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Three-Phase Solid–Liquid–Gas Equilibria for Three Carbon Dioxide–Hydrocarbon Solid Systems, Two Ethane–Hydrocarbon Solid Systems, and Two Ethylene–Hydrocarbon Solid Systems

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The pressure–temperature trace of the three-phase solid–liquid–gas curve starting at the melting point of the heavy solid and terminating at the upper critical end point was determined for CO_2–octacosane, CO_2–biphenyl, CO_2–naphthalene, ethane–octacosane, ethane–biphenyl, ethylene–octacosane, and ethylene–biphenyl. The results of this study are discussed in relation to previous studies of solid solubilities in supercritical fluids.

Introduction

Within the past decade there has been an active interest in using supercritical solvents (i.e., a solvent which is at a temperature above its critical temperature and a pressure above its critical pressure) as candidate solvents for difficult separations. Supercritical solvent extraction has been applied to separation problems ranging from removing caffeine from coffee beans (*1*) to deashing coal liquids (*2*).

Future applications of this separation technique are dependent on our ability to understand and predict the phase behavior which occurs for mixtures in their critical region. However, this can be a formidable task since even relatively simple binary mixtures, such as methane–*n*-octane (*3*), in which the components are chemically similar but differ in molecular size, can exhibit complex phase behavior.

As part of our research program in critical mixture phase behavior, we are interested in the phase behavior of a class of binary mixtures which consists of a well-characterized heavy solid and a light supercritical fluid. In this case, the melting point of the heavy solid, T_{M2}, is greater than the critical temperature of the lighter component, T_{C1}. Shown in Figure 1 is a typical pressure–temperature ($P-T$) diagram for a binary mixture in which the components do not differ appreciably. CD and MH are the pure-component vapor pressure curves, MN the heavy-component melting curve, and EM the pure-heavy-component sublimation curve. Points D and H represent pure-component critical points. The critical mixture curve representing different mixture compositions runs continuously from the critical point of the heavy component, H, to the critical point of the lighter component, D. For the binary mixture, the heavy-component melting curve, MN, exhibits a freezing point depression at elevated pressures due to the solubility of the light component in the heavy liquid phase. In Figure 1, this freezing point depression is depicted by the line MF, which represents the three-phase solid–liquid–gas (S–L–G) equilibrium. If the solubility of the light component is large, the freezing point depression will be appreciable, as shown in Figure 1. For a binary mixture of fixed composition, varying types of phase behavior are possible depending on the mixture composition as the pressure is increased isothermally at a temperature greater than T_{C1}, but less than T_{M2}, to pressures above the three-phase pressure (*4*). If the concentration of the heavy component in the mixture is slight, then liquid–gas equilibrium exists above the three-phase pressure until the vapor–liquid critical point is reached for the binary mixture (curve DH). Above this pressure a single fluid phase exists. However, if the concentration of the heavy component in the mixture is much greater than the previous case, then solid–gas equilibrium would exist at all pressures above the three-phase pressure.

Our interest is in binary mixtures where not only is the melting temperature of the heavier component greater than the critical temperature of the lighter component, but also the molecular size, shape, structure, and critical conditions of the two components differ substantially. The phase behavior for this type of binary mixture is depicted in the $P-T$ diagram in Figure 2, where the pure-component equilibrium curves have the same notation as in Figure 1. In this case, the melting curve, MN, will exhibit a small freezing point depression at elevated pressures due to the limited solubility of the light component in the liquid phase. At elevated pressures the S–L–G freezing point depression curve eventually intersects the critical mixture curve in two locations: the upper critical end point (UCEP) and the lower critical end point (LCEP). At these two intersections, the liquid and gas phases of the S–L–G freezing point depression curve merge into a single fluid phase in the presence of excess solid (*5*). At the UCEP the solubility of the heavy solid in the supercritical fluid phase can be quite substantial. At all pressures between the two branches of the S–L–G curve, solid–gas equilibrium exists.

In this study we experimentally determined the $P-T$ trace of the three-phase S–L–G curve starting at the melting point of the heavy solid and terminating at the UCEP for CO_2–octacosane, CO_2–biphenyl, CO_2–naphthalene, ethane–octacosane, ethane–biphenyl, ethylene–octacosane, and ethylene–biphenyl. This work, along with the fact that the LCEP occurs very near the critical temperature and critical pressure of the light component, defines the $P-T$ region in which solid–gas equilibrium exists at all pressures for the above systems. It is in this region where supercritical solvent extraction of heavy solids would take place.

Experimental Section

The supercritical fluid of interest is charged at ambient temperature to an air-operated gas/liquid compressor (Superpressure, Inc., Model 46-14025-1) where it is compressed and delivered to a high-pressure equilibrium view cell (Jerguson sight glass gauge, Jerguson Gauge and Valve Co., Model 11T51). The high-pressure view cell is immersed in a water bath which is controlled at a constant temperature to within ±0.1 °C (American Scientific Products, YSI 63RC controller). The temperature of the water is measured with an accuracy of ±0.1 °C by using a platinum resistance element (Degussa Inc.) calibrated on the 1968 IPTS scale. System pressure is measured with a Bourdon-tube Heise gauge (Dresser Industries, Model CM) with a range of 0–10 000 psig and an accuracy of ±10 psi. The cell contents are mixed when the cell is rocked approximately 180°, causing a small stirring bar previously inserted into the cell to move through the cell contents.

The $P-T$ trace of the three-phase solid–liquid–gas line is determined by using the following procedure. The view cell, loaded with heavy solid, is pressurized to approximately 50 psig with CO_2, ethane, or ethylene and then purged to remove any

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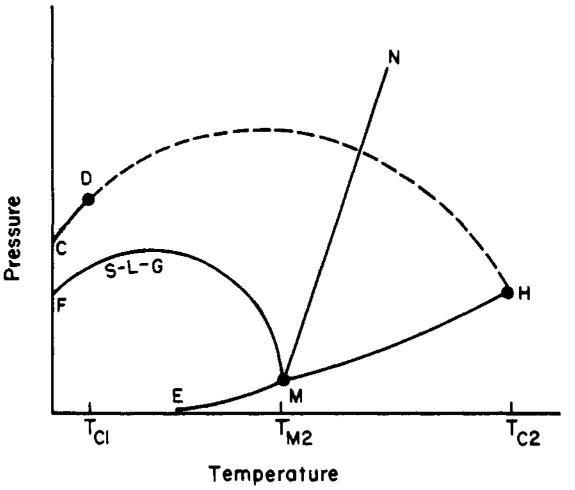

Figure 1. Pressure-temperature diagram for a binary mixture of similar components.

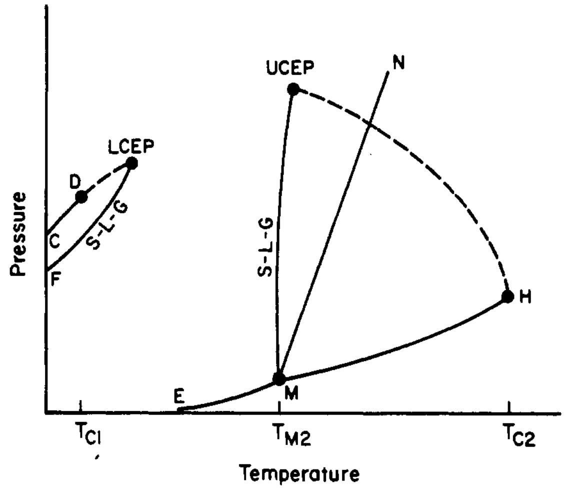

Figure 2. Pressure-temperature diagram for a highly asymmetric binary mixture.

Table I. Experimental Pressure-Temperature Data for the Ethylene-Biphenyl Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
10.9	65.8	70.7	49.6
17.0	64.0	77.5	48.1
24.5	62.5	86.4	46.3
30.6	60.6	107.5	44.7
36.0	59.0	127.5	43.7
40.8	57.7	174.8	42.8
52.3	54.3	202.7	41.7
57.6	52.7	225.5[a]	41.6[a]
64.6	50.9		

[a] UCEP.

Table II. Experimental Pressure-Temperature Data for the Ethylene-Octacosane Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
1.0	63.5	125.5	44.9
32.6	54.1	151.2	44.1
48.3	51.2	177.0	43.8
70.7	48.1	202.7	43.3
88.2	46.1	206.4[a]	43.0[a]

[a] UCEP.

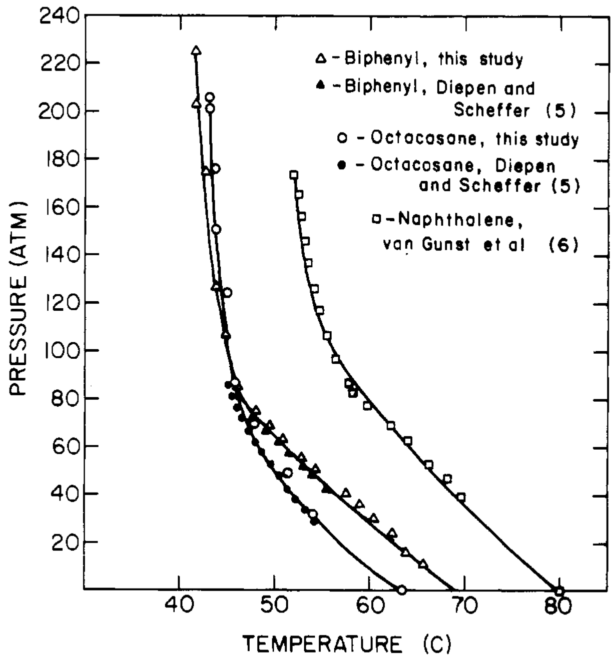

Figure 3. Pressure-temperature trace of the three-phase S-L-G line ending at the UCEP for three ethylene-hydrocarbon solid systems.

residual air from the system. After three to four purgings, the system is brought to the desired operating pressure and maintained there for approximately 30 min to ensure thermal equilibrium. Starting with a solid-fluid condition in the cell, the temperature is then adjusted until the solid begins to melt. This temperature is maintained with periodic stirring for 10-20 min to determine if complete melting occurs. If not, the procedure is repeated until a liquid-fluid condition exists in the cell. At that point, the three-phase temperature is in the interval between this liquid-fluid state and the previous solid-fluid state. The solid is alternately frozen and melted a number of times in an effort to decrease the solid-fluid, liquid-fluid temperature interval to within 0.1 °C.

The UCEP for these systems is defined to be the pressure and temperature at which critical opalescence is observed for a very slight change in either pressure or temperature. Also at the UCEP, a small change in temperature and/or pressure causes a dramatic change in the amount of supercritical fluid phase, liquid phase, or solid phase present in the view cell. For example, in certain instances adjusting the temperature approximately 0.1 °C changed the phases present in the cell in only a few seconds from a single supercritical fluid phase to about 90 vol % liquid phase and 10 vol % supercritical fluid phase.

Materials

Fisher Scientific Co. supplied the naphthalene; Aldrich Chemical Co. supplied the biphenyl; and Sigma Chemicals, Inc., supplied the octacosane. All of the solids were stated to be 99+% purity by the manufacturers and therefore were used without further purification.

The ethane, CP grade 99.0% minimum purity, the ethylene, CP grade 99.5% minimum purity, and the carbon dioxide, "bone-dry" grade 99.8% minimum purity, were supplied by Linde Co. The gases were used without further purification.

Results

The experimental pressure-temperature data for the three-phase S-L-G line for the ethylene-biphenyl system and the ethylene-octacosane system are listed in Tables I and II, respectively. These data are shown in Figure 3 along with the ethylene-naphthalene S-L-G line determined by van Gunst et al. (*6*). Diepen and Scheffer (*5*) have previously determined the *P-T* trace of the S-L-G line for ethylene-octacosane and ethylene-biphenyl to pressures of 87 atm and the data obtained

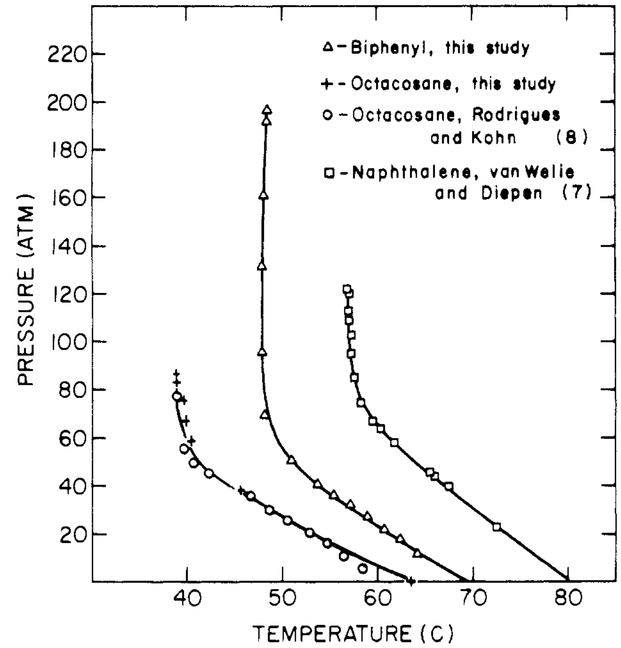

Figure 4. Pressure-temperature trace of the three-phase S-L-G line ending at the UCEP for three ethane-hydrocarbon solid systems.

Table III. Experimental Pressure-Temperature Data for the Ethane-Octacosane Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
1.0	63.5	75.8	39.5
38.1	45.8	83.0	38.9
58.8	40.6	86.4[a]	38.9[a]
67.0	39.8		

[a] UCEP.

Table IV. Experimental Pressure-Temperature Data for the Ethane-Biphenyl Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
12.2	64.2	50.5	51.0
18.3	62.4	70.2	48.2
23.3	60.7	96.1	48.0
28.2	59.0	131.9	48.0
32.6	57.2	161.5	48.2
36.7	55.4	191.8	48.5
41.0	53.7	196.6[a]	48.7[a]

[a] UCEP.

in this study are in good agreement with their results.

The UCEP for the ethylene-octacosane system is 206.4 atm and 43.0 °C while the UCEP for the ethylene-biphenyl system is 225.5 atm and 41.6 °C.

As shown in Figure 3, the S-L-G lines for the ethylene-octacosane and ethylene-biphenyl systems are very close to each other and both reach lower temperatures than the ethylene-naphthalene system. The UCEP's for both systems are also quite close. This suggests that the vapor pressure of the solid is the major variable which would determine whether octacosane or biphenyl would be more soluble in supercritical ethylene at a specific temperature in the solid-gas region of the phase diagram.

The experimentally determined *P*-*T* trace of the S-L-G lines for ethane-octacosane and ethane-biphenyl are listed in Tables III and IV, respectively. Shown in Figure 4 are these two systems along with the ethane-naphthalene system which was previously determined by van Welie and Diepen (*7*). Rodrigues and Kohn (*8*) have also determined the *P*-*T* trace of the S-L-G line for the ethane-octacosane system to 77 atm. The data obtained in this study are in fair agreement with their results.

Table V. Experimental Pressure-Temperature Data for the CO_2-Naphthalene Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
140.1	59.1	241.8	59.9
174.1	59.7	244.5	59.9
210.9	59.9	252.7[a]	60.1[a]
238.4	59.9		

[a] UCEP.

Table VI. Experimental Pressure-Temperature Data for the CO_2-Biphenyl Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
100.3	50.0	357.5	53.0
130.8	49.3	425.1	54.7
196.6	50.4	469.0[a]	55.1[a]
286.0	51.9		

[a] UCEP.

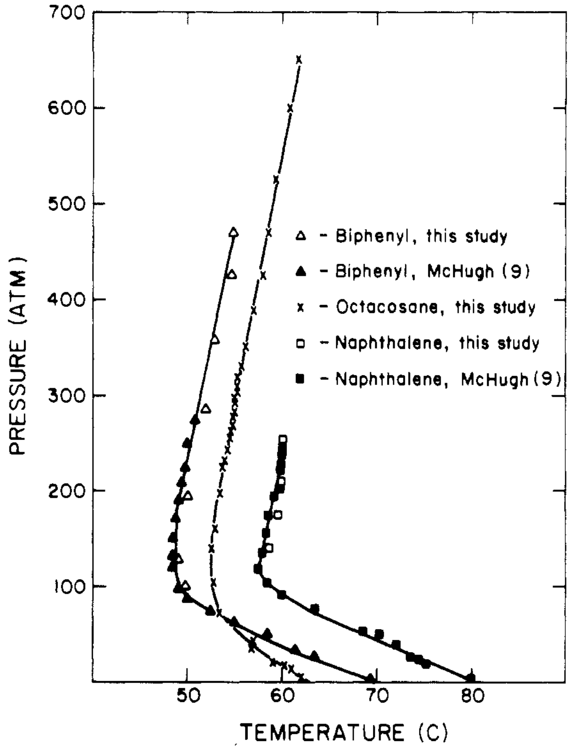

Figure 5. Pressure-temperature trace of the three-phase S-L-G line ending at the UCEP for three CO_2-hydrocarbon solid systems.

The UCEP for the ethane-octacosane system is 86.4 atm and 38.9 °C and the UCEP for the ethane-biphenyl system is 196.6 atm and 48.7 °C.

In this case, the S-L-G lines for the three ethane-solid systems exhibited distinctly different behavior. In fact, the ethane-biphenyl S-L-G exhibits a slight temperature minimum at approximately 96 atm and 48 °C (i.e., as the pressure is increased, the S-L-G line begins with a negative slope, passes through a temperature minimum, and then continues with a positive slope to the UCEP). The fact that the ethane-octacosane S-L-G line runs to lower temperatures and that its UCEP is lower than either of the other two systems suggests that the solubility of solid octacosane in supercritical ethane would be higher than the solubility of either biphenyl or naphthalene in supercritical ethane at comparable pressures and temperatures in the solid-gas region of the phase diagram.

The experimentally determined *P*-*T* traces of the S-L-G lines for CO_2-naphthalene, CO_2-biphenyl, and CO_2-octacosane are listed in Tables V-VII, respectively, and are shown in Figure 5. Two of these systems, CO_2-naphthalene and CO_2-biphenyl, were previously determined to pressures as high as 275 atm

Table VII. Experimental Pressure-Temperature Data for the CO_2-Octacosane Solid-Liquid-Gas Line

press., atm	temp, °C	press., atm	temp, °C
1.7	62.0	274.4	55.0
13.6	61.0	283.0	55.0
17.6	60.3	294.3	55.0
21.2	59.1	296.4	54.8
38.7	56.9	297.4	55.1
43.1	57.3	299.0	55.2
73.6	53.4	300.7	55.1
105.1	52.8	302.7	55.4
139.4	52.5	308.1	55.4
161.2	53.0	314.3	55.2
198.6	53.5	316.0	55.4
226.8	53.8	329.2	55.8
230.9	53.9	331.6	56.0
242.2	54.2	351.5	56.3
242.8	54.2	387.7	57.1
254.4	54.5	424.3	58.0
256.7	54.6	470.7	58.6
260.2	54.7	526.0	59.5
262.9	54.7	600.0	61.0
267.3	54.5	649.5	62.0

(*9*), and the results of this work are in good agreement with that previous study.

The UCEP's for the CO_2 systems are significantly higher than those for either the ethane or ethylene systems. For CO_2–naphthalene the UCEP is 252.7 atm and 60.1 °C. This measurement is in excellent agreement with the UCEP reported by McHugh (*9*) and with the UCEP deduced by McHugh and Paulaitis (*10*) based on the shapes of various naphthalene–supercritical CO_2 pressure–composition (P–x) isotherms. The CO_2–biphenyl UCEP is 469.0 atm and 55.1 °C. This result is also in excellent agreement with the value deduced by McHugh and Paulaitis (*10*) based on the shapes of various biphenyl–supercritical CO_2 P–x isotherms. The UCEP for the CO_2–octacosane system could not be determined due to the pressure limit of the view cell.

Unlike any of the above systems, the octacosane–CO_2 system exhibited a supercritical fluid–liquid phase inversion at approximately 260 atm and 54.7 °C (i.e., the supercritical fluid phase becomes denser than the liquid phase and hence at pressures greater than approximately 260 atm the clear supercritical fluid phase now is located below the liquid phase).

Another characteristic of the CO_2 systems which differs from either the ethane or ethylene systems is that all the S–L–G lines exhibit a large temperature minimum. This result is especially important when interpreting the solid solubility behavior for these systems. For instance, McHugh and Paulaitis (*10*) report solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide for a number of isotherms near their respective UCEP's. However, the results obtained in this study show that some of the P–x isotherms for both the CO_2–naphthalene and the CO_2–biphenyl system intersected their respective S–L–G lines. Therefore, over certain pressure ranges the reported solubilities represent liquid–fluid and not solid–fluid equilibria. This is especially evident for the CO_2–biphenyl system where the temperature minimum of the S–L–G line is approximately 49.3 °C.

The solubility behavior for systems which exhibit a temperature minimum in the S–L–G line is radically different from systems which have no temperature minimum. Operating isothermally very near the UCEP, the solubility of heavy solid in supercritical CO_2 first increases dramatically as the system pressure approaches the UCEP pressure but then decreases sharply as the system pressure is increased slightly above the UCEP pressure (*7*, *9*). McHugh (*9*) has shown that the solubility of solid biphenyl in supercritical carbon dioxide does indeed decrease sharply when the pressure is increased above the UCEP pressure at a constant temperature equal to the UCEP temperature. For the ethylene–solid and ethane–solid systems, where no (or only a slight) temperature minimum in the S–L–G line was observed, operating isothermally very near the UCEP the solubility of the heavy solid in the supercritical fluid phase increases dramatically as the system pressure approaches the UCEP pressure. However, as the system pressure is increased above the UCEP pressure, the solubility will continue to increase until at a higher pressure it reaches a limiting value. If the pressure were increased still further, the solubility would decrease but not as sharply as in the CO_2–solid systems (*7*, *10*). A temperature minimum in the S–L–G line has also been observed for the methane–naphthalene system (*11*) and therefore this behavior cannot be considered peculiar to CO_2–solid systems.

The results of this study indicate that it can be vitally important to obtain phase border curves prior to obtaining solubility data of a heavy solid in a supercritical fluid. By a fast and reliable determination of the S–L–G line starting at the melting point of the heavy solid and terminating at the UCEP one can also obtain a qualitative estimate of the selectivity of a supercritical fluid for various heavy solids.

Registry No. CO_2, 124-38-9; octacosane, 630-02-4; biphenyl, 92-52-4; naphthalene, 91-20-3; ethane, 74-84-0; ethylene, 74-85-1.

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