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Three-Phase Solid–Liquid–Vapor Equilibria in the Binary Hydrocarbon Systems Methane–*n*-Hexane and Methane–Benzene

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Pressure, temperature, liquid-phase compositions, and liquid-phase molar volumes are presented along the solid–liquid–vapor (SLV) loci of the binary systems methane–*n*-hexane and methane–benzene. The data were taken by using cryoscopic techniques and are compared to the solid–liquid (SL) data at elevated pressures of Kuebler and McKinley. The standard deviations of the smoothed SLV data for liquid-phase solute composition presented herein from the raw SLV data are 3.7% for the methane–*n*-hexane system and 8.6% for the low-temperature branch of the methane–benzene system. The corresponding standard deviation for the high-temperature (high solute composition) branch for the system methane–benzene is less than 0.7%.

Introduction

Solid solubility data of hydrocarbon components in low molecular weight solvents are important for use in the design of liquefaction, vaporization, and transport systems for liquefied natural gas (LNG) and liquefied petroleum gas (LPG). A major problem in the liquefaction processing of LNG is the precipitation of solids (hydrocarbons and CO_2) from the liquid phase. These solids can coat the surfaces of heat exchangers and foul turboexpansion devices, requiring liquefaction units to be shut down for cleaning and/or repair. We have been engaged in an extended program of obtaining and classifying three-phase solid–liquid–vapor data, primarily in the low solute concentration range.

In previous papers, we reported the solubility of three different hydrocarbon solutes in methane: *n*-heptane (*1*) and *n*-octane and cyclohexane (*2*). All of these data were for binary three-phase SLV systems. Earlier Kuebler and McKinley (*3*, *4*) reported SL data at elevated pressures for binary systems of methane and the solutes *n*-butane, *n*-pentane, benzene, toluene, *n*-hexane, and *n*-heptane. In the case of methane–*n*-heptane (*1*), it was shown that the SLV data exhibited significantly lower liquid-phase solute compositions than the SL data of Kuebler and McKinley (*3*) at the same temperatures.

In this present paper, we report the liquid-phase composition and the molar volume for the SLV loci for the binary systems methane–*n*-hexane and methane–benzene. The experimental results are compared with the SL phase behavior studies of Kuebler and McKinley (*3*) on these same binary systems.

Experimental Section

The apparatus was identical with that described by Lee and Kohn (*5*) which was used in the earlier cryogenic studies of methane–hydrocarbon SLV phase equilibria (*1*, *2*). The experimental procedures are similar to those employed in ref *1* and *2*; additional detail can be found in ref *6*.

The methane used in this study was Linde "ultrapure" grade stated to be 99.97 mol % pure. The gas was run through 13X molecular sieves at 100-atm pressure and room temperature before use. A -85 °C isotherm determined on the treated gas indicated a difference between the bubble-point and dew-point pressures of 0.2 atm, and the vapor pressure of 50 vol % liquid was within 0.1 atm of the data reported by Din (*7*).

Table I. Smoothed Data for the Solid-Liquid-Vapor Equilibria of the Methane-*n*-Hexane System

T, K	press., atm	liquid-phase compn (mole fraction n-C_6)	liquid-phase molar vol, mL/(g-mol)
164	17.01	0.339 5	66.0
162	16.54	0.077 52	50.4
160	15.50	0.042 06	48.6
158	14.33	0.027 79	47.5
156	13.20	0.022 66	47.0
154	12.15	0.018 26	46.2
152	11.18	0.014 87	45.6
150	10.25	0.012 22	45.1
148	9.36	0.010 13	44.7
146	8.59	0.008 46	44.3
144	7.80	0.007 14	43.8
142	7.22	0.006 02	43.3
140	6.48	0.005 05	42.8
138	5.80	0.004 22	42.4

The benzene was supplied by Mallinckrodt with a stated purity of 99%. Its refractive index was 1.5013 compared to the literature value of 1.5011 at 20 °C; its air-saturated freezing point was 0.32 K below the literature value of 5.53 °C. The *n*-hexane was supplied by Humphrey-Wilkinson ("pure grade") with a stated purity of 99%.

Results

Table I presents a portion of the smoothed SLV locus for the methane–*n*-hexane binary system. This locus is a continuous locus extending from the triple point of the solute *n*-hexane down to the Q point (S_1S_2LV) where the methane crystallizes as well. (This latter point would be near the triple point of pure methane.) Twenty raw SLV data were taken, and the standard deviation of the raw data from the smoothed data in Table I is 3.7%, with the worse agreement being in the reduced temperature region of $1/T^* < 1.1$, where the locus is steepest. In this region, the standard deviation is 5.6%.

Table II presents data for the methane–benzene binary SLV locus. In pressure–temperature space, there are upper and lower branches. The upper branch extends from the triple point of benzene sharply up to an eventual K-point terminus, where the liquid and vapor phases are critical in the presence of the solid benzene crystals. The experiments herein did not extend to that K point. The lower branch extends from a second K point, estimated to be close to 190.5 K and 45.66 atm, down in temperature to a Q point (S_1S_2LV) near the triple point of pure methane. As can be seen, there is a dramatic drop in solute liquid-phase composition between the upper and lower branches of the SLV locus. The standard deviation of the solute liquid-phase composition for the upper branch is 0.5% for pressures less than 85 atm, based on 20 raw data, and 0.7% for pressures greater than 85 atm, based on 7 raw data. The high-pressure data were taken in a metal Jerguson cell with

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Table II. Smoothed Data for the Solid-Liquid-Vapor Equilibria of the Methane-Benzene System

press., atm	T, K	liquid-phase compn (mole fraction benzene)	liquid-phase molar vol, mL/(g-mol)
		Upper Branch	
10	277.7	0.9815	86.8
20	276.8	0.9635	86.1
30	275.8	0.9433	85.1
40	274.9	0.9247	84.2
50	273.9	0.9019	83.1
60	273.1	0.8824	82.2
70	272.2	0.8598	81.0
80	271.6	0.8444	80.1
90	270.9	0.8249	78.9
100	270.4	0.8092	78.0
110	269.9	0.7931	77.0
120	269.4	0.7775	76.1
130	269.0	0.7642	75.3
140	268.7	0.7537	74.7
150	268.4	0.7409	74.0
160	268.2	0.7308	73.4
170	268.1	0.7246	73.0
		Lower Branch	
45.66	190.5[a]	0.000150	70.2
38.4	185	0.000170	63.5
32.8	180	0.000165	58.7
29.7	175	0.000150	54.8
23.3	170	0.000135	52.1
19.5	165	0.000110	49.8

[a] Estimated location of K point of the lower branch.

site-glass window, and it is not as precise as the smaller all-glass cells used at the lower pressures (less than 85 atm). The lower branch of the SLV locus is characterized by very low benzene solute concentration. The standard deviation is 8.6%, based on 10 raw SLV data.

Compositions of the equilibrium vapor phases for both binary SLV studies were not measured and therefore are not reported. At the low temperatures studied, the vapor phases are assumed to be virtually pure methane.

Discussion

Figure 1 is a comparison of the raw and smoothed data for the two binary SLV loci. Since no definition of deviations between raw and smooth data for the upper branch can be easily shown, the raw data are not illustrated in Figure 1. The coordinates chosen for this plot are ln X_{solute} vs. $1/T^*$, where T^* is the reduced temperature (by the solute triple-point temperature) in each binary system. Also shown in Figure 1 are the ideal solubility curves for each binary system

$$\ln X_I = \frac{\Delta h_{\text{FUS}}}{RT_T}\left(1 - \frac{1}{T^*}\right)$$

As can be seen, both binary systems are highly nonideal. The methane-benzene data are suggestive of the behavior of the methane-*n*-octane and methane-cyclohexane systems (*2*); the benzene liquid-phase fractions along the lower branch are smaller than those of either cyclohexane or *n*-octane.

Previous work by Shim and Kohn (*8*) on the SLV locus of methane-*n*-hexane appears to be consistent with the data of the present study; three of these data are shown in Figure 1.

Figure 1 also includes for illustrative purposes approximate loci of the SL data of Kuebler and McKinley (*3*) at pressures of 10 MPa. In the case of benzene, the solute concentrations are higher along the domain of the lower SLV branch. This also holds for the solute *n*-hexane except at temperatures $1/T^* < 1.09$, where the Kuebler-McKinley data fall below the data in Table I.

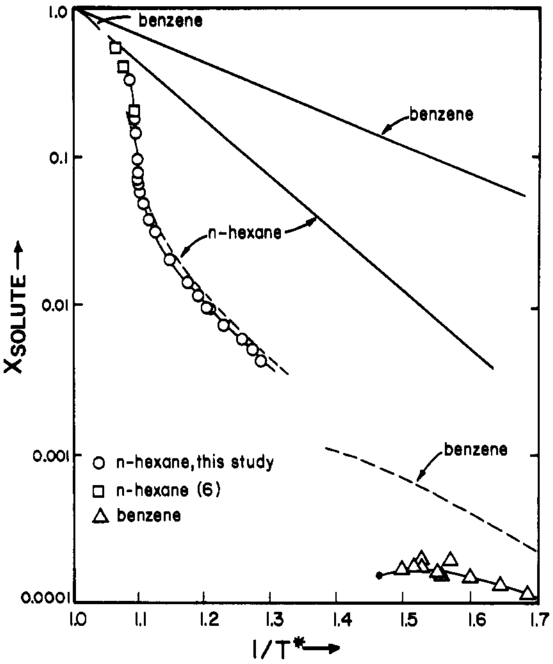

Figure 1. A plot of the raw data (denoted by symbols) and the smoothed data (denoted by solid curves) for the binary SLV systems methane-*n*-hexane and methane-benzene. The solid circle (●) is the estimated K point for the lower branch of the methane-benzene system. The raw data are not shown for the upper branch of the same system. Ideal solubility is shown by the thin straight lines for both systems. The dashed curves are approximate locations of the Kuebler-McKinley (*3*) SL data and should be considered as only illustrative.

Glossary

Δh_{FUS}	heat of fusion for a solute at its triple point: 3.114 kcal/(g-mol) for *n*-hexane, 2.351 kcal/(g-mol) for benzene
K	K point, or critical end point, where L and V are critical in the presence of S
L	liquid phase
P	pressure
Q	Q point, or four-phase point, where S_1, S_2, L, and V are in equilibrium
R	gas constant
S	solid phase
S_1, S_2	solid phases, one of which is pure solute and the other is pure methane
T	temperature
T_T	Triple-point temperature of solute: 177.84 K for *n*-hexane, 278.69 K for benzene
T^*	$= T/T_T$
V	vapor phase
X_{solute}	mole fraction of the solute in the L phase
X_I	ideal solubility of the solute in the L phase

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