Three-Phase Solid–Liquid–Vapor Equilibria of the Binary Hydrocarbon Systems Methane–*n*-Octane and Methane–Cyclohexane

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Pressure–temperature profiles along with liquid compositions and molar volumes are presented for two hydrocarbon solutes with methane as a common solvent. The data were taken employing cryoscopic techniques. In the case of the methane–cyclohexane system, the liquid compositional range covered extended from solute-rich solutions to very dilute solute solutions. Since reliable data on the methane–*n*-octane system in the solute-rich solution range are available, only the dilute solute range of this system was studied. The liquid compositional data when represented as the logarithm of composition vs. T_{FUS}/T (where T_{FUS} = freezing temperature of each pure solvent) are smooth curves, with both binary systems possessing a maximum in composition at temperatures slightly below the critical temperature of methane. The curves become quite linear in the lower temperature range. The standard deviations of the liquid composition data are different for each system and for certain composition ranges as follows: methane–*n*-octane system, 5.0% for $191 > T > 155$; methane–cyclohexane system, 0.76% for $279 > T > 190$, 2.5% for $190 > T > 154$.

Solid solubility data of hydrocarbons 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). The authors are engaged in an extended program of obtaining such pertinent data. These data, being in the low-concentration range, are scarce, as indicated by Kurata's review (*9*) of experimental data on the solid solubility of hydrocarbons in liquefied methane. The best existing data on the solid solubility of hydrocarbons in methane are those of Kuebler and McKinley (*6, 7*), which includes *n*-alkanes up through *n*-heptane and also benzene and toluene.

In earlier papers (*5, 11*), the authors examined six binary systems, in which ethane was the solvent, by cryoscopic means. The data were taken along the three-phase solid–liquid–vapor locus for each binary system. In this present paper, the authors investigate the corresponding behavior of the binary systems methane–*n*-octane and methane–cyclohexane. In addition to adding to existing knowledge of hydrocarbon solubility behavior in methane, this study extends the cryoscopic approach to systems with very low solute concentrations compared to our earlier studies. Furthermore, the cryoscopic approach avoids some of the difficulties that would hamper traditional sampling methods of liquid-phase analysis of S–L–V systems (*4*), arising simply from the inherent phase behavior of such S–L–V systems. For example, removal at constant pressure of a liquid-phase sample along the low solute concentration locus mandates the handling of a solid–vapor system, from which solute can precipitate on the walls of sampling devices and/or plug the sampling tube altogether. This problem is discussed in detail in ref 4. The present study, being cryoscopic in design, avoids this problem.

Experimental Section

The apparatus used in this study was identical with that reported by Lee and Kohn (*10*) which was used in other cryoscopic studies (*2, 8*). The experimental procedure, as described in the earlier papers in which ethane was the gaseous component (*5, 11*), was followed closely in taking data on the methane–cyclohexane binary system at temperatures between the triple point of cyclohexane and 193 K. In this range the liquid phase has a high concentration of cyclohexane, and the previous procedure was used without modification. Briefly, the procedure involved charging the liquid component to a glass equilibrium cell which had an inside volume of between 10 and 17 mL. The component mass was determined accurately by weighing techniques. The air was vented from the cell by repeated flushing with methane. The cell was thermostated in a liquid bath confined in a Dewar flask, and the bath could be chilled by means of a cascade refrigerator or liquid nitrogen or both. Methane was added to the cell from a reservoir using a calibrated positive displacement mercury pump. The bath was cooled slowly while agitation of the cell contents was effected by a steel ball actuated by an override magnet. When crystals were observed inside the cell, the cell contents were very slowly heated until only a trace of crystals remained. It was possible visually to detect as little as a few tenths of a milligram of crystals in the cell. This was regarded as an equilibrium crystal point with known liquid-phase composition. Temperature, pressure, and liquid volume were taken. Temperatures were taken on a platinum-resistance thermometer which was accurate to at least ±0.03 °C of the 1968 IPTS scale. Pressures were taken on a calibrated Heise bourdon tube gauge which was accurate to at least ±0.07 atm. Liquid volumes were read from calibration marks on the cell or by use of a cathetometer. Volumes could generally be read to 0.02 mL.

Repeated additions of methane to the cell allowed observation of additional crystal points at lower temperatures, which concluded when the cell was full of liquid phase or the lowest temperature desired was attained.

At temperatures below 195 K the experimental procedure had to be modified due to the extremely small concentrations of dissolved solids in the liquid phase. After a number of procedural modifications were tried which gave partially satisfactory results, the following procedure evolved as the most precise and reliable. The initial part of the modified procedure was the same as before up through flushing the air from the cell with methane gas. Then sufficient methane was added to the cell (the temperature of the cell at this point being below 191 K) to form 2 or 3 mL of liquid phase. The cell contents were cooled and agitated until extensive crystallization had occurred. The temperature was then held constant, and additional small increments of methane gas were added to the cell. Agitation of the cell contents resulted in dissolving some of the crystals and incremental additions of methane continued until only a few tenths of a milligram of crystals remained in the cell. This point was taken as the crystal point as before. In some cases the cell contents could be further cooled with sufficient crystal growth to give an additional crystal point or two at lower temperatures. In many cases, however, cooling below the initial crystal point resulted in only a very tenuous crystal film forming on the inside walls of the cell. In this case it was difficult if not impossible to detect when the crystal mass was in a trace amount (0.2 mg or so) and thus only one crystal point could be determined from each initial cell solute loading. This procedure was followed for both binary systems with greater care being taken in the case of the methane–*n*-

Table I. Vapor–Liquid–Solid Three-Phase Smoothed Data: Methane–*n*-Octane Binary System

Temp, K	Pressure, atm	Liquid-phase comp (mole fraction C_8)	Liquid-phase vol, mL/g-mol
191.15[a]	45.9	0.000 592	—
190.00	44.4	0.000 653	75.3
188.00	41.7	0.000 766	68.2
186.00	39.1	0.000 836	63.8
184.00	36.7	0.000 837	61.4
182.00	34.5	0.000 809	59.4
180.00	32.3	0.000 772	57.7
178.00	30.2	0.000 730	56.2
176.00	28.3	0.000 689	54.8
174.00	26.4	0.000 638	53.6
172.00	24.6	0.000 589	52.6
170.00	23.0	0.000 538	51.7
168.00	21.4	0.000 483	50.8
166.00	19.8	0.000 431	50.0
164.00	18.4	0.000 380	49.2
162.00	17.0	0.000 331	48.4
160.00	15.7	0.000 288	47.7
158.00	14.5	0.000 250	47.0
156.00	13.4	0.000 214	46.3

[a] *K* point (V–L critical point in presence of solid).

octane system because of the extremely small concentrations of *n*-octane in the liquid phase, comparatively speaking.

Materials

The methane used in this study was Linde "ultra pure" 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 the dew point pressure of 0.2 atm and the vapor pressure at 50 vol % liquid was within 0.1 atm of the data reported in Din (*1*).

The cyclohexane used was Eastman reagent "ACS" grade chemical. The *n*-octane was Humphrey–Wilkinson "pure grade" petroleum-derived product. Both of these components were used without further purification.

Results

Tables I and II present the smoothed experimental data for the two systems studied. The pressures are precise to ±0.1 atm, the temperatures to ±0.2 °C, and the liquid molar volume to 0.4 mL/g-mol. The liquid composition data were smoothed prior to tabulation by use of the same procedure as was reported for the ethane systems (*5, 11*). In this procedure, the ideal solubility for each solute component was determined by use of a simple version of the Van't Hoff isochore for freezing point lowering

$$\ln x_{\mathrm{I}} = (\Delta H_{\mathrm{FUS}}/RT_{\mathrm{FUS}})(1 - 1/T^*) \qquad (1)$$

where $T^* = T/T_{\mathrm{FUS}}$, ΔH_{FUS} = enthalpy of fusion of the solute, and T_{FUS} = triple point temperature of the solute. The enthalpies of fusion and the triple point temperatures were taken from Rossini (*12*). The ratio of the ideal solubility to the experimental solubility is the estimated activity coefficient of the solute.

The activity coefficients were plotted as log γ vs. $1/T^*$ and smoothed by eye. Then smoothed values of the mole fraction of solute component x were computed from

$$x = x_{\mathrm{I}}/\gamma \qquad (2)$$

where x_{I} is calculated from eq 1. These are the composition values listed in Tables I and II.

Table II. Vapor–Liquid–Solid Three-Phase Smoothed Data: Methane–Cyclohexane Binary System

Temp, K	Pressure, atm	Liquid-phase comp (mole fraction C_6)	Liquid-phase vol, mL/g-mol
279.83	—	1.000	—
270.0	9.3	0.9632	102.2
265.0	14.4	0.9441	100.4
260.0	19.6	0.9243	98.6
255.0	24.4	0.9040	96.7
250.0	28.9	0.8834	94.8
245.0	33.2	0.8629	93.1
240.0	37.0	0.8411	91.3
235.0	40.7	0.8183	89.6
230.0	43.8	0.7944	87.8
225.0	46.3	0.7693	86.1
220.0	48.4	0.7436	84.4
215.0	50.1	0.7169	82.5
210.0	51.4	0.6890	80.5
205.0	52.3	0.6544	78.1
200.0	52.9	0.6193	75.4
197.5	53.6	0.5998	73.6
195.0	59.0	0.5790	71.1
193.0	75.0	0.5622	68.0
192.74[a]	47.5	0.00410	—
190.0	43.6	0.00518	69.5
188.0	41.2	0.00588	64.6
186.0	38.8	0.00629	61.8
184.0	36.4	0.00651	59.5
182.0	34.2	0.00661	57.8
180.0	32.0	0.00652	56.1
178.0	30.0	0.00635	54.8
176.0	28.0	0.00617	53.7
174.0	26.2	0.00591	52.7
172.0	24.4	0.00572	52.0
170.0	22.7	0.00540	51.1
168.0	21.2	0.00511	50.4
166.0	19.6	0.00483	49.6
164.0	18.1	0.00453	48.9
162.0	16.8	0.00420	48.3
160.0	15.5	0.00391	47.5
158.0	14.3	0.00358	47.0
156.0	13.2	0.00334	46.5
154.0	12.1	0.00310	46.0

[a] *K* point (V–L critical point in presence of solid).

In the case of the methane–cyclohexane system at temperatures between 280 and 192 K, two runs were taken at two different cell loadings—a total of 18 raw data points. The standard deviation between the smoothed compositions in Table I and the raw data in this temperature range is ±0.76%. In the temperature range between 193 and 154 K the standard deviation for the methane–cyclohexane system is ±2.5% based on a total of 13 data points taken from four separate loadings. For the methane–*n*-octane system in the temperature range between 191 and 156 K, there were 17 runs (17 different loadings on several different size cells). There was a total of 36 data points and the standard deviation between the smoothed data points and the raw data points for this system was ±5.0%. The raw data for the two binary systems are shown in Figure 1. Noteworthy in the composition behavior of the two binary systems is the maximum in the composition which occurs at the high-temperature end of the low-composition branch of the S–L–V locus. At these points the systems, already extremely dilute in hydrocarbon solute, are approaching the vicinity of the critical point of pure methane. Apparently the increase in molar volume of the liquid phase effects a decrease in composition, in contrast to what one experiences at lower temperatures. To the authors' knowledge, this is the first report of such a phenomenon for binary S–L–V systems with methane as the solute. The work of Kuebler and McKinley (*6, 7*) was carried out at "over-pressures", which procedure in effect creates a solid–liquid system substantially removed from the critical region (no vapor phase

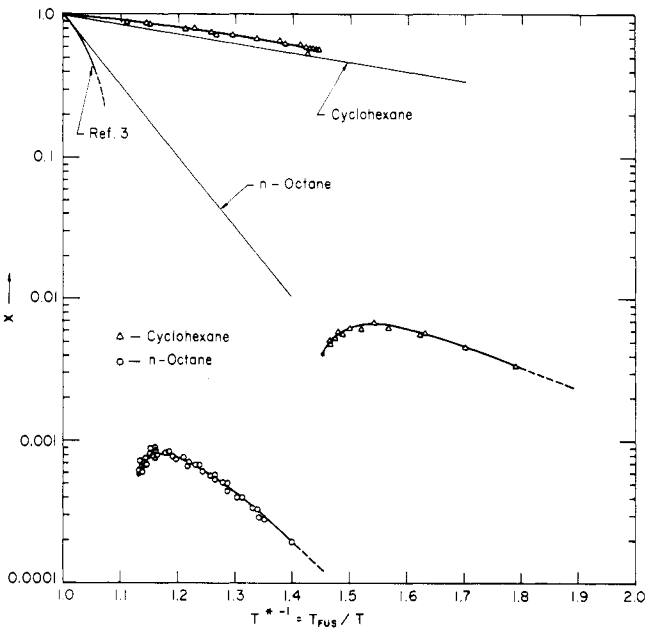

Figure 1. Experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions for the two binary systems studied. The heavy lines are the smoothed data presented in Tables I and II, while the light straight lines are the ideal composition loci for the two solutes. The heavy line for CH_4–*n*-octane at high concentrations is taken from Kohn and Bradish (*3*). The heavy dots (●) are *K* points.

present), which would probably mask the phenomenon reported here.

A comparison of the P–T loci of the two binary systems is interesting. See Figure 2. Whereas CH_4–*n*-octane behaves typically like a system where the triple point of the solute substantially exceeds that of the critical point of the solvent, the locus of the system CH_4–cyclohexane at high solute concentrations bends toward the low solute concentration locus (much in the manner of CH_4–*n*-hexane or CH_4–*n*-heptane) but then proceeds to adopt a behavior at $T < 200$ K similar to that of the CH_4–*n*-octane system, with the locus rising sharply to high pressures.

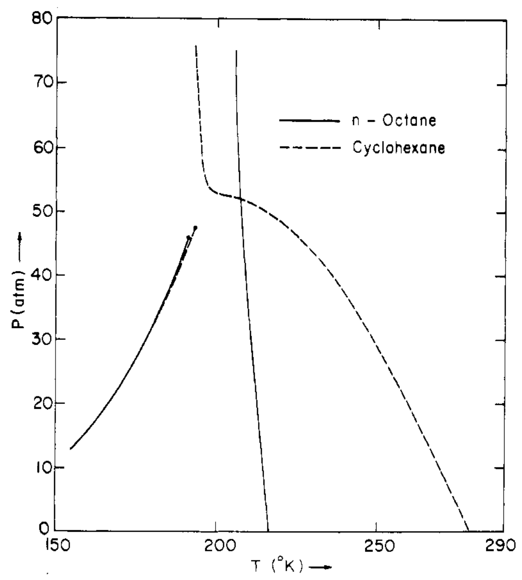

Figure 2. The P–T loci of the solid–liquid–vapor systems for the two binary systems studied. The heavy dots (●) are K points. The loci at low temperatures, being extremely dilute in solute, are virtually coincident.

Glossary

R	universal gas constant (1.987 cal/(g-mol K))
P	pressure (atmospheres absolute)
T_{FUS}	triple point temperature in K
T	temperature in K
T^*	T/T_{FUS}
v	liquid-phase molar volume in mL/g-mol
x	solute mole fraction
x_I	ideal solute mole fraction, computed from eq 1
γ	activity coefficient of solute = x_I/x
ΔH_{FUS}	enthalpy of fusion of pure solute component (cal/g-mol)

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