

Vapor-Liquid Two-Phase and Vapor-Liquid-Solid Three-Phase Behavior in Three Ternary Hydrocarbon Systems Containing Methane

W. F. O'Reilly, T. E. Blumer, K. D. Luks,* and J. P. Kohn

Department of Chemical Engineering, University of Notre Dame, Notre Dame, Ind. 46556

Vapor-liquid isotherms at temperatures near the freezing point of the highest molecular weight component in each system are presented for the ternary systems methane-*trans*-decalin-phenanthrene, methane-*n*-butylbenzene-*n*-dotriacontane, and methane-*n*-butylbenzene-phenanthrene. Binary vapor-liquid isotherms are run for methane-*n*-butylbenzene at 70 and 100 °C. Vapor-liquid-solid three-phase behavior is also presented for the same ternary systems. Cryoscopic solid-liquid two-phase data are presented for the binary systems *trans*-decalin-phenanthrene, *n*-butylbenzene-*n*-dotriacontane, and *n*-butylbenzene-phenanthrene.

The effect of dissolved methane under pressure on the solid solubility of high molecular weight components in complex mixtures such as crude oil is a technological question which has not been completely answered. Recent work in our laboratory on vapor-liquid and vapor-liquid-solid behavior of several ternary hydrocarbon systems which contain methane has been reported (1-3). The present study reports data on three additional ternary systems which contain methane. The ternary mixtures contain various combinations of paraffinic, naphthenic, and aromatic components. The data should prove useful in solution modeling and in predictions of solubility in multicomponent systems which contain other combinations of hydrocarbons.

Experimental

The apparatus and experimental techniques were identical to those reported previously (1). The components methane, *trans*-decalin, phenanthrene, and *n*-dotriacontane were used in the same purities as in the previous studies. The *n*-butylbenzene was obtained from the Aldrich Chemical Co. and was certified to be better than 99% pure.

Constant molar ratio mixtures of the two heavier components of each ternary system were prepared from the pure components by weighing techniques. The mixtures were kept in closed bottles. Each sample bottle was heated prior to use so that the entire sample material was in the completely melted condition. The liquid sample was withdrawn from the sample bottle by means of an hypodermic syringe which had an 8-in. long capillary neck, and was introduced into the glass equilibrium cell. The mass of the material added to the equilibrium cell was determined by accurate weighing techniques.

During experimental vapor-liquid two-phase runs, methane was added to the equilibrium cell as superheated gas from a thermostated high-pressure bomb through use of a positive displacement mercury pump. The mass of gas added to the equilibrium cell was determined by straightforward stoichiometric computations. Methane dissolution into the liquid phase was greatly facilitated by stirring with a steel ball which was actuated by an override magnet outside the cell. At each equilibrium pressure, readings were taken of the

mass of gas added to the cell and liquid volume, noted from cell calibration markings or from cathetometer readings relative to a fiducial mark on the cell wall.

The experimental runs involving vapor-liquid-solid three-phase equilibria were similar to the vapor-liquid two-phase runs. The sole difference was that after each methane addition and stirring of the cell contents, the temperature of the cell was slowly lowered until crystallization could be observed; then the temperature of the cell was raised until only a few crystals remained in equilibrium with the liquid and vapor phases inside the cell. Generally, the procedure of cooling down to finite levels of crystallization and reheating to the true thermodynamic crystal point was repeated several times at slower rates. At the final crystal point, the cell tem-

Table I. Smoothed Values of Temperature vs. Composition Locus of Freezing Point Depression of Phenanthrene upon Addition of *trans*-Decalin at 1 atm abs

Temp, K	x_H , mol fraction of phenanthrene
371.77	1.0
365.2	0.9
359.1	0.8
353.5	0.7
348.2	0.6
343.3	0.5
337.8	0.4

Table II. Smoothed Values of Temperature vs. Composition Locus of Freezing Point Depression of *n*-Dotriacontane upon Addition of *n*-Butylbenzene at 1 atm abs

Temp, K	x_H , mol fraction of <i>n</i> -dotriacontane
342.41	1.0
341.2	0.9
339.3	0.8
337.8	0.7
336.3	0.6
334.8	0.5

Table III. Smoothed Values of Temperature vs. Composition Locus of Freezing Point Depression of Phenanthrene upon Addition of *n*-Butylbenzene at 1 atm abs

Temp, K	x_H , mol fraction of phenanthrene
371.77	1.0
364.6	0.9
357.8	0.8
350.9	0.7
344.1	0.6

perature, pressure, liquid volume, and stoichiometric methane gas addition data were taken.

Results

Tables I-III present the freezing point depression of phenanthrene by *trans*-decalin, dotriacontane by *n*-butylbenzene, and phenanthrene by *n*-butylbenzene, respectively. It is estimated that the temperatures are good to ± 0.2 °C.

Table IV gives the methane mole fraction and the liquid molar volume as a function of pressure at 70 and 100 °C for the binary system methane-*n*-butylbenzene. The average deviation in x_1 is ± 0.0029 , and the average deviation in v is ± 0.44 cc/g-mol.

Tables V-VII present the methane mole fraction and the liquid molar volume as a function of pressure for the three ternary vapor-liquid systems studied for several values of composition. For the systems containing phenanthrene (Ta-

Table VI. Smoothed Values of Methane Mole Fraction and Molar Volume as Function of Pressure Along Vapor-Liquid Isotherms at 70 °C for Mixtures of Ternary System Methane-*n*-Butylbenzene-*n*-Dotriacontane

P , atm	x_1 , mol fraction	v , cc/g-mol
	$(X_M/X_H) = 0.3053$	
10	0.0520	457.3
20	0.1012	436.3
30	0.1480	416.2
40	0.1914	398.0
50	0.2288	382.2
60	0.2591	369.5
	$(X_M/X_H) = 0.7757$	
10	0.0505	364.5
20	0.0989	353.6
30	0.1441	342.7
40	0.1840	331.8
50	0.2167	320.9
60	0.2419	310.0

Table IV. Smoothed Values of Methane Mole Fraction and Molar Volume as Function of Pressure for Vapor-Liquid System of Methane-*n*-Butylbenzene at Two Temperatures

P , atm	x_1 , mol fraction	v , cc/g-mol
	$T = 70$ °C	
10	0.0268	160.08
20	0.0529	156.90
30	0.0782	154.10
40	0.1029	151.51
50	0.1262	149.02
60	0.1476	146.61
	$T = 100$ °C	
10	0.0245	166.06
20	0.0491	163.00
30	0.0732	160.09
40	0.0968	157.48
50	0.1196	155.00
60	0.1411	152.59

Table VII. Smoothed Values of Methane Mole Volume as Function of Pressure Along Vapor-Liquid Isotherms at 100 °C for Mixtures of Methane-*n*-Butylbenzene-Phenanthrene

P , atm	x_1 , mol fraction	v , cc/g-mol
	$(X_M/X_H) = 0.3082$	
10	0.0160	164.33
20	0.0279	162.84
30	0.0410	161.39
40	0.0512	159.99
50	0.0617	158.70
60	0.0720	157.52
	$(X_M/X_H) = 0.9252$	
10	0.0177	164.58
20	0.0322	162.82
30	0.0463	161.13
40	0.0600	159.49
50	0.0734	157.86
60	0.0864	156.26

Table V. Smoothed Values of Methane Mole Fraction and Molar Volume as Function of Pressure Along Vapor-Liquid Isotherms at 100 °C for Mixtures of Ternary System Methane-*trans*-Decalin-Phenanthrene

P , atm	x_1 , mol fraction	v , cc/g-mol
	$(X_M/X_H) = 0.2885$	
10	0.0118	165.30
20	0.0423	163.97
30	0.0345	162.63
40	0.0454	161.31
50	0.0562	159.99
60	0.0666	158.67
	$(X_M/X_H) = 0.9123$	
10	0.0165	165.96
20	0.0317	164.18
30	0.0468	162.39
40	0.0616	160.60
50	0.0762	158.81
60	0.0904	157.01
	$(X_M/X_H) = 1.2619$	
10	0.0138	166.58
20	0.0310	164.55
30	0.0477	162.50
40	0.0642	160.46
50	0.0803	158.43
60	0.0963	156.40

Table VIII. Ternary Solid-Liquid-Vapor Data Points for Three Systems Studied at Several Values of (X_M/X_H) , Mole Ratio of Middle to Heavy Hydrocarbon Present

T , K	P , atm	x_1 , mol fraction	(X_M/X_H)	v , cc/g-mol
	Methane- <i>trans</i> -decalin-phenanthrene			
356.98	22.22	0.0303	0.2885	161.41
356.59	36.24	0.0471	0.2885	159.20
356.22	49.57	0.0632	0.2885	157.17
344.06	21.80	0.0398	0.9123	159.82
343.60	37.25	0.0625	0.9123	156.85
343.47	49.29	0.0803	0.9123	154.92
	Methane- <i>n</i> -butylbenzene- <i>n</i> -dotriacontane			
337.40	21.39	0.0938	0.3053	436.56
336.87	35.75	0.1746	0.3053	400.53
336.52	49.36	0.2238	0.3053	380.24
334.34	21.45	0.0987	0.7757	356.64
333.90	37.03	0.1684	0.7757	332.32
333.52	50.51	0.2207	0.7757	314.34
	Methane- <i>n</i> -butylbenzene-phenanthrene			
354.79	20.85	0.0276	0.3082	160.55
354.40	36.77	0.0439	0.3082	158.36
354.08	50.38	0.0605	0.3082	156.18
337.90	20.30	0.0301	0.9252	158.48
337.93	36.43	0.0534	0.9252	155.73
337.89	51.46	0.0739	0.9252	153.44
337.75	62.76	0.0892	0.9252	151.54

bles V and VII), the average deviation is ± 0.0012 in methane mole fraction and ± 0.21 cc/g-mol in v . For the system containing *n*-dotriacontane (Table VI), the average deviation is ± 0.0077 in methane mole fraction and ± 3.41 cc/g-mol in v . The latter deviations are larger due in part to the larger x_1 and v encountered in the *n*-dotriacontane systems.

Table VIII gives some data points for the three ternary S-L-V surfaces. For these points the major unreliability is in the temperature, which is good to ± 0.2 °C. The other data are at least good to the accuracies stated for Tables V-VII. Pressure could be read to ± 0.07 atm. Since Table VIII is "raw" data, the temperature is tabulated to two decimals, since our Pt resistance thermometer was accurate to ± 0.02 °C (1).

Nomenclature

P = pressure, atm
 T = temp, K

v = liquid mixture molar volume, cc/g-mol
 x = mole fraction

Subscripts

1 = methane
M = middle weight hydrocarbon
H = heavy hydrocarbon

Literature Cited

- (1) Cordeiro, D. J., Luks, K. D., Kohn, J. P., *Ind. Eng. Chem. Process Des. Dev.*, **12**, 47 (1973).
- (2) Cordeiro, D. J., Luks, K. D., Kohn, J. P., *AIChE J.*, **19**, 186 (1973).
- (3) Tan, F. O., Cordeiro, D. J., Luks, K. D., Kohn, J. P., *ibid.*, p 846.

Received for review August 28, 1975. Accepted December 1, 1975. Work supported by the American Petroleum Institute (Research Project No. 135). Comprehensive report on entire project available from API.

Equilibrium-Phase Properties of Carbon Dioxide-*n*-Butane and Nitrogen-Hydrogen Sulfide Systems at Subambient Temperatures

Harish Kalra, Thamra R. Krishnan,¹ and Donald B. Robinson*

Department of Chemical Engineering, University of Alberta, Edmonton, Alta., Canada T6G 2E1

Vapor and liquid equilibrium-phase compositions were determined at 50.0, 1.1, and -49.3 °F for the carbon dioxide-*n*-butane system and at -49.3 and -99.4 °F for the nitrogen-hydrogen sulfide system. The data for the 50.0 °F isotherm for the carbon dioxide-*n*-butane system were taken in a variable volume cell, and the remaining data in a constant volume cell designed for operation at low temperatures. Refractive index measurements of the equilibrium phases were made for the carbon dioxide-*n*-butane system at 50.0 and 1.1 °F. These measurements were used to determine phase densities by use of the Lorentz-Lorenz molar refractivity relationship.

To perform reliable design calculations with petroleum reservoir fluids or natural gas systems, it is desirable to have good data on all binary pairs that constitute the system. Binary data are necessary to determine the interaction parameters required in equations used to predict multicomponent phase behavior. Previous work on the carbon dioxide-*n*-butane system by Poettman and Katz (6), Olds et al. (5), and Besserer and Robinson (7) covered a temperature range from 80 to 280 °F. Earlier work on the nitrogen-hydrogen sulfide system by Besserer and Robinson (2) was in the range from 0 to 160 °F. However, increased interest in industrial processes which operate at temperatures significantly lower than those referred to above suggested that it would be useful to extend the data on these systems down to the -50 or -100 °F range.

¹ Present address, Black, Sivals, and Bryson Ltd., Edmonton, Alta., Canada.

Accordingly, the information presented in this paper is based on a study of the coexisting phase properties of the carbon dioxide-*n*-butane system between 50 and -50 °F at pressures between the vapor pressures of normal butane and carbon dioxide and of the nitrogen-hydrogen sulfide system at -50 and -100 °F to pressures of 2000 psia.

Experimental Method

The data at 50 °F for the carbon dioxide-*n*-butane system were obtained using a variable volume cell in which the vapor and liquid mixture under investigation was confined between two movable pistons. The pressure of the cell contents and the location of the phases within the cell were varied by altering the relative position of the pistons using a double-acting two-cylinder Ruska pump. The refractive index of either phase viewed in the observation port was calculated from measurements made with a special window and mirror arrangement and an autocollimating telescope. These made it possible to obtain the minimum angle of deviation of a ruby laser ray passed through the window and cell contents, reflected off the mirror, and back out through the window. The details of this equipment and the method of operation have been given by Besserer and Robinson (7).

The data at all other temperatures were obtained in a recently designed constant volume cell capable of operating at much lower subambient temperatures. The materials under investigation were charged to the cell at the required pressure and at a temperature determined by the surrounding cryostat. Equilibrium between phases was obtained by a magnetic stirrer coupled externally to rotating magnets. This cell was also provided with a window and mirror arrangement and an autocollimating telescope for making refractive index