EQUILIBRIUM DATA DETERMINATION FOR SYSTEM OF METHANE AND HEPTANE

J. Alaei and M. Tajerian

Research Institute of Petroleum Industry-Tehran IRAN

Abstract. This work presents vapor-liquid equilibrium determination for a binary system of methane and heptane. The static method and an equipment like the one that Van Ness used for this research has been used. Temperature and pressure ranges for operation are 80.6-205 °F and 100-3120 Psia, respectively. *Key words:* methane, heptane, equilibrium

Introduction

Various techniques are applied for phase equilibrium determination that generally are divided into two methods:

1) Static methods 2) Dynamic methods.

In static methods, the mixture of liquid and gas reaches to the equilibrium in a closed chamber and then sampling for analyzing is taken. At low pressures, since density of vapor phase is low, therefore sampling from vapor phase is taken (Inoue, 1975) [1] or concentration of vapor phase is calculated by gas chromatography technique (Holldrof & knapp, 1988) [2], (Lepori and Matteoli, 1988) [3].

Also, another analyzing method of vapor phase concentration is "Infrared Spectrum" (Mckeigue & Gualri, 1986) [4]. At high pressures, the concentration of liquid phase is determined by other methods (Prausnitz & Hermsen, 1962) [5]. A simpler method in static equilibrium instead of sampling, is the recording of variables of system such as equilibrium temperature and pressure (Van Ness & Gibbs, 1972) [6].

It should be mentioned that during this method, the liquid feed should be degassed before experiment because, in determination of real vapor pressure in the chamber, little quantity of gases in liquid feed causes some problems. For degassing, there are different methods: purification method with vacuum (bell, 1968) [7]and/ or vacuum distillation (Abbot and Van Ness, 1978) [8].

The second method in VLE calculation, is dynamic method in which there are one or two continuous phases. For the first time, the concept of continuous flow in phase equilibrium determination invented by Simnick, et al., 1977. The specialty of this method is that, a lot of samples may be simply taken and the residence time for equilibrium is short time. Another method of dynamic methods, is circulation method based on circulation of one phase, for example volatile substance as a gas is entered to the liquid and the exit gas is analyzed (Setier & Blanc, 1988)[9].

This method idiomatically is named" Recirculation of Gas Phase".

Hala (1967) reviewed over these equipments until 1965. A good type of these equipment was constructed by Malanoswki: (1980). In this apparatus, there was the possibility of circulation of two phase (vapor and liquid). Malanoswki (1982) reviewed different types of these apparatuses completely [11].

The selected method in this research is static method for equilibrium pressure determination that is the best and fast method with a high accuracy. The advantage of this method is that no sample from vapor or liquid is taken during experiments, therefore all problems and difficulties related to their analyses is eliminated.

Experimental Apparatus

The apparatus used in this research is similar to the apparatus that Van Ness and Gibbs used [6].

The instruction of this equipment is very simple. This apparatus has an equilibrium cell that is equipped with an air bath. This cell works at a constant temperature and is equipped with a shaker. This cell is able to work from atmospheric pressure to 6000 Psia for transferring the vapor and liquid phase to this cell, two separate pumps are used that work with mercury piston and the accuracy of them is about 0.001 meat constant pressure. Before transferring each phase, the liquid phase should be degassed. For this purpose" Rasca cylinder" is used. The schematic diagram of this apparatus is in Figure 1.

Experimental Procedure

The procedure of determination of experimental equilibrium data for Methane- Heptane system is as follows:

1. First, Heptane liquid with purity about 99.5% should be degassed. For this purpose, this liquid is transferred to rasca cylinder and with decreasing pressure by vacuum pump, the in solved gases in liquid is separated. This stage is repeated several times.

2. After degassing, Heptane is transferred to the equilibrium cell by injection pump. The volume of injected liquid is recorded.

3. The density of liquid is calculated by dens meter with accuracy about 0.0001, and the amount of injected mole or weight is indicated.

4. Then the second component (Methane) with purity about 99.99% is entered to the cell. Temperature and pressure should be constant during the injection, thus the amount of Methane mole is calculated.

5. For reaching to the thermal and thermodynamic equilibrium, system should be held under a specific conditions for six hours. Then equilibrium pressure and liquid volume is recorded.

6. For saving time and material, we keep this cell at various

temperatures and after reaching to the thermal equilibrium, the equilibrium pressure and liquid volume is recorded again.

7. Then the cell is drained and washed and then repeat all the stages with another amount of Methane for having various mole fractions (z).

Experimental Example

First, 73.7288 cm³ of Heptane is injected to the cell. This amount is equal to 0.5 mole of Heptane at 80.6 °F. Then 2.5 cm³ Methane at a pressure about 3675 psig and ambient temperature (68 °F) is injected to the cell. The equilibrium pressure after several hours will be 100 psig.

Determination of equilibrium pressure and liquid volume is done at 105, 130, 155, 180 and 205 °F temperatures. For reaching to the thermal and thermodynamic equilibrium of each temperature, system is held for 6 hours. These experimental results are given in table 1.

Experimental Results

The above experiment is repeated by adding other amounts of Methane

 $(5, 12.5, 21, 33, 45 \& 50 \text{ cm}^3)$ to the cell at pressure about 3675 psig and ambient temperature. These results are given in the tables 2 to 7.

Table 1. Experimental Results of 2.5 cc Methane injection to the	
system	

	system					Methar	ne Injection
68 °F	=	-	70.:	5°F	=		•
		-	12.5	5 cc	=		ne Injection e
73.7288 cc		5	73.7288	8 cc	=		e Injection e
3675psi	=	-	3675	5psi	=		re Injection re
Equilibrium temperature (°F)	•	• • •	Equilibrium temperature (°F)]	pressu	ıre	Liqu'id pl volum (cc)
80.6	100	75.131					
			80.6		368		75.39
			105		394		77.75
			130		420		78.39
155	120	79.670	155		450		80.09
180	130	81.501	180		490		83.13
205	140	82.951	205		519		83.97
	3675psi Equilibrium temperature (°F) 80.6 105 130 155 180	$\begin{array}{rcl} 68 & F & = & T \\ 2.5 & cc & = & M \\ \hline 2.5 & cc & = & M \\ \hline 73.7288 & cc & = & H \\ \hline 3675 & psi & = & M \\ \hline P1 \\ \hline Equilibrium \\ temperature \\ (^{\circ}F) & (psig) \\ \hline 80.6 & 100 \\ \hline 105 & 107 \\ \hline 130 & 118 \\ \hline 155 & 120 \\ \hline 180 & 130 \\ \end{array}$	$\begin{array}{rcl} 68 \ {}^{\mathrm{o}}\mathrm{F} &=& \begin{array}{c} \mathrm{Methane\ lnjection\ Temperature\ }}\\ 2.5 \ \mathrm{cc} &=& \ \mathrm{Methane\ lnjection\ Volume\ }}\\ 73.7288 \ \mathrm{cc} &=& \ \mathrm{Heptane\ lnjection\ Volume\ }}\\ 3675 \ \mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ lnjection\ }\\ \mathrm{Methane\ lnjection\ }\\ \mathrm{Pressure\ }\\ \end{array}$	$\begin{array}{rcl} 68\ {}^{\circ}\mathrm{F} &=& \displaystyle \underset{\mathrm{Temperature}}{\operatorname{Methane Injection}} & 70. \\ 68\ {}^{\circ}\mathrm{F} &=& \displaystyle \underset{\mathrm{Temperature}}{\operatorname{Temperature}} & 12. \\ 2.5\ \mathrm{cc} &=& \displaystyle \operatorname{Methane Injection Volume} & 73.728 \\ 73.7288\ \mathrm{cc} &=& \displaystyle \operatorname{Heptane Injection} & \operatorname{Volume} & 73.728 \\ 3675\mathrm{psi} &=& \displaystyle \underset{\mathrm{Pressure}}{\operatorname{Methane Injection}} & 367. \\ \hline \\ $	$\begin{array}{rcl} 68\ {}^{\circ}\mathrm{F} &=& \begin{array}{c} \mathrm{Methane\ Injection\ Temperature\ }} & 70.5\ {}^{\circ}\mathrm{F} \\ 2.5\ \mathrm{cc} &=& \mathrm{Methane\ Injection\ Volume\ }} & 12.5\ \mathrm{cc} \\ 73.7288\ \mathrm{cc} &=& \mathrm{Heptanc\ Injection\ Volume\ }} & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ Injection\ } & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ Injection\ } & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ Injection\ } & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ Injection\ } & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ Injection\ } & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} &=& \begin{array}{c} \mathrm{Methane\ Injection\ } & 73.7288\ \mathrm{cc} \\ 3675\mathrm{psi} & 3675\mathrm{psi} \\ \end{array} \end{array}$	$68 \ ^{\circ}F$ =Methane Injection Temperature70.5 \ ^{\circ}F= $2.5 \ cc$ =Methane Injection Volume $12.5 \ cc$ = $73.7288 \ cc$ =Heptane Injection Volume $73.7288 \ cc$ = $3675psi$ =Methane Injection Pressure $3675psi$ =Equilibrium temperature (°F)Equilibrium (psig)Liquid phase volume (cc)Equilibrium (°F)Equilibrium (psig) 80.6 100 75.131 80.6 368 105 107 76.694 105 394 130 118 78.933 130 420 180 130 81.501 180 490	Nethane Injection TemperatureTemperature $.68 \ ^{\circ}F$ =Methane Injection Temperature $70.5 \ ^{\circ}F$ =Methane Temperature $2.5 \ cc$ =Methane Injection Volume $12.5 \ cc$ =Methane Volume $73.7288 \ cc$ =Heptane Injection Volume $73.7288 \ cc$ =Heptane Volume $3675psi$ =Methane Injection Pressure $3675psi$ =Methane Methane PressureEquilibrium temperature ($^{\circ}F$)Equilibrium (psig)Liquid phase volume (cc)Equilibrium ($^{\circ}F$)Equilibrium (psig) 80.6 100 75.131 80.6 368 105 107 76.694 105 394 130 118 78.933 130 420 155 120 79.670 155 450 180 130 81.501 180 490

Density of injected Methane at the above temperature and pressure is (0.1884 gr/cc).

Table 2. Experimental Results of 5cc Methane injection to the system

	syste	em			
70 °F	=	Methane Injection Temperature			
5 cc	=	Methane Injection Volume			
73.7288 сс	=	Heptan	e Injection Volume		
3675psi	=	Methar Pressur	e Injection e		
Equilibrium temperature (°F)	Equili press (ps	sure	Liquid phase volume (cc)		
80.6	18	0	74.197		
105	18	4	76.360		
130	18	8	77.075		
155	20	0	78.096		
180	21	5	81.017		
205	23	0	82.056		

Density of injected Methane at the above temperature and pressure is (0.1873 gr/cc).

Table 3. Experimental Results of 12/5cc Methane injection to the system

me	12.5 c	c =	Methane Injection Volume
me	73.7288 c	c =	Heptane Injection Volume
	3675ps	si =	Methane Injection Pressure
e	Equilibrium temperature (°F)	Equilib pressu (psig	ure volume
	80.6	368	3 75.390
	105	394	4 77.755
	130	420	78.395
	155	450	80.094
	180	490	83.134
	205	519	83.973

Density of injected Methane at the above temperature and pressure is (0.1869 gr/cc).

	system		
69.5 °F		Methane Injection Temperature	
21 cc		Methane Injection Volume	
73.7288 сс		Heptane Injection Volume	73.7
3675psi	=	Methane Injection Pressure	:
Equilibrium H temperature (°F)	Equilibriu pressure (psig)		Equilibrium temperature (°F)
80.6	648	77.272	80.6
105	724	79.242	105
130	748	80.282	130
155	155 790		155
180	853	84.866	180
205	900	86.707	205

Table 4. Experimental Results of 21cc Methane injection to the

Density of injected Methane at the above temperature and pressure is (0.1876 gr/cc).

Table 5. Experimental Results of 33cc Methane injection to the system			Table 7. Experimental Results of 50cc Methane injection to the system				
63 °F	=	Methane Tempera	Injection ture	60 °F	=	Methane I Temperatu	
33 cc	=	Methane Volume	Injection	50 cc	=	Methane I Volume	njection
73.7288 cc	=	Heptane Vo lu me	Injection	73.7288 сс	c = Heptane Injection Volume		njection
3675psi	=	Methane Injection Pressure		3675psi	=	Methane Injection Pressure	
Equilibrium E temperature (°F)	Quilib pressu (psig	ıre	Liquid phase volume (cc)	Equilibrium temperature (°F)	pre	librium ssure sig)	Liquid phase volume (cc)
80.6	104	7	77.894	80.6	1.	591	79.817
105			80.466	105	1	670	83.489
130	130 1247		82.816	130	1	740	87.634
155	155 1390		84.068	155	1	860	89.614
180	180 1420		87.310	180	2000		94.465
205			90.050	205	2	120	98.114

Density of injected Methane at the above temperature and pressure is (0.1913 gr/cc).

Table 6. Experimental Results of 45cc Methane injection to the system

=

=

=

=

Equilibrium

pressure

(psig)

1360

1460

1585

1692

1808

1923

60 °F

45 cc

73.7288 cc

3675psi

Methane Injection

Heptane Injection

Methane Injection

Liquid phase

volume

(cc)

78.112

80.586

83.437

86.685

89.034

91.282

Temperature Methane Injection

Vo lu me

Vo lu me

Pressure

Density of injected Methane at the above temperature and pressure is (0.1931 gr/cc).

Density of injected Methane at the above temperature and pressure is (0.1931 gr/cc).

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