

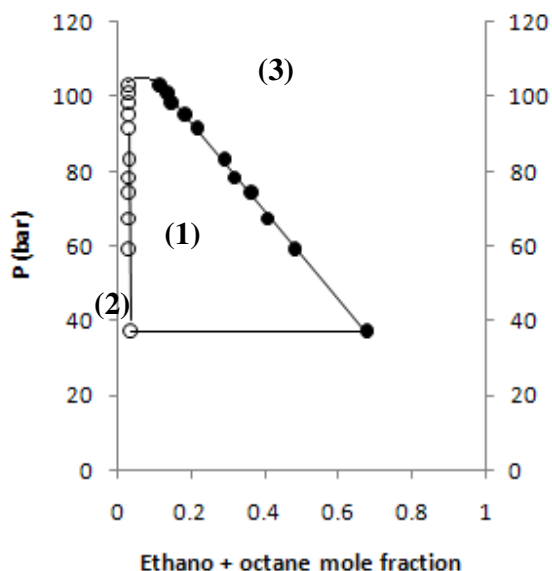
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PHASE EQUILIBRIUM DATA STUDY WITH CARBON DIOXIDE SOLVENT FOR 80.52:19.48 OF ETHANOL-OCTANE MIXTURE AT ELEVATED PRESSURE

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GRAPHICAL ABSTRACT

Solubility data of a mixture containing 80.52 % ethanol and 19.48 % octane was measured in carbon dioxide solvent using a high-pressure type phase equilibrium apparatus at pressures up to 100 bar and at temperature of 75 °C. The experimental results showed that considerable separation was not achieved in this ethanol and octane ratio using carbon dioxide. From the point of view of the phase diagram for the current ternary system, the experimental results showed a closed loop. There was a two-phase region (vapor-liquid) in area (1) for ethanol-octane and CO₂ mixture. Furthermore, there was a one-phase region (liquid phase) in area (2) for the studied mixture. There also was a one-phase region (vapor phase) in area (3) for current mixture. According to the ethanol mole fractions extracted from the ternary system was investigated no effect of pressure on the solvent-free molar fraction of ethanol in both, the vapor and liquid phases.



Two Phases Equilibrium Data (Phase Diagram) Based on Experiment for Ethanol-Octane (Heavy Component) Substances. o: Ethanol-octane liquid phase data, ●: Ethanol-octane vapor phase data.

Keywords: Ethanol-Octane; Solubility; Supercritical CO₂; Vapor-liquid equilibria

INTRODUCTION

Many researchers have proven that carbon dioxide is chemically reactive toward alcohols, general oxygen-containing compounds and it also produces weak complexation in condensed mixtures of these substances [1-5].

However, percentage of octane and ethanol extraction by high pressure CO₂ solvent increases with a decrease of pressure in the binary systems of CO₂-octane and CO₂-ethanol respectively, but extraction percentage of ethanol is more than octane at the same conditions [5]. Furthermore, the azeotrope of the ethanol-octane systems occurs at around a ratio of ethanol: octane = 84: 16 [4], similar to the chosen ethanol-octane ratio in this study.

Recently some researchers have theoretically studied mutual solubilities of some natural hydrocarbons from petroleum production as a function of pressure [6, 7]. They predicted equilibrium data for binary water-hydrocarbon, alcohol-hydrocarbon and other complex mixtures systems by applying associating fluid equations of state.

Browarzik (2004) theoretically studied vapor-liquid equilibrium for ethanol-octane system and the other binary systems containing alkane-alkanol [8]. The research for the case of ethanol-octane system was conducted at two temperatures of 75 °C and 45 °C.

According to this case, two closed loops were observed at temperature of 45 °C and 75 °C respectively. The former was at pressure less than 0.2 bar whereas the later was at pressure between 0.2 bar and 0.9 bar. An azeotrope point was observed at ethanol mole fraction of 0.864 for this mixture in both of loops. On the other hand, these results were supported by experimental data reported by Goral et al. [9].

Gupta et al. have studied solubilities of ethanol in compressed CO₂ at pressures ranging from 10 to 60 bar and at temperatures of 25, 50 and 75 °C [3]. They clearly showed that temperature increased ethanol solubility in CO₂. Furthermore, solubility decreased with increasing pressure of CO₂.

Solubilities of octane in CO₂ at temperatures of 17 °C and 38 °C and pressures up to 36.7 bar were studied by Wang et al. [10]. They concluded that solubility decreased with increasing pressure. Furthermore, temperature increased octane solubility in CO₂ at the similar pressures.

In this research, the mutual feasibility of a ternary system containing 24.2 % mole ratio octane to ethanol (as heavy component), using supercritical and slightly sub critical carbon dioxide solvent was studied.

MATERIALS

A solution of ethanol (99.9 %, J.T. Baker) and octane (99.8 %, J.T. Baker) involving 80.52 % ethanol and 19.48 % octane used for supercritical extraction process, using CO₂ (99.99 %) which purchased from MOX factory. Extracted samples from the apparatus were analyzed by gas chromatography (GC).

EXPERIMENTAL PROCEDURE

The equipment used was the phase equilibrium re-circulation high-pressure type apparatus as shown in Fig. 1 (fabricated by Alpha Dynamic Sdn. Bhd).

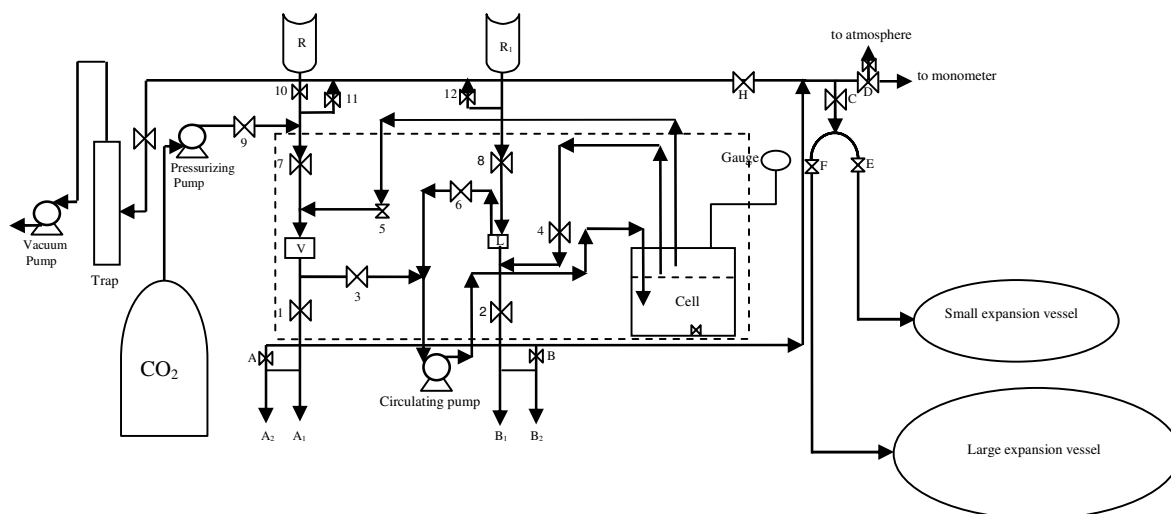


Figure 1: Supercritical Apparatus Scheme

In this apparatus the attainment of equilibrium was further assisted by magnetic stirrer which was installed in the equilibrium vessel. All units of the apparatus, i.e. the equilibrium cell (volume 500 cm³), the joining tubes, vapor and liquid sample bombs (volume 50 and 40 cm³), couplings and valves were made of stainless steel and designed to withstand a working pressure of 500 bar. The part of the equipment shown within the dash line was immersed in an air bath. The temperature in the equilibrium cell was measured using a digital thermocouple.

When the cell and the circuit were under vacuum, the heavy component under study (ethanol-octane as feed) was fed into the equilibrium cell. This was accomplished by first filling the reservoir (R₁) with about 120 cm³ of this liquid. The liquid heavy component was then allowed to go directly into the cell by turning on valve 8 and turning off valve 6. Having charged the cell with the heavy component, CO₂ at cylinder pressure was admitted to the cell. A high pressure pump connected between the cylinder containing the contacting CO₂ and the cell was then switched on to pressurize the cell. In the filling process, the heaters for the cell, the air bath and also the bath fan were switched on. As the cell was brought to the desired pressure, valve 6 and 3 were turned off, and the cell was carefully brought to the desired temperature. This was accomplished using a fine control on the heater outputs, which were gradually increased to obtain the required temperature. Equilibration and sampling would be achieved when the required temperature (by controlling and observing the temperature indicator) and pressure (by controlling and observing the pressure gauge) were reached and remained constant (equilibrium condition); the pneumatic re-circulating pump and the magnetic stirrer were turned on at the same time. Then valve 6 was opened and after a few seconds valve 3 was also opened. The reason for this was to avoid any droplets of solvent passing through the vapor sample bomb flow section. The pump and stirrer were left on for about 30 minutes, to ensure that equilibrium has been achieved. When equilibrium was resumed, the pump and stirrer were turned off and internal valves 3, 5, 4 and 6 were kept open. The phases were then allowed to stand in contact with each other for about 30 minutes to allow any

bubbles in the liquid to become disengaged. After the period of 30 minutes, the vapor sample bomb and the liquid sample bomb were isolated by turning off valves 3 and 5 (for the vapor sample bomb) and valves 4 and 6 (for the liquid sample bomb). Samples of the gas and liquid phases were then extracted from vapor bomb and the liquid bomb through valves 1 and 2 respectively.

The samples taken from A and B were vapor and liquid sample respectively, then it were analyzed by GC (Perkin Elmer) which had been equipped with a capillary GC column (length \times I.D. 30 m \times 0.32 mm, d_f 1.00 μ m, Supelco brand).

In term of uncertainty, the validity of the experimental data was already proposed by King et al. [11]. The experimental data were produced based on the average of the two repeat runs performed for each data point. The repeat runs ensured that the experiments could be repeated within an experimental error of $\pm 2\%$.

RESULTS AND DISCUSSION

A) The mutual solubility of CO₂-ethanol-octane ternary system was studied at temperature of 75 °C and at various pressures. The composition of the equilibrium phases was obtained at each pressure. The mole fractions of ethanol in the liquid and vapor phases on a carbon dioxide free basis were calculated from following equations:

$$X_1 = \frac{(nx_1)^L}{[(nx_1)^L + (nx_2)^L]} = \frac{\bar{R}}{1 + \bar{R}} \quad (1)$$

$$Y_1 = \frac{(nx_1)^G}{[(nx_1)^G + (nx_2)^G]} = \frac{\bar{R}_1}{1 + \bar{R}_1} \quad (2)$$

where,

$(nx_1)^L$: number of moles of ethanol in the liquid phase on a carbon dioxide free basis.

$(nx_1)^G$: number of moles of ethanol in the vapor phase on a carbon dioxide free basis.

$(nx_2)^L$: number of moles of octane in the liquid phase on a carbon dioxide free basis.

$(nx_2)^G$: number of moles of octane in the vapor phase on a carbon dioxide free basis.

$$\bar{R} = (nx_1)^L / (nx_2)^L$$

$$\bar{R}_1 = (nx_1)^G / (nx_2)^G$$

\bar{R} and \bar{R}_1 were taken directly from the calibration chart when the ratio of the corresponding peak heights obtained from the chromatographic analyses of the liquid and vapor samples.

The calculations for the mole fraction of carbon dioxide in the liquid phase (X) and in the vapor phase (Y) of this system were carried out using the following equations:

$$Y = \frac{(ny)^G}{[(nx)^G + (ny)^G]} \quad (3)$$

$$(1 - X) = \frac{(nx)^L}{[(ny)^L + (nx)^L]} \quad (4)$$

where,

$(ny)^G$: number of moles of carbon dioxide in the vapor sample bomb.

$(nx)^G$: number of moles of heavy component in the vapor sample bomb.

$(ny)^L$: number of moles of carbon dioxide in the liquid sample bomb.

$(nx)^L$: number of moles of heavy component in the liquid sample bomb.

The values of $(nx)^L$ and $(nx)^G$ were calculated from the following relationship:

$$(nx)^L \text{ or } (nx)^G = \frac{(\text{weight of extracted heavy components})}{(x_A M_A + x_B M_B)}$$

where,

x_A = mole fraction of ethanol in the liquid sample bomb (or in the vapor sample bomb).

x_B = mole fraction of octane in the liquid sample bomb (or in the vapor sample bomb).

M_A = molecular weight of ethanol (46.07 g. mole⁻¹).

M_B = molecular weight of octane (114.23 g. mole⁻¹).

In the liquid bomb calculations, x_A and x_B were calculated from \bar{R} by using the following equations:

$$x_A = \frac{\bar{R}}{1 + \bar{R}}$$

$$x_B = \frac{1}{1 + \bar{R}}$$

In order to calculate $(ny)^G$ and $(ny)^L$ it is necessary to consider deviation from the perfect gas law pressure for the present situation it may be conveniently expressed by the following equation:

$$P V = n(RT + B_v P)$$

P : pressure, V : system volume, n : number of moles of gas, B_v : second virial coefficient.

This equation leads directly to the expression

$$(ny)^G = V \left[\frac{P_2}{RT + B_v P_2} - \frac{P_1}{RT + B_v P_1} \right] = VP_2 \left[\frac{1 - \left(\frac{P_1}{P_2}\right) \left(\frac{RT + B_v P_2}{RT + B_v P_1}\right)}{(RT + B_v P_2)} \right] \quad (5)$$

for the number of mole of gas in the vapor sample bomb.

where, P_1 and P_2 are expansion vessel pressure before and after expansion and V is the volume of the system (35 liters).

The number of moles of CO₂ in the liquid sample bomb, $(ny)^L$, was calculated by using exactly the same procedure as that given above except that total volume of the expansion system (V) was taken as 7 liters.

Because of the proportion of heavy component extracted into the vapor phase was comparatively small, majority of it was maintained in the liquid phase without changing throughout the tests. The mole fraction of ethanol in the liquid and vapor phases were calculated on a carbon dioxide free basis at the pressures studied. The results obtained are given in Table 1.

Table 1: Composition of the Equilibrium Vapor and Liquid Phase for System CO₂-Ethanol- Octane

P (bar)	Vapor phase, ethanol mole fraction on CO ₂ free basis	Liquid phase, ethanol mole fraction on CO ₂ free basis	Vapor phase, CO ₂ mole fraction	Liquid phase, CO ₂ mole fraction
102.75	0.8118	0.8048	0.9688	0.8850
100.75	0.8121	0.8048	0.9692	0.8625
98.25	0.8124	0.8052	0.9686	0.8508
95.00	0.8128	0.8052	0.9692	0.8150
91.50	0.8133	0.8048	0.9693	0.7851
83.00	0.8144	0.8050	0.9698	0.7115
78.50	0.8149	0.8048	0.9694	0.6851
74.00	0.8156	0.8052	0.9693	0.6351
67.50	0.8164	0.8049	0.9695	0.5951
59.00	0.8176	0.8048	0.9684	0.5211
36.90	0.8260	0.8051	0.9642	0.3250

This table also shows no effect of pressure on the solvent-free molar fraction of ethanol in both, the vapor and liquid phases. The equilibrium data of the two phases in equilibrium given in Table 1, based on ethanol-octane (heavy component) substances are plotted as function of pressure in Fig. 2.

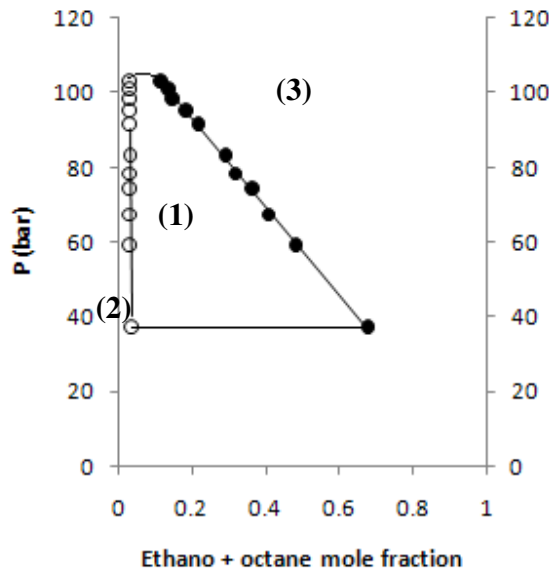


Figure 2: Two Phases Equilibrium Data (Phase Diagram) Based on Experiment for Ethanol-Octane (Heavy Component) Substances. o: Ethanol-octane liquid phase data, ●: Ethanol-octane vapor phase data

It was observed that the saturation curves for the vapor and liquid phase are nearly linear. The results also showed that there was a two-phase region (vapor-liquid) in area (1) for ethanol-octane and CO₂ mixture. Furthermore, there was a one-phase region (liquid phase) in area (2) for the studied mixture. There also was a one-phase region (vapor phase) in area (3) for current mixture.

Fig. 3 shows that the liquid phase composition for the system CO₂-ethanol-octane at 75 °C as a function of pressure (these data interpolated from the data in Table 1)

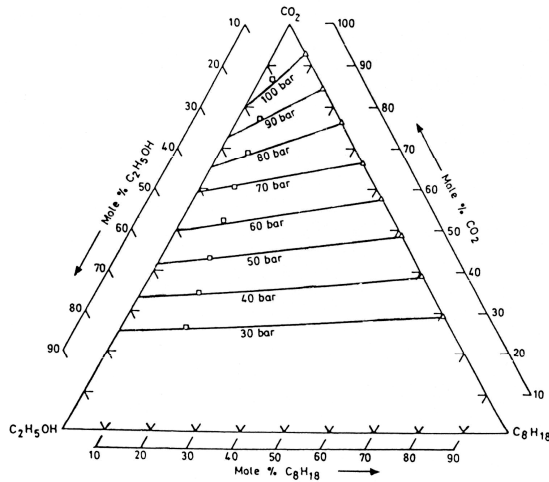


Figure 3: Liquid Composition for the System CO₂- Ethanol-Octane as a Function of Pressure at 75°C. □: This work, Δ: Interpolated from [12]

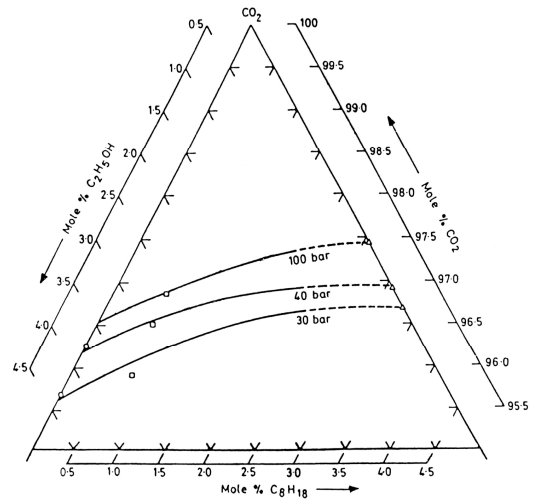


Figure 4: Vapor Composition for the System CO₂- Ethanol-Octane as Function of Pressure at 75°C. □: This work, Δ: Interpolated from [12], o: Interpolated from [3]

It is observed that the saturation curve for the liquid phase is nearly linear. The liquid phase data for the CO₂-ethanol binary were also obtained and illustrated in Figure 4. The data for CO₂-octane binary were interpolated from the reported data by Alderson [12]. Vapor phase data for the CO₂-ethanol binary system were obtained from another reference [3] and illustrated in Fig. 4.

Fig. 4 shows vapor phase composition as a function of pressure at the same temperature for the same system (these data also interpolated from the data in Table 1) but the saturation curves for the vapor phase are not as linear.

Fig. 5 shows the compositions of both the vapor and liquid phases at 75 °C and at pressure of 100 bar. The tie lines are also shown in this figure. It is observed that for the applied ethanol-octane ratio in this study, the ratio in the vapor phase was greater than that in the liquid phase. Along the azeotrope tie line the mole ratio of octane-ethanol was constant.

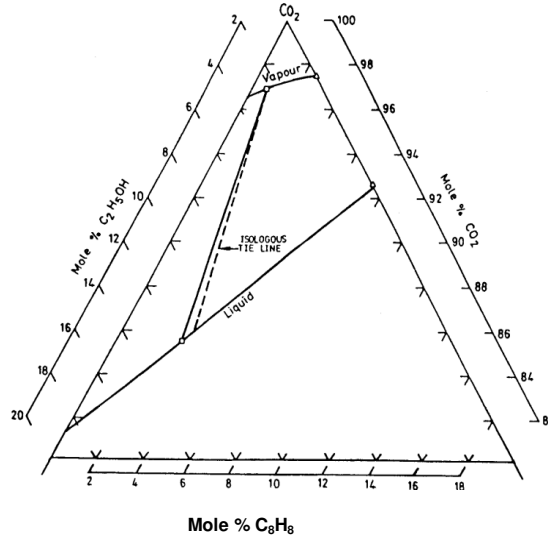


Figure 5: Vapor and Liquid Compositions for the CO₂ -Ethanol-Octane System at 100 bar and at 75 °C. □: This work, Δ: Interpolated from [12]. azeotrope composition extracted from [4]

The precision of the experimental results due to vapor phase composition is the overall weight fraction of the heavy components for the ternary system as followed:

$$X_w = \frac{m}{m + 44.01 \times n_G} \approx \frac{m}{44.01 n_G} \quad (6)$$

where n_G is number of molecules of CO₂ entering the expansion system and is given approximately by:

$$n_G = \frac{V \Delta P}{RT} \quad (7)$$

where V , ΔP , T and m are volume of the expansion system, pressure rise in the expansion system, absolute temperature of the expansion system and mass of heavy component collected respectively. The overall mole fraction of heavy component in the vapor phase is likewise given by:

$$X_M = \frac{m/M}{m/M + n_G} \approx \frac{m}{M n_G} \quad (8)$$

where, M is the molecular weight of the heavy component (or the average molecular weight of the heavy components in the case of the ternary system).

Examination of Eqs. (6), (7) and (8) shows that the calculated mole and weight fraction are affected by the errors in the pressure rise, in the absolute temperature of the expansion system and in the mass of heavy component collected. The error function $\varepsilon(x_w)$ arising from errors $\varepsilon(\Delta P)$ in ΔP , $\varepsilon(T)$ in T and $\varepsilon(m)$ in m may be obtained by differentiation [13].

In the vapor phase composition the errors in the weight $\varepsilon(x_w)$ and mole $\varepsilon(x_M)$ fraction of CO₂-ethanol-octane system at 75 °C are shown in Table 2. These are equal to

the absolute errors $\varepsilon(x_w)$ and $\varepsilon(x_M)$ in the overall weight and mole fraction of the heavy component present.

Table 2: Uncertainties $\varepsilon(x_w)$ in the Vapor Phase Weight and Mole Fraction from the System Carbon Dioxide-Ethanol-Octane at 75 °C

P (bar)	$x_M \times 10^2$	$x_w \times 10^2$	$\varepsilon(x_M) \times 10^4$	$\varepsilon(x_w) \times 10^4$	$\varepsilon(x_M)/x_M \times 10^2$
30	2.129	3.880	1.75	3.19	0.82
40	2.464	4.494	1.86	3.38	0.76
75	2.697	4.916	1.29	2.35	0.48
100	2.884	5.270	0.98	1.78	0.34

Table 3: Uncertainties $\varepsilon(x_w)$ in the Liquid Phase Weight and Mole Fraction from the System Carbon Dioxide-Ethanol-Octane at 75 °C

P (bar)	$x_M \times 10^2$	$x_w \times 10^2$	$\varepsilon(x_M) \times 10^4$	$\varepsilon(x_w) \times 10^4$	$\varepsilon(x_M)/x_M \times 10^2$
30	0.64	0.764	1.52	1.190	0.238
40	0.407	0.555	0.974	0.997	0.239
75	0.097	0.164	0.236	0.369	0.243
100	0.022	0.039	0.058	0.103	0.269

A maximum error (of 0.82%) was observed at pressure of 30 bar while a minimum error (of 0.34%) was obtained at pressure of 100 bar. The errors in the individual weight and mole fraction in the ethanol and octane are expected to be greater than that arising from the chromatographic analysis of the condensate, but it is believed that these are trustworthy over the entire range. In the liquid phase composition the absolute errors in the weight and mole fractions of CO₂ in the CO₂-ethanol-octane system at 75 °C are shown in Table 3. These are equal to the absolute errors $\varepsilon(x_w)$ and $\varepsilon(x_M)$ in the overall weight and mole fraction of the heavy component.

A maximum error (of 0.269%) was observed at pressure of 100 bar while a minimum error (of 0.238%) was obtained at pressure of 30 bar. In this case, the errors in the individual weight and mole fraction in the ethanol and octane are expected to be greater than that arising from the chromatographic analysis of the condensate.

CONCLUSIONS

In this research, feasibility of a ternary system involving CO₂-ethanol-octane at various pressures and at temperature of 75 °C was studied however the binary systems of ethanol-CO₂, octane-CO₂ and ethanol-octane were already studied by other researchers. Although the similar trend was observed for binary systems of ethanol-CO₂ and octane-CO₂ but azeotrope points were observed for closed loops of binary system of ethanol-octane while similar behavior was observed for current ternary system. On the other hand, from view point of phase diagram, ethanol-octane binary system has shown two closed loops (two-phase) from pressure ranging 0.2 bar to 0.9 bar and ethanol mole fractions ranging from zero to 0.864 and from pressure ranging 0.8 bar to 0.9 bar and ethanol mole fractions ranging from 0.864 to one. Ethanol mole fractions increases with increasing the pressure in the vapor and liquid phases for ethanol mole fractions ranging from zero to 0.864 while ethanol mole fractions increased with decreasing pressure for ethanol mole fractions from ranging 0.864 to one. The experimental results showed that

considerable separation was not achieved in this ethanol and octane ratio. Ethanol-octane-CO₂ ternary system phase diagram with phases behavior was described in detail in this research.

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