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Experimental Measurement and Equation of State Modeling of Liquid Saturated Properties (Solubility, Density, and Viscosity) of (Ethane + *n*-Octadecane) Binary Systems

Hossein Nourozieh, Mohammad Kariznovi, and Jalal Abedi*

Department of Chemical & Petroleum Engineering, University of Calgary, Calgary, Canada

ABSTRACT: The liquid saturated properties (solubility, density, and viscosity) data for binary system of ethane + *n*-octadecane at three temperatures (323, 373, and 423) K and pressures up to 8 MPa were measured using a designed pressure−volume−temperature (PVT) apparatus. The experimental data (saturated liquid phase composition and density) were compared with the modeling results obtained using the Peng−Robinson and Soave−Redlich−Kwong equations of state. Both models were capable of representing the solubility data well; however, the Peng−Robinson equation of state gave better estimation of liquid saturated densities both with and without volume translation.

INTRODUCTION

The knowledge of phase equilibrium properties of hydrocarbon mixtures are fascinating and of great fundamental and practical importance. Isothermal (vapor + liquid) equilibrium data of binary mixtures are of great interest for the development of new correlations to describe the phase behavior of multicomponent systems. Among the binary hydrocarbon mixtures, the phase behavior of binary mixtures of a light and heavy hydrocarbon component is of particular importance because it provides an investigation about the nonideal behavior that caused by differences in chain length in these binary systems. The present study was attempted to provide a better understanding of the phase behavior of binary systems with largely different molecular sizes. Therefore, the experimental phase equilibrium information for binary systems of ethane + *n*-Octadecane at elevated temperatures and pressures were considered.

During the course of this study, a literature survey on the phase behavior of ethane-containing systems has been done. Table 1 summarizes the available experimental data[1−16] in the literature for these systems. Although no experimental information for vapor−liquid equilibrium of binary systems of ethane + *n*-Octadecane has been reported, there is also a lack of experimental data for density and viscosity of saturated liquid phase. Of the thermodynamic properties of the fluid mixtures in reservoirs that are of significance, the density and viscosity are of especial importance because they determines the fluid flow properties as well as an estimation about the total mass of reserves.

In the present study, the vapor−liquid equilibrium properties for a binary system of ethane + *n*-octadecane were measured using a designed experimental apparatus. The solubility, density, and viscosity of ethane-saturated *n*-octadecane were reported at three temperatures (323, 373, and 423) K and pressures up to 8 MPa. Alongside the experimental measurements, one aim of the present study is to evaluate and compare the ability of conventional cubic equations of state to correlate and predict the liquid saturated properties (solubility and density) of binary fluid mixtures. Since the experimental measurement of phase equilibria is time-consuming and expensive, the Soave−Redlich−Kwong (SRK)[17] and Peng−Robinson (PR)[18] equations of state were adjusted by the generated experimental data to determine the interaction parameters. The estimated parameters combined the equation of state can be used to predict the phase equilibria of binary mixtures.

EXPERIMENTAL SECTION

Apparatus. In previous studies,[19,20] a designed PVT apparatus for gas solubility measurement was described in detail. The apparatus consists of two feeding cells, an equilibration cell, four sampling cells, a density measuring cell, a viscometer, and two Quizix automated pressure activated pumps.

The equilibration and sampling cells, density measuring cell, and viscometer are placed in a temperature-controlled Blue M oven. The oven is equipped with a temperature controller capable of maintaining the temperature within ± 0.1 K. The uncertainty of temperature measurements is estimated to be ± 0.1 K. An Anton Paar density measuring cell equipped with a DMA HPM external high-pressure unit is calibrated using nitrogen and water. The density measurements are precise to ± 0.5 $\text{kg}\cdot\text{m}^{-3}$ with an uncertainty of ± 1 $\text{kg}\cdot\text{m}^{-3}$. The Cambridge viscometer (ViscoPro 2000) is factory calibrated; and, the accuracy of measurements was tested with pure hydrocarbons and some standard fluids. The average deviation for the measurements was less than 5%.

Materials. The ethane used in these measurements was supplied by Praxair. The *n*-octadecane was obtained from Alfa Aesar Company. All materials were found to be within acceptable purity specifications and were used without further purifications. Table 2 summarizes the chemical sample descriptions.

Measurements. Prior to each experiment, the entire system was thoroughly cleaned to remove any contaminant. To ensure no contaminants were left inside the system, cells and lines were successively evacuated and flushed with helium and ethane.

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Table 1. Available Literature Experimental Data at Temperature T, and Pressure p, for the Binary Ethane-containing Systems

ref	pure light hydrocarbon	pure heavy hydrocarbon	T/K	p/MPa	data
Reamer and Sage[1]	ethane	*n*-decane	278−511	up to 69	two-phase boundary and molal volumes
Ng et al.[2]	methane, ethane, propane, ethylene, and propylene	octadecane, eicosane, and docosane	303−473	low pressure	solubility
Cuker and Prausnitz[3]	methane, ethane, and hydrogen	*n*-hexadecane, bicyclohexyl, and diphenylmethane	298−473		Henry's constant
Chappelow and Prausnitz[4]	methane, ethane, propane, *n*-butane, isobutane, and hydrogen	*n*-hexadecane, *n*-eicosane, squalane, bicyclohexyl, octamethylcyclotetrasiloxane, diphenylmethane, and 1-methylnaphthalene	298−473	low pressure	solubility
Kaul and Prausnitz[5]	methane, ethane, and ethylene	hexadecane, bicyclohexyl, diphenylmethane, and 1-methyl naphthalene	323−443	1−8	vapor-phase solubilities
	methane, ethane, and ethylene	eicosane and squalane	438−545		
Richon and Renon[6]	methane, ethane, propane, and *n*-butane	*n*-hexadecane, *n*-octadecane, and 2,2,4,4,6,8,8-heptamethylnonane	298 and 323	low pressure	Henry's constant
Specovius et al.[7]	ethane	*n*-octadecane, *n*-nonadecane, and *n*-eicosane	∼313		critical end points
Bufkin et al.[8]	ethane	*n*-decane	278−511	up to 8	solubility and molar volume
Peters et al.[9]	ethane	*n*-hexadecane, *n*-eicosane, *n*-docosane, *n*-tricosane, *n*-tetracosane, *n*-pentacosane, *n*-hexacosane, and *n*-octacosane	up to 335	up to 9	two-phase and three-phase boundary
Peters et al.[10]	ethane	eicosane	up to 450	up to 12	solubility
Peters et al.[11]	ethane	tetracosane	280−360	up to 12	two-phase and three-phase boundary, molar volume
Peters et al.[12]	ethane	pentacosane	300−315	up to 8	three-phase boundary
Peters et al.[13]	ethane	docosane	290−370	up to 16	two-phase and three-phase boundary, molar volume
Huang et al.[14,15]	methane, ethane, and carbon dioxide	*n*-octacosane and *n*-eicosane	up to 573	up to 5	solubility
Gasem et al.[16]	ethane	*n*-eicosane, *n*-octacosane, *n*-hexatriacontane, and *n*-tetratetracontane	348−423	up to 8	solubility

Table 2. Chemical Sample Specifications

chemical name	source	initial purity	purification method
ethane	Praxair	0.99999 mol fraction	none
n-octadecane	Alfa Aesar	0.99 mass fraction	none

After cleaning, *n*-octadecane was charged into the equilibration cell using the two Quizix pumps. The ethane was then charged into the cell. During the measurements, about (200−300) cm^3 of equilibrium cell was filled with the ethane and *n*-octadecane. To measure the solubility at a specific temperature and pressure, the experimental pressure and temperature were fixed: the Quizix pumps kept a constant pressure with an error of less than ± 5 kPa.

The equilibration cell was rocked to achieve effective mixing and to reach the equilibrium condition for the ethane + *n*-octadecane systems. During the mixing period, the volume of mixture to keep a constant pressure in the equilibration cell was recorded. When there was no change in the volume, equilibrium was achieved. Thus, the volume change in the mixing of binary systems was the criteria for equilibrium condition. Prior to the discharge of the equilibrium fluids, the equilibration cell was first kept in an upright position (vertical position) for a few hours to obtain single bulk volumes of each phase vertically segregated in the order of phase density. Then, the equilibrium fluids were discharged through the density measuring cell and viscometer, while maintaining a constant temperature and pressure. The pressure was measured by both the in-line and Quizix pump pressure transducers. The uncertainty of pressure measurements was ± 10 kPa.

The phase samples were collected with steady readings of the viscometer and the density measuring cell; any change in viscosity and density indicated a passage of a phase boundary through the measuring instruments. Vapor and liquid phases were transferred into sampling cells, and the last sampling cell was used to purge the phase boundary portion and clean the transition between the phases. Saturated samples could be collected through the sampling port for compositional analysis or further studies.

To measure the solubility of the saturated liquid(s), the collected samples were flashed at atmospheric pressure. The volume of the evolved gas was measured by the Chandler Engineering Gasometer (model 2331) with a 0.2% accuracy of the reading. The composition of gas phase was also measured with gas chromatography (GC).

Table 3. Experimental Equilibrium Data for Temperature T, Pressure p, Pure n-Octadecane Density ρ, Saturated Liquid Density ρ_s, Saturated Liquid Viscosity μ_s, Mole Fraction of Ethane in Saturated Liquid Phase x, for the System Ethane + n-Octadecane[a]

T (K)	p (MPa)	ρ (kg·m^{-3})	ρ_s (kg·m^{-3})	μ_s (mPa·s)	$10^2 \cdot x$
323.1	1.15	755	732	1.59	27.0
323.1	1.95	756	715	1.09	41.5
323.3	3.01	756	691	0.81	54.6
323.3	3.97	757	662	0.55	65.4
323.1	5.23	757	606	0.31	78.9
323.1	5.89	758	572	0.23	84.4
372.8	0.94	730	719	0.87	12.7
372.8	2.18	731	703	0.70	29.8
372.8	2.92	731	692	0.62	37.2
372.8	4.08	733	676	0.52	47.4
372.8	4.94	733	664	0.46	53.6
372.8	5.98	734	648	0.39	59.9
372.8	7.12	735	628	0.32	66.6
372.8	7.98	736	614	0.29	70.1
422.6	0.95	695	688	0.55	9.6
422.6	1.93	697	679	0.49	19.4
422.6	3.06	699	667	0.43	29.6
422.6	3.97	700	659	0.40	36.5
422.6	5.00	701	648	0.37	42.7
422.6	5.94	702	640	0.33	47.7
422.5	7.16	703	624	0.29	54.7
422.5	8.17	704	613	0.27	58.8

[a] $u(T) = 0.1$ K, $u(p) = 0.01$ MPa, $u(\rho) = 1$ kg·m^{-3}, $u(\mu) = 0.05\ \mu$, and $u(x) = 0.001$.

RESULTS AND DISCUSSIONS

The experimental liquid saturated properties (solubility, density, and viscosity) of ethane + n-octadecane system at three temperatures are summarized in Table 3. The density of pure n-octadecane at each temperature and pressure is also measured and summarized in the third column of Table 3 for comparison. Caudwell et al.[21] was also measured the density and viscosity of pure n-octadecane for temperatures (298−473) K and high pressure conditions (up to 200 MPa). The precision and uncertainty of the measurements for compositions were 0.001 mol fraction. The equilibrium gases for all experiments were virtually pure ethane due to low volatility of n-octadecane.

The experimental data obtained were modeled with the conventional SRK and PR equations of state using van der Waals mixing rule. The critical temperature and pressure and the acentric factor were obtained from Yaws.[22] The binary interaction parameters for the SRK and PR equations of state were considered as tuning parameters and were evaluated as 0.01628 and 0.00705 from the experimental data, respectively. The average absolute deviations ($\Delta x = [1/N]\Sigma|x_{\text{calcd}} - x_{\text{exptl}}|$) were 0.014 and 0.015 for the SRK and PR equations of state, respectively. The modeling results with the equations of state are shown in Figure 1. In these plots, the lines denote the calculation results by the equations of state for the three temperatures of (323.1, 372.8, and 422.6) K. For comparison, the experimental data are also shown by dots. Both equations of state reasonably correlated the composition of ethane at the three temperatures over the studied pressure range.

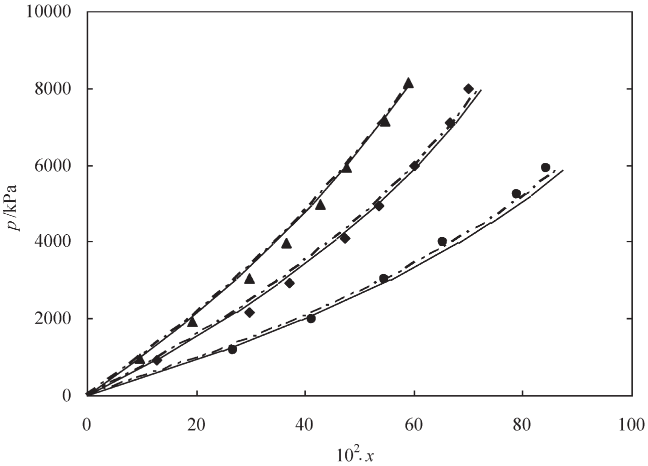

Figure 1. Phase equilibria for ethane + n-octadecane system; p, pressure; x, mole fraction of ethane in saturated liquid phase; ●, ◆, and ▲, experimental data; —·—, SRK EOS; —, PR EOS (1978); ●, T = 323.1 K; ◆, T = 372.8 K; ▲, T = 422.6 K.

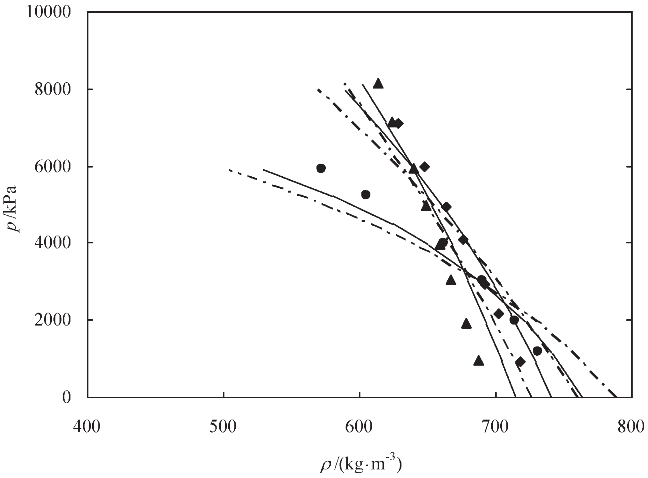

Figure 2. Saturated liquid densities ρ for ethane + n-octadecane system; p, pressure; ●, ◆, and ▲, experimental data; —·—, SRK EOS; —, PR EOS (1978); ●, T = 323.1 K; ◆, T = 372.8 K; ▲, T = 422.6 K.

To improve the predictions for the saturated liquid densities, the volume translation technique of Peneloux et al.[23] was applied. The average absolute deviations for densities ($\Delta\rho = [1/N]\Sigma|\rho_{\text{calcd}} - \rho_{\text{exptl}}|$) were 179 and 120 for the SRK and PR equations of state, respectively before any volume translation was applied. The SRK equation of state resulted in the best agreement with volume shift of 0.35328 while this value is 0.23646 for PR equation of state. The average absolute deviations for densities with volume translation were 21 and 12 for the SRK and PR equations of state, respectively. The modeling results for both equations of state with the volume translation were shown in Figure 2. The saturated liquid density was closely modeled using the PR equation of state, while the SRK equation of state under and or overpredicted the liquid density. To have a better representation of modeling results, the numerical values obtained for each temperature and pressure were also summarized in Table 4.

Finally, the saturated liquid phase viscosities were plotted in Figure 3. As depicted in the figure, the viscosity reduction with pressure would be less at higher temperatures. This is caused by the decrease in the

Table 4. **Experimental versus Modeling Results for Temperature T, Pressure p, Saturated Liquid Density ρ_s, Mole Fraction of Ethane in Saturated Liquid Phase x, for the System Ethane + n-Octadecane**[a]

T	p	$\rho_s/(\mathrm{kg \cdot m^{-3}})$			$10^2 \cdot x$		
K	MPa	experiment	SRK EOS	PR EOS	experiment	SRK EOS	PR EOS
323.1	1.15	732	758	741	27.0	24.3	24.8
323.1	1.95	715	732	721	41.5	38.6	39.4
323.3	3.01	691	689	689	54.6	54.9	55.8
323.3	3.97	662	641	650	65.4	67.2	68.2
323.1	5.23	606	559	579	78.9	80.8	81.7
323.1	5.89	572	504	528	84.4	86.8	87.6
372.8	0.94	719	745	729	12.7	12.6	12.7
372.8	2.18	703	721	711	29.8	27.2	27.4
372.8	2.92	692	705	699	37.2	34.9	35.2
372.8	4.08	676	678	678	47.4	45.7	46.0
372.8	4.94	664	657	661	53.6	52.7	53.0
372.8	5.98	648	630	639	59.9	60.3	60.6
372.8	7.12	628	597	611	66.6	67.6	67.8
372.8	7.98	614	571	588	70.1	72.3	72.6
422.6	0.95	688	715	705	9.6	9.4	9.4
422.6	1.93	679	700	694	19.4	18.3	18.3
422.6	3.06	667	683	680	29.6	27.6	27.5
422.6	3.97	659	668	668	36.5	34.4	34.3
422.6	5.00	648	650	653	42.7	41.5	41.4
422.6	5.94	640	633	639	47.7	47.4	47.3
422.5	7.16	624	610	620	54.7	54.3	54.2
422.5	8.17	613	590	602	58.8	59.6	59.5

[a] $u(T) = 0.1$ K, $u(p) = 0.01$ MPa, $u(\rho) = 1\ \mathrm{kg \cdot m^{-3}}$, and $u(x) = 0.001$.

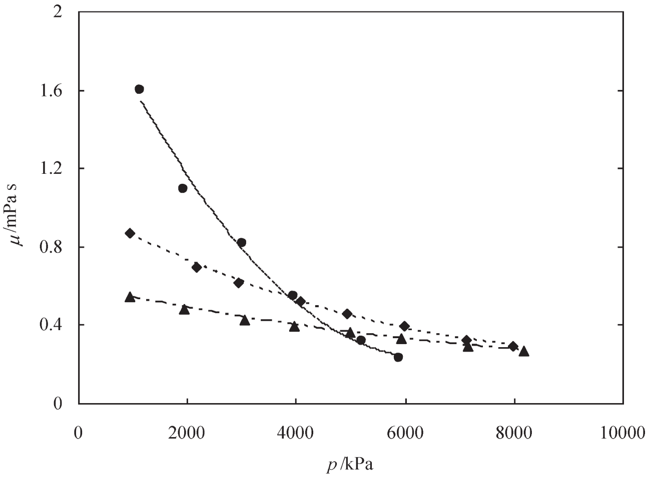

Figure 3. Saturated liquid viscosities μ for ethane + n-octadecane system; p, pressure; ●,—, T = 323.1 K; ◆,· · ·, T = 372.8 K; ▲,— · —, T = 422.6 K.

solubility with temperature. Worthy mentioned that the saturated liquid viscosity exhibits almost a linear trend at higher temperatures.

CONCLUSION

The experimental saturated liquid properties for binary system of ethane + n-octadecane were measured at three different temperatures. The experimental data (saturated liquid solubility and density) obtained were modeled using the PR and SRK equations of state. To tune the equations of state, the binary interaction parameters were adjusted. Both equations of state considered here closely modeled the composition of ethane in the liquid phase. To improve the predictions for the saturated liquid densities, the volume translation technique was applied. The PR equation of state provided better correlations for the saturated liquid densities compared to those of the SRK equation of state with and without volume translation.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jabedi@ucalgary.ca. Tel: 403-220-5594.

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