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

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ABSTRACT: The liquid saturated properties (solubility, density, and viscosity) data for the binary system of ethane + *n*-tetradecane at three temperatures (323, 373, and 423) K were measured using a designed pressure−volume−temperature (*PVT*) apparatus. The saturated liquid phase properties were measured for pressures up to 8 MPa. 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.

INTRODUCTION

The phase behavior of binary mixtures of a light and heavy hydrocarbon component is of particular importance in the design and development of many industrial processes such as enhanced oil recovery methods and the processing of petroleum products. Apart from the application point of view, these studies enable the development of new correlations to describe the phase behavior of multicomponent systems involving ethane. In addition, it provides an investigation about the nonideal behavior caused by differences in chain length in these binary systems. The present study was aimed to obtain more insight into the phase behavior of binary systems with largely different molecular sizes.

In the past, some experimental studies on the phase behavior of binary systems containing volatile components and heavy normal hydrocarbons have been reported. Reamer and Sage[1] have reported the properties and phase equilibria of mixtures of ethane + *n*-decane at pressures to 69 MPa and temperatures from 40 to 460 °F (277.6 to 510.9 K). Bufkin et al.[2] have also measured the solubility of ethane in *n*-decane as a function of pressure at five temperatures (277.6, 310.9, 344.3, 377.6, and 410.9 K). The liquid phase molar volumes for two lowest temperatures are also reported.

Peters et al.[3−7] have presented experimental data of the binary ethane + eicosane, ethane + tetracosane, ethane + pentacosane, and ethane + docosane. Huang et al.[8,9] have measured the solubility of carbon dioxide, methane, and ethane in *n*-octacosane and *n*-eicosane at temperatures up to 300 °C (573.2 K) and pressures to 50 atm (5.1 MPa). Gasem et al.[10] have reported the solubility of ethane in *n*-eicosane, *n*-octacosane, *n*-hexatriacontane, and *n*-tetratetracontane over the temperature range 348 to 423 K and pressures up to 7.8 MPa.

In the present study, the vapor−liquid equilibrium properties for the binary system of ethane + *n*-tetradecane are measured using a designed experimental apparatus. The solubility, density, and viscosity of ethane-saturated *n*-tetradecane are reported at three temperatures 323, 373, and 423 K and pressures up to 8 MPa. Finally, the phase compositions and densities are modeled using Peng−Robinson (PR) and Soave−Redlich−Kwong (SRK) equations of state.

EXPERIMENTAL SECTION

Apparatus. The schematic diagram of the apparatus is shown in Figure 1. It consisted of feeding cells, an equilibration cell, four sampling cells, a density measuring cell, a viscometer, and two Quizix automated pressure activated pumps. The Quizix pumps charged and discharged water to displace the fluids or to keep the pressure constant. The equilibration, sampling, and feeding cells were equipped with pistons to prevent contamination of the mixture with water. The pistons were sealed with the Viton O-rings.

The equilibration and sampling cells, density measuring cell, and viscometer were placed in a temperature-controlled Blue M oven. The oven was equipped with a temperature controller capable of maintaining the temperature within ±0.1 K. The uncertainty of temperature measurements was estimated to be ±0.1 K. The two pumps (Quizix pumps) controlled the system pressure by charging or discharging the fluids with an accuracy of $\pm 0.001\ \mathrm{cm}^3$. The rocking action of the equilibration cell with the rolling ball expedited the process of mixing and reaching equilibrium. The rocking equilibration cell had a total volume of about $900\ \mathrm{cm}^3$, which allowed for a sufficiently saturated phase volume for measurement of physical properties, such as density and viscosity. In addition, it provided ease of phase detection and enough phase volume for further analyses.

The density measuring cell and viscometer were used for phase detection. They were installed in a series to improve the phase detection. Their in-line measurements provided data of higher accuracy than separately sending very small samples to the viscometer and to the density measuring cell.

The sample fluid was discharged from the top of the rocking cell through the viscometer and density measuring cell, while the temperature and pressure were kept constant. This methodology allowed us to detect the phase variation within the system as the data were collected from the density measuring cell and/or viscometer. In this design, the sample volume was large enough that a visual evaluation of phases was not required. The density measuring cell had the capability of detecting small changes in density over a wide range of pressures and temperatures.

An Anton Paar density measuring cell equipped with a DMA HPM external high-pressure unit was used to measure the

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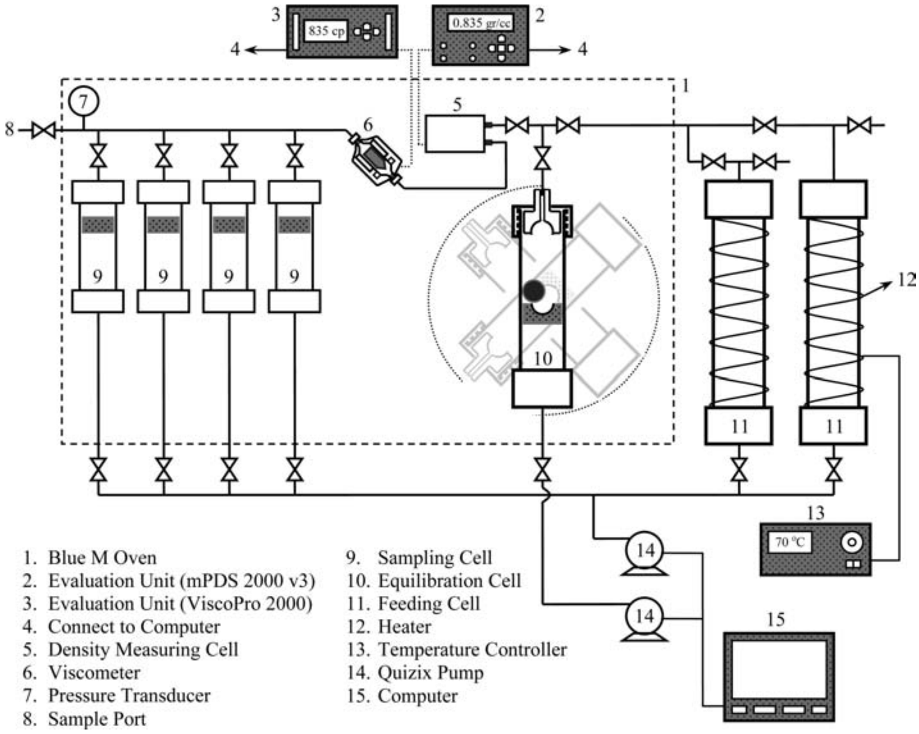

Figure 1. Schematic diagram of experimental apparatus.

density of the fluids. The fluid was transferred into a U-shaped Hastelloy tube. The tube was electronically vibrated at its characteristic frequency, and depending on the density of the fluid, the characteristic frequency changed. By precise determination of the characteristic frequency and a mathematical conversion, the density of the fluid would be calculated. The external unit was calibrated using nitrogen and water for pressures from 690 to 13 800 kPag (100 to 2000 psig) and temperatures between 283.15 and 463.15 K (10−190 °C). The data for the densities of nitrogen and water at specific temperatures and pressures were taken from the National Institute of Standards and Technology (NIST) database. The density measurements were precise to $\pm 0.5\ \mathrm{kg \cdot m^{-3}}$ with an uncertainty of $\pm 1\ \mathrm{kg \cdot m^{-3}}$.

The Cambridge viscometer (ViscoPro 2000) had the capability to measure viscosity in the range 0.02 to 10 000 mPa·s with an accuracy of ±1.0% of full scale and at temperatures up to 463 K and pressures up to 140.6 MPa (20 000 psi). The piston-style viscometer used two magnetic coils within a stainless steel sensor and a magnetic piston inside the pipe line. The piston was forced magnetically back and forth within a predetermined distance. The fluid sample surrounded the piston, and depending on the viscosity, the piston's round trip travel time was measured at constant force exerted. The time required to complete a two-way cycle was an accurate measure of viscosity. The viscometer was factory calibrated, and the accuracy of measurements was tested with pure hydrocarbons and some standard fluids. The average error for the measurements was less than 5%.

Materials. The ethane (grade 5, 99.999% mole) used in these measurements was supplied by Praxair. The *n*-tetradecane was minimum 99% (mass) purity obtained from Spectrum Chemical Mfg. Corp. All materials were found to be within acceptable purity specifications and were used without further purifications.

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.

After cleaning, *n*-tetradecane was charged into the equilibration cell using the two Quizix pumps. The ethane was then charged into the cell. 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*-tetradecane 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 a constant temperature and pressure were maintained. 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 density and viscosity indicated a passage of a phase boundary through the measuring instruments. Vapor and liquids were transferred into sampling cells 1−3, 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

Table 1. Experimental Liquid Saturated Properties for Ethane + *n*-Tetradecane Systems at $T = (323, 373, \text{and } 423)$ K[a]

T/K	P/MPa	$\rho/(\text{kg}\cdot\text{m}^{-3})$		$\mu/(\text{mPa}\cdot\text{s})$	10^2x
		n-tetradecane	saturated		
323.2	1.05	741	719	0.86	22.5
323.2	2.02	742	695	0.63	40.2
323.2	3.16	743	661	0.45	57.2
323.2	4.07	744	632	0.32	66.8
323.2	5.06	745	579	0.21	79.1
323.3	5.94	745	503	0.13	87.8
373.6	1.01	706	691	0.53	12.1
373.4	2.08	707	677	0.46	25.9
373.5	2.97	708	664	0.41	35.2
373.4	4.05	709	647	0.34	44.9
373.5	5.01	710	631	0.30	51.9
373.4	6.01	710	611	0.26	59.4
373.4	7.07	711	590	0.22	65.8
422.5	1.08	672	660	0.34	10.2
422.5	2.14	673	648	0.32	20.1
422.6	3.02	675	639	0.29	27.2
422.6	4.02	676	628	0.27	34.5
422.6	5.04	677	615	0.24	41.7
422.6	6.05	679	604	0.22	47.0
422.7	7.00	680	590	0.21	52.5
422.7	8.00	681	576	0.18	57.5

[a] P, pressure; ρ, densities; μ, saturated liquid viscosity; x, mole fraction of ethane in saturated liquid phase.

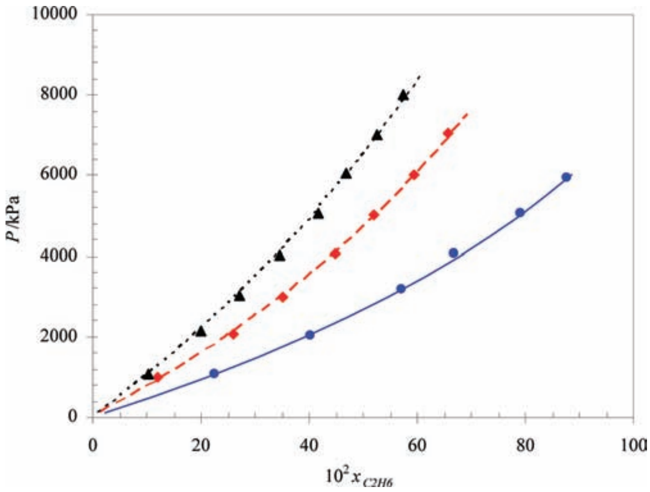

Figure 2. Phase equilibria for ethane + *n*-tetradecane system (P, pressure; $x_{C_2H_6}$, mole fraction of ethane in saturated liquid phase): ●, ◆,▲, experimental data; —, SRK EOS (1978); ●, —, T = 323.2 K; ◆, — — —, T = 373.5 K; ▲, ---, T = 422.6 K.

Gasometer (Model 2331) with a 0.2% accuracy of the reading. The composition of gas phase was also measured with gas chromatography (GC).

■ RESULTS AND DISCUSSION

The experimental liquid saturated properties (solubility, density, and viscosity) of ethane + *n*-tetradecane system at three temperatures are summarized in Table 1. The densities of pure *n*-tetradecane at each temperature and pressure are also summarized in the third column of Table 1 for comparison. The precision and uncertainty of the measurements for compositions are 0.001. The equilibrium gases for all experiments are virtually pure ethane due to low volatility of *n*-tetradecane.

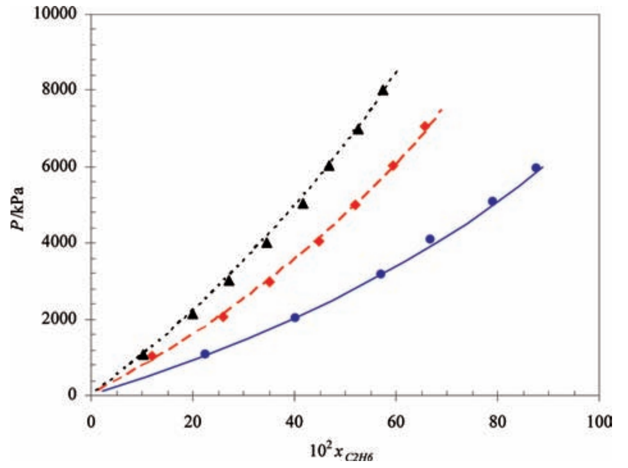

Figure 3. Phase equilibria for ethane + *n*-tetradecane system (P, pressure; $x_{C_2H_6}$, mole fraction of ethane in saturated liquid phase): ●, ◆,▲, experimental data; —, PR EOS (1978); ●, —, T = 323.2 K; ◆, — — —, T = 373.5 K; ▲, ---, T = 422.6 K.

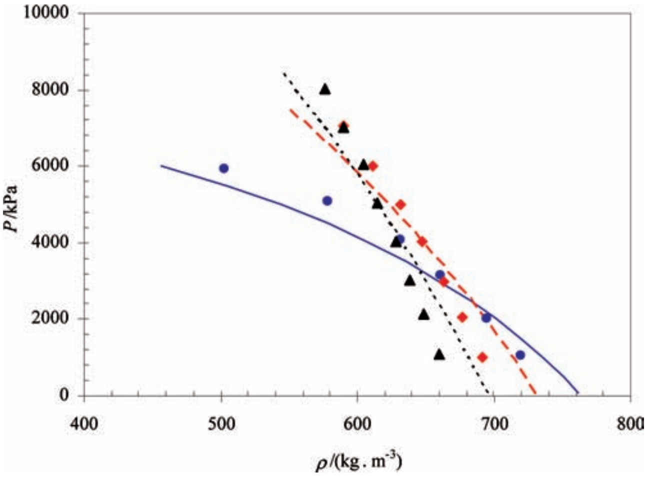

Figure 4. Saturated liquid densities ρ for ethane + *n*-tetradecane system (P, pressure): ●, ◆,▲, experimental data; —, SRK EOS (1978); ●, —, T = 323.2 K; ◆, — — —, T = 373.5 K; ▲, ---, T = 422.6 K.

The experimental data obtained are modeled with the conventional SRK[11] and PR[12] equations of state. The critical temperature and pressure and the acentric factor are obtained from Yaws.[13] The binary interaction parameters for the SRK and PR equations of state are considered as tuning parameters and are evaluated as 0.0055 and 0.00307 from VLE experimental data, respectively. The modeling results with the equations of state are shown in Figures 2−3. In these plots, the lines denote the calculation results by the equations of state for the three temperatures of 323.2, 373.5, and 422.6 K. For comparison, the experimental data are also shown by dots. Both equations of state reasonably predict the composition of ethane at the three temperatures over the studied pressure range.

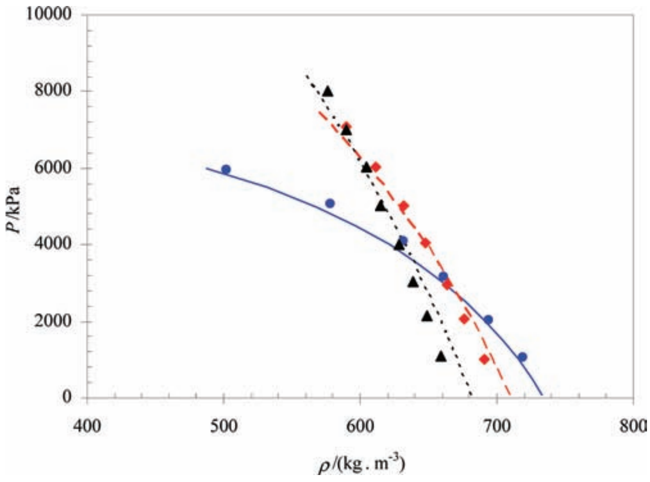

Figure 5. Saturated liquid densities ρ for ethane + *n*-tetradecane system (P, pressure): ●, ◆,▲, experimental data; —, PR EOS (1978); ●, —, T = 323.2 K; ◆, − − −, T = 373.5 K; ▲, ---, T = 422.6 K.

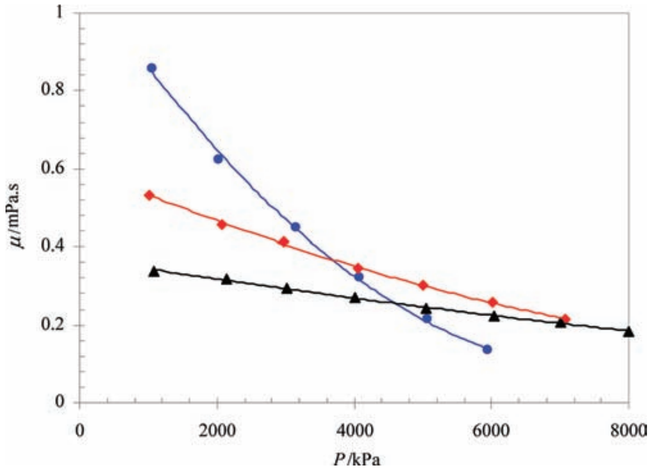

Figure 6. Saturated liquid viscosities μ for ethane + *n*-tetradecane system (P, pressure): ●, —, T = 323.2 K; ◆, —, T = 373.5 K; ▲, —, T = 422.6 K.

To improve the predictions for the saturated liquid densities, the volume translation technique of Peneloux et al.[14] is applied. The SRK equation of state results in the best agreement with volume shift of 0.2599, while this value is 0.11878 for the PR equation of state. The modeling results for both equations of state are shown in Figures 4−5. The saturated liquid density is closely modeled using the PR equation of state, while the SRK equation of state underpredicts or overpredicts the liquid density.

Finally, the saturated liquid phase viscosities are plotted in Figure 6. As depicted in the figure, the viscosity reduction with pressure will be less at higher temperatures. This is caused by the decrease in the solubility with temperature. It is worth mentioning that the saturated liquid viscosity exhibits almost a linear trend at higher temperatures.

■ CONCLUSION

The experimental saturated liquid properties for the binary system of ethane + *n*-tetradecane 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. Both equations of state considered here closely modeled the composition of ethane in the liquid phase. The PR equation of state provided better predictions for the saturated liquid densities compared to those of the SRK equation of state.

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