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Equilibrium Phase Densities, Interfacial Tensions for the Ethane + *n*-Pentane System at 294.15 K

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ABSTRACT: The equilibrium phase densities and interfacial tensions of the binary mixture (ethane + *n*-pentane) have been measured simultaneously using the pendant drop method at 294.15 K. The experimental pressure was in the range of (6 to 30) bar. The measured phase densities are compared with calculated equilibrium densities by applying the GERG2004 equation. The deviations of the measured interfacial tension at each experimental condition are calculated on the basis of ISO combined standard uncertainty calculation recommendations. No open interfacial tension data for the system have been reported at any isothermal conditions. The measurement results extend the range of previous interfacial tension data of the hydrocarbon mixtures in the open literature.

1. INTRODUCTION

Surface tension is regarded as an important parameter for modeling the thermophysical behavior of real petroleum fluids in the oil and gas industry. The study here is part of our research project on high-pressure gas—liquid separation. It is well-known that that there are strong dependencies between gas—liquid interfacial tensions and separation performance since both droplet size distribution and re-entrainment are sensitive to interfacial tension values in the separation scrubber. Furthermore, reliable surface tension data are also a key factor for the accurate simulation of droplet—droplet interactions and droplet—liquid film interactions which can give a detailed picture of the coalescence, deposition, and entrainment phenomena in the separation conditions.

In this study the ethane + *n*-pentane system is utilized as a synthetic condensate to mimic the thermodynamic behavior of a real nature gas in high-pressure gas—liquid separation systems. The experimental temperature is set to 294.15 K since it is close to the normal scrubber working temperature. The experimental data will be used to correlate our own model for interfacial tension computation of the real gas condensate. Both the phase densities and interfacial tensions of the ethane + *n*-pentane system are measured in a high-pressure interfacial tension cell. The experimental investigation of the ternary system methane + ethane + *n*-pentane will form the basis of one future publication. In the laboratory the high pressure Anton Paar oscillation tube densimeter is employed for density measurement, and the pendant drop method is used to generate the interfacial tension data. The results will extend our database, and in addition it is very useful for the understanding, experimental characterization, and modeling of interfacial properties and phase behavior governing the high-pressure gas—liquid separation process, which is the main purpose of this research work.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

2.1. Experimental Apparatus. In this study the interfacial tension of a vapor—liquid interface is determined by using a video-enhanced pendant drop tensiometer. Lots of investigations have been done to improve the accuracy of the curve fitting the drop edge coordinates to the Young—Laplace equation.[1−5] Axisymmetric drop shape analysis (ADSA) is a powerful and robust technique for the measurement of the interfacial properties from the shape of pendant drops,[6−9] which was utilized to measure the equilibrium interfacial tensions of the ethane + *n*-pentane mixture in the work. A vapor—liquid interfacial tension facility was employed to conduct the measurement. It is capable of measuring high-pressure phase densities and steady interfacial tensions at gas—liquid equilibrium conditions.

The main components of the experimental system are illustrated in Figure 1, and the apparatus information can be found in Table 1. The experimental facility consists of an interfacial tension cell, two densimeters for measuring vapor and liquid phase densities, and a high-pressure liquid circulation pump, all housed in a temperature-controlled environmental chamber [(−30 to 100) °C] from Heraeus Vötsch. The key apparatus of the measurement system is a see-through windowed high-pressure interfacial tension cell, which has a chamber volume of 41.5 cm^3. Inside the pendant drop cell there is a self-designed inlet port. There is no physical contact between liquid and gas in the inlet port section, and a pendant droplet hangs at its end (0.75 mm inner diameter supplied by Teknolab AS, material is Hastelloy C). One lying U-tube is located at a position 2 cm above valve 5 and used to accumulate the extra amount of liquid necessary to make the droplet. There is one pressure gauge with the temperature compensation placed in liquid line (see Figure 1). Both temperature sensors are integrated in the high-pressure densimeter.

2.2. Experimental Procedure. *2.2.1. Calibrations.* The liquid pressure gauge and temperature sensors are already calibrated

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Table 1. List of Apparatus Information

no.	apparatus name	description
1	pendant drop cell	tensiometer (Temco Inc., USA) type: IFT − 2 serial no.:1118 maximum pressure: 690 bar maximum temperature: 177 °C software: Dropimage
2	liquid circulation pump	Eldex laboratories Inc. type: B − 100 − S − 2CE flow rate: (0.2 to 8) $\text{mL}\cdot\text{min}^{-1}$ maximum pressure: 345 bar
3	densimeter	Anton Paar GmbH external measuring cell: DMA HPM evaluation unit: mPDS 2000v3 temperature range: (−10 to 200) °C pressure range: (0 to 1400) bar density range: (0 to 3) $\text{g}\cdot\text{cm}^{-3}$
4	pressure sensor	pressure sensor 01 in vapor phase (see Figure [1]) absolute pressure transducer (HBM) type: P6 F. No.: 49244 pressure range: up to 1000 bar pressure sensor 02 in liquid phase (see Figure [1]) oil operated pressure gauge Paroscientific, Inc. transducer model: 410KR-HHT-101 serial no.: 117257 range: (3 to 690) bar accuracy: 0.01 % of reading above 14 bar or 0.14 kPa at lower pressure
5	CCD video camera module	lens: COSMICAR Television lens, 50 mm, 1:1.8
6	light system	light source: BODSON GBE 75 1 diffuse reflection glass 2 m fiber optical cable METREL type: HSN0103 Us :(0 to 220) V 5A 1.25 KVA
7	back pressure regulator	Swagelok Fluid System Technologies model no.: SS-4R3A5 red spring kit: 177-R3A-K1-G pressure range: (275 to 344) bar
8	tube size	supplier: Teknolab AS material: stainless steel gas circulation line: 1/8″ liquid circulation line: 1/8″ tube from liquid pump to valve 3: 1/16″ lying U tube above valve 5: 1/4″

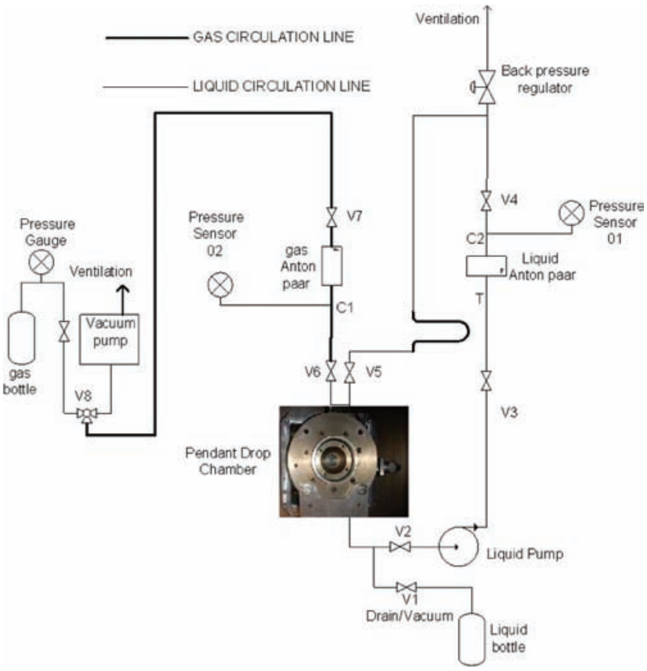

Figure 1. Experimental apparatus (showing the vapor and liquid circulation path).

beforehand by the manufacturer. The temperature sensors are integrated in the high-pressure densimeters. The position of the gas densimeter is standing, and the liquid densimeter is lying on the platform. The maximum uncertainties of the temperature measurement are lower than 0.1 °C in the adjusted ranges and equal to ± 0.1 °C in the not adjusted ranges. The accuracy of the liquid pressure gauge is listed in Table 1, and the vapor pressure gauge is calibrated in this work with an accuracy 0.01 % of the reading pressure. The calibrated pressure range is between (1 and 115) bar.

Liquid and vapor densities are determined in an Anton Paar DMA HPM unit based on the vibrating U-tube method. The apparatus measures the oscillating period of the U-tube filled with sample that is automatically converted to phase density after proper calibration. Two calibration fluids, methane and *n*-pentane, have to be selected for calibrations at pressures ranging from (1 to 115) bar and the temperature interval (20.5 to 21.5) °C. The uncertainty of the phase density is within ± 0.004 $\text{g}\cdot\text{cm}^{-3}$ for the vapor and liquid phase.

2.2.2. Materials. Ethane was supplied by YARA Industrial AS with a reported purity of 99.995 %. The *n*-pentane was supplied by LAB SCAN Limited with a reported purity of 99 % (code no.: A40A11X; batch no.: 4336/8). No further purification of the chemicals was attempted.

2.2.3. Measurement Process. In the first step the *n*-pentane in the cylinder bottle is filled into the facility via valve 1 with the help of a volume displacement pump (Temco, Inc., MOD: HAT-100-10-SS, work pressure: 690 bar). The filled liquid volume can also be read in the filling process. It is circulated from the bottom to the top of the pendant drop cell with the help of the high-pressure liquid pump through the whole liquid circulation path. In the second step, an amount of ethane gas will be pressurized via valve 6 into the cell directly from the gas bottle. The gas volume is not measured in the work. It was noticed that the cell pressure was much higher than the saturation pressure of *n*-pentane at 294.15 K. In the third step, the mixing process, the liquid flow falls at the bottom of the pendant drop cell from the inlet port and gets "physical" contact with the vapor phase there; a mount of *n*-pentane liquid is evaporated and transferred into the gas phase; and the ethane gas is diffused into the liquid phase.

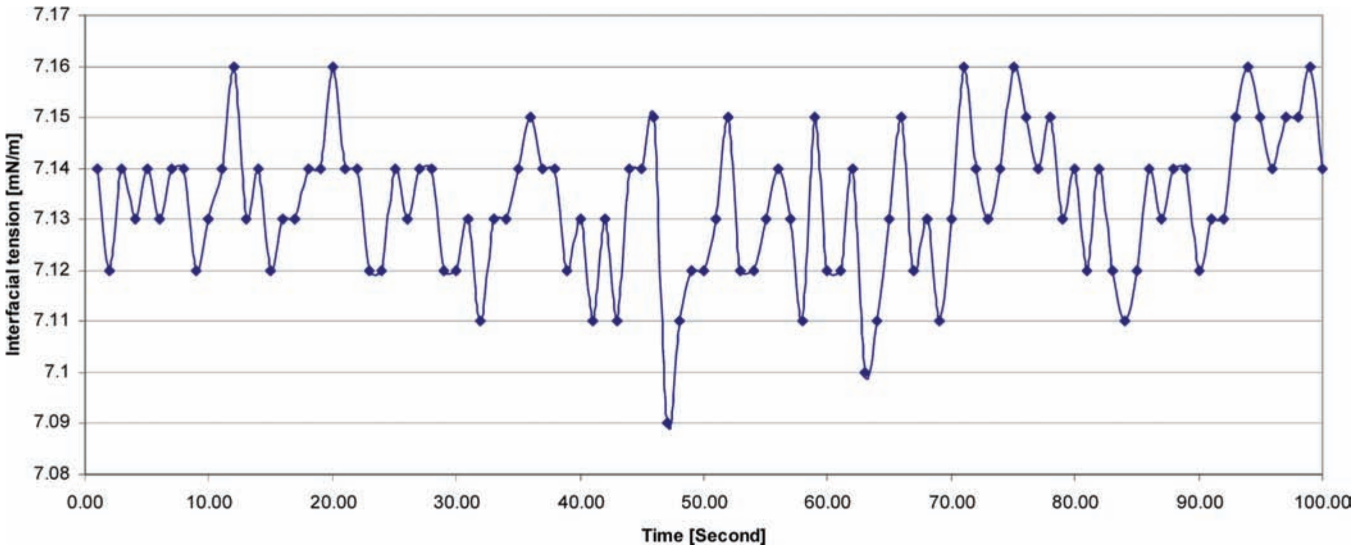

Figure 2. Droplet 6 @ 16.03 bar: interfacial tensions versus time for an ethane + *n*-pentane mixture.

At the beginning the mass convection between the bulk phases is very fast, and it can be noticed that the pressure is rapidly reduced in the interfacial tension facility. When the condensation and vaporization process reach the equilibrium condition in the rig, both phase pressures will become stable. After several hours the liquid pump will be turned off when gas–liquid equilibrium conditions are assumed in the experimental facility. The phase temperatures, pressures, and periods of the densimeters were written down, and the drop was made and hangs inside in the Temco pendant drop cell. Interfacial tensions are calculated based on droplet initial shape analysis.

About 15 droplets will be made in the pendant drop cell at each pressure condition, and for every droplet about 100 pictures were taken for droplet shape analysis for the interfacial tension measurement. The time interval between each picture is 1 s. In Figure 2 the interfacial tension versus time is plotted. Small interfacial tension fluctuations can be observed, and the changes of interfacial tension values with time are caused mainly by dynamic convection of ethane between the droplet interface and the bulk phase. However, the range of tension fluctuation is so small that we can conclude that the gas–liquid equilibrium in the measurement process is stable.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The measured data for the ethane + *n*-pentane system is listed in Tables 2 and 3 which include the measured phase densities and interfacial tensions. According to Table 2 the calculated average liquid density deviation is −0.05 % for the ethane + *n*-pentane mixture, and the average vapor phase is 1.8 % in comparison with computed results from the GERG2004 equation.[10] In Figure 3 are plotted the experimental phase densities and calculated densities by the GERG2004 equation.

In Table 3 are data pertaining to interfacial tension measurements. The total deviation of measurement is made up of two parts. One is uncertainty based on drop shape analysis at each taken picture which can be calculated based on eq 1: N is the total number of pictures which are taken at every experimental condition, and the symbol $\overline{\sigma}$ is the average interfacial tension at each measuring condition.

Table 2. Comparison of Experimental and Calculated Phase Densities for the Ethane + *n*-Pentane System at 294.15 K

pressure	phase density/[g·cm^{-3}]		deviation
[bar]	experimental	calculated (GERG2004)	(%)
	Liquid Phase		
5.90	0.6001	0.6036	0.6
7.11	0.5940	0.5982	0.7
11.56	0.5717	0.5759	0.7
16.03	0.5458	0.5493	0.6
20.38	0.5164	0.5190	0.5
22.05	0.5086	0.5061	−0.5
24.08	0.4985	0.4895	−1.8
27.74	0.4594	0.4567	−0.6
29.87	0.4389	0.4360	−0.7
		average	0.0
	Vapor		
5.90	0.0085	0.0088	3.4
7.11	0.0104	0.0105	0.9
11.56	0.0169	0.0171	1.1
16.03	0.0243	0.0244	0.5
20.38	0.0323	0.0324	0.3
22.05	0.0357	0.0357	0.1
24.08	0.0383	0.0401	4.4
27.74	0.0481	0.0488	1.4
29.87	0.0526	0.0546	3.6
		average	1.8

$$e_1(\sigma) = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\sigma_i - \overline{\sigma})^2} \qquad (1)$$

The other deviation is the combined standard uncertainty related to the measured phase densities, shape factor, and apex

Table 3. Experimental Interfacial Tensions for the Ethane + n-Pentane System at 294.15 K

pressure	experimental interfacial tension	deviation		
[bar]	[mN/m]	e1/[mN/m]	e2/[mN/m]	(e1 + e2)/Exp./(%)
5.90	10.8	0.03	0.12	1.4
7.11	10.6	0.05	0.12	1.6
11.56	8.8	0.05	0.11	1.8
16.03	7.2	0.05	0.09	2.0
20.38	5.6	0.04	0.08	2.0
22.05	5.1	0.02	0.07	1.8
24.08	4.6	0.01	0.06	1.7
27.74	3.4	0.01	0.05	1.8
29.87	2.7	0.01	0.05	2.0
			average	1.8

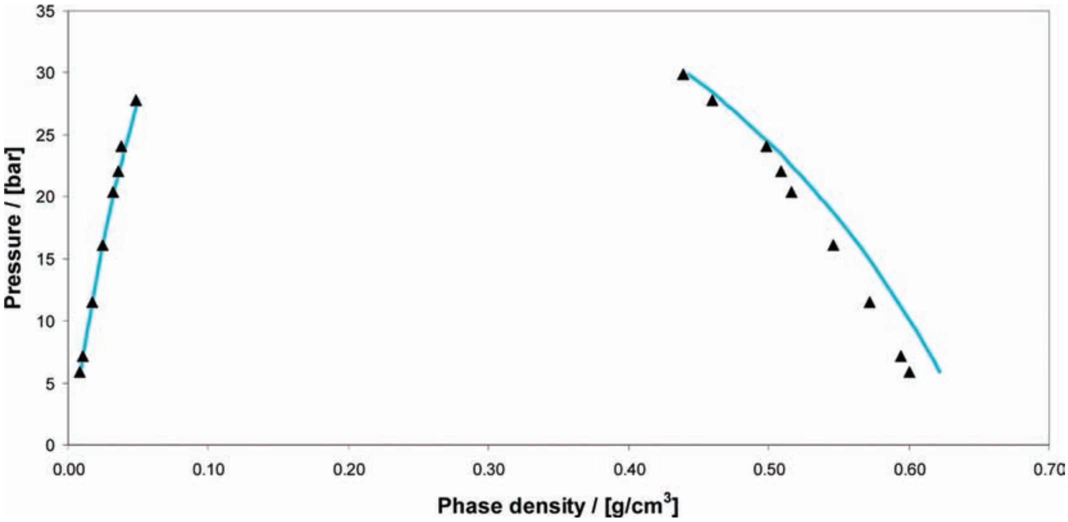

Figure 3. Phase densities for the ethane + n-pentane system at 294.15 K: ▲, experimental density (this work); blue line, calculated density of GERG2004.

radius. According to ISO recommendations of the combined standard uncertainty calculation,[11] the combined standard uncertainty of the measured interfacial tensions can be computed based on the following equation

$$e_2(\sigma) = \sqrt{\left(\frac{\partial\sigma}{\partial\rho_{\text{liq}}}e(\rho_{\text{liq}})\right)^2 + \left(\frac{\partial\sigma}{\partial\rho_{\text{vap}}}e(\rho_{\text{vap}})\right)^2 + \left(\frac{\partial\sigma}{\partial\beta}e(\beta)\right)^2 + \left(\frac{\partial\sigma}{\partial R_0}e(R_0)\right)^2} \quad (2)$$

It is shown in Table 3 that the average deviation is 1.8 % for the ethane + n-pentane mixture. It can be noticed that the relative deviation of the experimental interfacial tensions is well distributed at each pressure condition, and no systematic error exists in our experimental process. For the ethane + n-pentane system no open interfacial tension data have been reported. The experimental interfacial tension versus the pressure is plotted in Figure 4. The measured interfacial tensions decrease with increasing pressure. The lowest measured interfacial tension value is about 2.7 mN·m^{-1}.

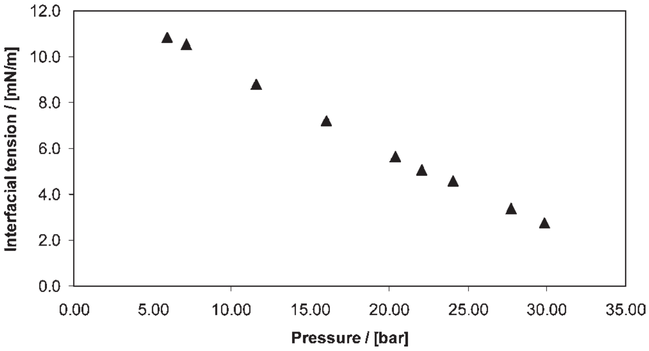

Figure 4. Interfacial tensions for the ethane + n-pentane system at 294.15 K: ▲, this work.

4. CONCLUSIONS

New data of experimental phase densities and interfacial tensions have been collected for ethane + n-pentane at 294.15 K. The precision of the liquid phase density data is excellent by comparing to PT flash simulation results from the GERG2004 equation. Even though there are high deviations of measured vapor densities, these cannot influence the uncertainty of the gas−liquid density difference because the value of the vapor density is very low compared with the measured liquid density. The standard deviation and relative standard deviation of the interfacial tension data are well distributed over the entire experimental pressure range, which proves that the experimental methodology works robustly for the system with no indication of systematic errors in the laboratory facility and measuring process. In this work the newly acquired experimental data for ethane + *n*-pentane extend the thermodynamic property database and are useful for the development and verification of the interfacial tension simulation for hydrocarbon mixtures.

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