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Compressed-liquid densities of two highly polar + non-polar binary systems ☆

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ABSTRACT

The binary systems ethanol + 2,2,4-trimethylpentane and 2-butanol + 2,2,4-trimethylpentane were studied as models for blends of gasoline with biofuels. Their densities were measured with a vibrating-tube densimeter at compressed-liquid states of three compositions of each of the binary systems. The temperature and pressure ranges of the measured data are from 270 K to 470 K, and 0.5 MPa to 50 MPa. There are no compressed-liquid density data for the binary system ethanol + 2,2,4-trimethylpentane in the literature, thus data reported here are compared to literature data at atmospheric pressure in order to establish their quality. No literature data for the system 2-butanol + 2,2,4-trimethylpentane were found, thus data reported here fill a void and help to further the understanding of molecular interactions in binary systems of a polar and a non-polar compound.

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1. Introduction

Governments in countries around the world are increasingly mandating the use of biofuels. In 1988, Denver, Colorado was the first in the United States to mandate the use of ethanol oxygenated fuel during winter months in order to reduce carbon dioxide emissions [1]. Every year from November to March, the gasoline sold in that metropolitan area is blended with 10% ethanol by volume, some of which is provided from the waste streams of a nearby brewery. In April of 2009, Directive 2009/28/EC of the European Parliament included the goal of a minimum of 10% use of biofuels or other renewable energy in the transport sector by 2020. The US Renewable Fuel Standard calls for 136 billion liters of biofuel blended into the US domestic auto and truck fuel supply by early 2022.

In spite of the widespread adoption of the use of biofuels, there is still much to learn about the thermophysical properties of these complex mixtures. Knowledge of such properties is necessary for many purposes such as the efficient design of engines and determining if the existing infrastructure will be adequate for large-scale distribution of the fuels. Biofuels often include blends of highly polar compounds with non-polar hydrocarbons. The interactions of the dissimilar molecules in these types of blends are difficult to model accurately, because they are strongly non-ideal. Measurements of such systems are more difficult than those of nonpolar compounds and their mixtures because of the physical attributes of polar compounds such as their hygroscopicity. As a result, accurate literature data for the development of non-ideal property models are sparse or non-existent. The systems investigated in this work are examples for both.

In an effort to better understand how polar + non-polar interactions affect the thermophysical properties of mixtures, the primary goal of the work presented here was to select binary systems whose pure fluid components are representative of those found in biofuel blends and then to measure their compressed-liquid densities over a wide range of temperature and pressure. Measurements such as those presented here help to reveal the non-ideal behavior of the mixtures. The binary mixtures chosen for this study were ethanol + 2,2,4-trimethylpentane and 2-butanol + 2,2,4-trimethylpentane. They are considered as model mixtures for blends of gasoline with biofuels where 2,2,4-trimethylpentane represents gasoline while ethanol and 2-butanol are first- and second-generation biofuels derived from biomass. Measurements of compressed-liquid densities were carried out for three compositions of each of the binary mixtures with nominal mole fractions of 2,2,4-trimethylpentane of 0.25, 0.5, and 0.75 over the temperature range from 270 K to 470 K with pressures from 0.5 MPa to 50 MPa.

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2. Sample liquids

Each of the three pure fluids used to prepare the mixtures studied in this work was obtained from a commercial source. The 2-butanol (CAS number 78-92-2) had a stated minimum purity of 99.5% by mole. Because of its hygroscopicity, activated molecular sieve type 5A, grade 521, with an effective pore size of 0.5 nm was added to the sample bottle to keep the 2-butanol dry. Prior to mixture preparation, the water content was just at the detection limit of approximately 20 ppm as measured by Karl Fischer coulombic titrimetry. The 2,2,4-trimethylpentane (CAS number, 540-84-1, here after referred to as iso-octane) had a stated molar purity of 99.8% and the ethanol (CAS number 78-92-2) one of 99.5%. Both were used without further purification.

The binary mixtures of ethanol + iso-octane and 2-butanol + iso-octane measured in this work were prepared gravimetrically in cleaned and dried glass bottles. The balance used in the mixture preparation had a manufacturer's stated repeatability of 0.3 g. Prior to measurements, each of the samples was transferred to a clean, dry, stainless steel bottle. The samples were then subjected to a series of being frozen with liquid nitrogen, evacuating the space above the frozen sample, and thawing the sample. This was done in order to remove air and/or any other volatile impurities from the sample, and did not affect the mixture composition.

3. Experimental

The densities of the compressed test liquids were measured with the automated densimeter that was used in our previous studies [2–9]. Central to the apparatus is a commercial vibrating-tube densimeter. Several physical and procedural improvements have been implemented beyond that of the commercial instrument operated in a stand-alone mode in order to minimize the uncertainty in the measurements. Some of these improvements include more accurate measurements of temperature and pressure, better temperature control, complete automation of the instrument control and data acquisition, and a comprehensive assessment of uncertainty. The temperature range of the instrument is 270 K to 470 K with pressures up to 50 MPa. The instrument was calibrated with propane and toluene over the entire temperature and pressure range. Further details of the calibration procedure can be found in the paper by Outcalt and McLinden [2]. The overall combined expanded uncertainty ($k=2$) in density is 1.5 $kg \cdot m^{-3}$, corresponding to a relative uncertainty in density of 0.19% to 0.30%. This uncertainty is far greater than the 0.81 $kg \cdot m^{-3}$ reported for measurements of pure fluids with this instrument. This is because it includes all of the uncertainties associated with pure fluids plus the uncertainty in the composition of the mixture.

4. Results and discussion

Tables 1 to 3 list the measured density values of three compositions of compressed-liquid ethanol + iso-octane from 270 K to 470 K to pressures of 50 MPa. A total of 375 data points are reported for this system. Tables 4 through 6 list the measured density values of the three compositions of compressed-liquid 2-butanol + iso-octane from 270 K to 470 K to pressures of 50 MPa. A total of 357 data points are reported for this system. No measurements of the mixture with 25.1% 2-butanol were conducted at 470 K. This is due to difficulties during the course of the measurements which completely depleted the supply of the standard mixture prior to measuring the final isotherm. For all

Table 1
Compressed-liquid densities of the binary system ethanol + iso-octane (25.1/74.9 mol%) measured in the high pressure vibrating-tube densimeter along isotherms from 270 K to 470 K.

270 K		290 K		310 K		330 K		350 K		370 K	
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ
MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$
50.00	755.0	49.97	742.7	50.03	730.5	50.01	717.9	50.02	705.0	50.02	691.9
40.00	749.3	39.99	736.4	39.99	723.7	40.00	710.5	40.01	696.9	40.00	683.1
29.99	743.1	30.01	729.6	30.01	716.3	30.00	702.3	30.00	687.8	30.00	673.1
20.01	736.4	20.00	722.2	20.00	708.0	20.00	693.1	20.00	677.6	20.01	661.7
10.00	729.0	10.00	713.9	10.00	698.8	10.00	682.6	10.01	665.7	10.01	648.0
5.00	725.0	5.00	709.4	5.00	693.6	5.00	676.7	5.00	658.8	4.99	639.9
4.00	724.2	4.00	708.5	4.00	692.6	4.00	675.4	3.99	657.3	4.00	638.2
3.00	723.4	2.99	707.5	3.00	691.4	3.00	674.2	3.00	655.8	3.00	636.3
2.00	722.5	2.00	706.5	2.01	690.3	2.00	672.8	2.00	654.2	2.00	634.5
0.99	721.6	1.00	705.5	1.00	689.2	0.99	671.5	1.00	652.7	1.00	632.5
0.50	721.2	0.49	705.0	0.50	688.6	0.50	670.8	0.50	651.8	0.50	631.5

390 K		410 K		430 K		450 K		470 K	
Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ	Pressure p	Density ρ
MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$	MPa	$kg \cdot m^{-3}$
50.01	679.3	50.01	666.5	50.02	654.0	50.02	641.4	50.01	628.6
40.00	669.6	40.00	656.0	40.00	642.5	40.00	628.9	40.00	615.1
30.00	658.6	30.00	643.8	30.00	629.1	30.00	614.2	30.00	598.8
20.00	645.7	20.00	629.3	20.00	612.7	20.00	595.7	20.01	578.0
10.00	629.9	10.00	610.9	10.00	591.2	10.00	570.3	10.00	548.0
5.00	620.3	5.00	599.2	5.01	576.7	5.01	552.1	5.00	524.5
4.00	618.1	4.00	596.5	4.49	575.0	4.50	549.9	4.50	521.4
3.00	615.9	3.00	593.7	3.99	573.2	4.00	547.5	4.00	518.1
2.00	613.5	2.00	590.8	3.51	571.5	3.51	545.2	3.50	514.6
0.99	611.1	1.00	587.7	3.00	569.6	3.00	542.4	3.00	510.9
0.50	609.9	0.50	586.0	2.50	567.7	2.50	539.7	2.50	506.8
				2.01	565.8	1.99	536.8	2.00	502.3
				1.50	563.7	1.50	533.9		
				1.00	561.5				

The combined expanded uncertainties U_c are $U_c(T)=30$ mK, $U_c(p)=10$ kPa, $U_c(\rho)=1.5$ $kg \cdot m^{-3}$ (level of confidence = 0.95).

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