

Density, Viscosity, Speed of Sound, Bulk Modulus, Surface Tension, and Flash Point of Binary Mixtures of *n*-Hexadecane + Ethylbenzene or + Toluene at (293.15 to 373.15) K and 0.1 MPa

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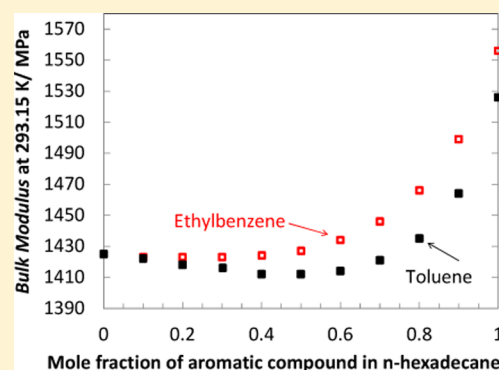
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S Supporting Information

ABSTRACT: In this work, the physical properties of binary mixtures of *n*-hexadecane with toluene or ethylbenzene were measured. Density and viscosity were measured at temperatures ranging from (293.15 to 373.15) K, and the speed of sound was measured at temperatures ranging from (293.15 to 333.15) K. Density mole fraction and temperature data were fit to a fourth-order polynomial. Viscosity mole fraction data were fit using the three-body McAllister model, while the viscosity deviations were fit to a Redlich–Kister type equation. For both two-component mixtures, the speed of sound at 293.15 K decreased as the mole fraction of the aromatic compound increased until a minimum was reached after which the speed of sound increased slightly to the value of the pure aromatic compound. The bulk modulus was calculated from density and speed of sound data. For both 2-component mixtures, the bulk modulus at 293.15 K decreased slightly as the mole fraction of the aromatic compound increased until a minimum was reached after which the bulk modulus increased to its highest value, which is the value for the aromatic compound. Flash points for the mixtures ranged from (278.5 to 408) K, and surface tension values ranged from (27.3 to 29.2) mN·m⁻¹.



1. INTRODUCTION

Liquid fuels derived from petroleum and from alternative sources such as algae, camelina, tallow, and forestry residual biomass can have a mixture of a large number of organic components such as linear and branched alkanes, aromatic compounds, and cycloparaffinic compounds. The modeling of the combustion of these fuels requires many input parameters for the various fuel components. For example, to model the combustion of only linear alkanes up to 16 carbons in length, over 10 000 reactions are included in a model developed by Lawrence Livermore Laboratories.¹ Researchers have sought to reduce the complexity of the combustion modeling of these fuels by developing surrogate mixtures, which contain a small number of known components, that match “key” physical and combustion properties of the fuel of interest.^{2–25} Some surrogate mixtures contain a variety of components such as a 14-component surrogate for jet fuel¹⁰ and an 8-component surrogate for diesel fuel,¹⁶ while other surrogates contain only a few components such as 2-component surrogates for hydrotreated renewable diesel fuel.^{5,21–25}

Unlike petroleum fuel which contains a significant fraction of aromatic compounds, alternative sourced fuels such as hydrotreated renewable diesel and jet fuels contain almost exclusively aliphatic compounds. These differences in the chemical composition cause engine seals to swell less in the presence of alternative fuels than in the presence of petroleum fuels,

which can result in fuel leaks in aircraft systems.²⁶ One way to counteract this problem is to add aromatic compounds to the alternative fuels. Recent work by DeWitt et al. studied the impact of adding various mixtures of aromatic compounds to alternative fuels on the level of swelling of nitrile rubber, fluorosilicone, and fluorocarbon o-rings.²⁷ They found that adding 10% by volume or more of an aromatic mixture to the aromatic-free alternative fuel increased the swell volume to the volume found for these o-rings in contact with petroleum-based fuels. Further work by Graham et al.²⁸ showed enhanced swelling of nitrile rubber in contact with a synthetic fuel, S-5, when various aromatic compounds, including toluene and ethylbenzene, were added at volume percentages of 10%.

The addition of aromatic compounds to alternative fuels necessitated by the need for seal swelling will change their physical properties, thereby affecting their combustion and delivery to the engine. Consequently, it is important to understand and ultimately model the impact of the addition of aromatic compounds on alternative fuel properties. It is the goal of this study to examine the properties of a surrogate mixture for an aromatic and aliphatic hydrocarbon system. Specifically this

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Table 1. Sample Information

chemical name	molar mass/(g·mol ⁻¹)	source	mole fraction purity	analysis method
<i>n</i> -hexadecane	226.44	Alfa Aesar	0.994	GC ^a
		Aldrich	0.995	GC ^a
ethylbenzene	106.165	Aldrich	0.9976	GC ^a
toluene	92.138	Pharmco-AAper	> 0.997	GC ^a

^aGas–liquid chromatography.

study focuses on two-component mixtures of the model reference compound for diesel fuel, *n*-hexadecane, which is also found in hydrotreated renewable diesel,³ and toluene or ethylbenzene, which have been studied in the seal-swelling experiments. The properties of the mixtures are compared with those of a hydrotreated renewable diesel made from algae (algal HRD-76) and a direct sugar to hydrocarbon diesel (DSH-76) to help determine the impact that the addition of aromatic compounds could have on those fuels. The physical properties of these fuels have been reported previously.^{5,21}

The “key” properties used to develop surrogate mixtures include those that impact the physical transport of the fuel into the combustion chamber as well as the physical and chemical processes in the combustion chamber itself. Some commonly measured properties are density, speed of sound, bulk modulus, viscosity, and distillation curve.^{2,3,5,7,9,12,14,23,25} The bulk modulus, which is calculated from density and speed of sound measurements, directly affects fuel injection time.^{3,29} The viscosity, surface tension, and density have been used as input parameters in the simulation of the vaporization of multi-component fuel droplets.^{30,31} In addition, the flash point has also been used as a metric for the development of some surrogate fuel mixtures because it is an indicator of the combustibility of the fuel.^{3,5,21,23,32}

In this work, the density, viscosity, surface tension, speed of sound, and flash point were measured for binary mixtures of *n*-hexadecane with toluene or ethylbenzene. Density and viscosity values of mixtures of *n*-hexadecane and these aromatic compounds have been reported at temperatures of (293.15, 298.15, 308.15, and 313.15) K.^{33–35} The current study expands the temperature range for the density and viscosity measurements of these mixtures and also measures the speed of sound, surface tension, and flashpoint. From the speed of sound and density measurements, the bulk modulus was calculated. Results from this work will provide an improved understanding of physical fuel properties at elevated fuel temperatures, which is of notable concern for engine operation in hot climates. Knowledge of the physical properties of these two-component surrogate mixtures will be help modelers who are trying to simulate their transport and combustion in engines and will provide a context for assessing the impact of aromatic compound addition on alternative fuels containing no aromatic components. Having correlations that smoothly fit the data will allow numerical simulations to test conditions where the physical properties may depend on temperature or composition.

2. MATERIALS

The *n*-hexadecane, toluene, and ethylbenzene were used as received from supplier (Table 1). Mixtures of *n*-hexadecane and each aromatic compound were prepared at room temperature by weighing each component on a Mettler Toledo AG204 analytical balance with an error of 0.0005 g. The error in mole fraction of the aromatic compound in *n*-hexadecane as given by

the combined expanded uncertainty is 0.0001, which is the same as found for other mixtures prepared the same way.²³

3. METHODS

The speed of sound of the *n*-hexadecane, toluene, ethylbenzene, and their mixtures was measured using an Anton Paar DSA 5000 density and sound analyzer. The viscosity of the compounds and mixtures was measured using an Anton Paar SVM 3000 Stabinger viscometer. Both instruments were used to measure the density. The DSA 5000 was cleaned and calibrated with degassed distilled water each day as specified by the manufacturer. For this device, two or more samples of each individual liquid or liquid mixture were measured at five temperatures between (293.15 and 333.15) K, and these replicates were used to determine the precision of the measurement. The accuracy of the SVM 3000 was tested using a NIST certified/traceable viscosity/density reference standard (Standard S3, Cannon Instrument Company) as recommended by the manufacturer. If the density deviated by more than 0.1 % from the reference value or if the viscosity deviated by more than 1 % from the reference value, then the instrument was cleaned and retested. The instrument was also tested using NIST traceable low viscosity standards (N.4 and N.8, Cannon Instrument Company). Using this instrument, two or more samples of each individual liquid or liquid mixture were measured at nine temperatures between (293.15 and 373.15) K, and these replicate measurements were used to determine the precision of the measurement. The accuracy of both instruments for their density measurements was tested using a NIST certified toluene liquid density standard-extended range (211d).

The surface tension of the liquids was measured using an axisymmetric drop shape analyzer (Krüss DS100). To determine the surface tension, an image was taken of the organic liquid droplet formed in air using a syringe and needle of known diameter. This image was magnified and fit using the Young–LaPlace equation to determine the surface tension.^{36,37} The input parameters in the fitting process are the needle diameter and the densities of the air and the organic liquid phase. Over 15 surface tension measurements were taken for a minimum of three droplets of each liquid, and these values were used to calculate the standard deviation of each measurement.^{3,5,21,23}

The flash points of the mixtures were measured using a Setafash Series 8 closed cup flash point tester model 82000-0 (Stanhope-Seta) using a temperature ramping setting. The manufacturer’s literature specifies that this flash point tester conforms to ASTM D3828 (gas ignition option), ASTM D1655 (gas ignition option), ASTM D3278, ASTM D7236, and ASTM E502. Two measurements were taken for each mixture from which the average and standard deviation were determined.

To determine the combined expanded uncertainty of density, viscosity, speed of sound, surface tension, and flash point, the standard deviation of the measurements (taken at each temperature as described above) were multiplied by 2. When a

Table 2. Experimental Values of Density ρ ($\text{kg}\cdot\text{m}^{-3}$), Dynamic Viscosity μ ($\text{mPa}\cdot\text{s}$), and Kinematic Viscosity ν ($\text{mm}^2\cdot\text{s}^{-1}$) of Mixtures of Toluene (1) + *n*-Hexadecane from $T = (293.15 \text{ to } 373.15) \text{ K}$ and 0.1 MPa^a

X_1	ρ kg·m ⁻³	μ mPa·s	ν mm ² ·s ⁻¹	ρ kg·m ⁻³	μ mPa·s	ν mm ² ·s ⁻¹	ρ kg·m ⁻³	μ mPa·s	ν mm ² ·s ⁻¹
	$T = 293.15 \text{ K}$			$T = 303.15 \text{ K}$			$T = 313.15 \text{ K}$		
0.0000	773.49	3.44	4.44	766.55	2.72	3.55	759.63		
0.1002	776.71	3.03	3.90	769.70	2.42	3.15	762.70		
0.2000	780.38	2.64	3.38	773.29	2.14	2.77	766.20		
0.3018	784.83	2.28	2.90	777.64	1.87	2.41	770.44		
0.4001	789.87	1.96	2.48	782.56	1.63	2.08	775.24		
0.5000	796.10	1.66	2.09	788.63	1.40	1.78	781.15		
0.6001	803.76	1.40	1.74	796.11	1.19	1.50	788.42		
0.7005	813.44	1.16	1.42	805.54	1.00	1.24	797.59		
0.8001	825.95	0.94(7)	1.15	817.73	0.82(8)	1.01	809.46		
0.8999	842.77	0.76(2)	0.90(4)	834.11	0.67(4)	0.80(8)	825.38		
1.0000	866.84	0.59(1)	0.68(2)	857.53	0.52(8)	0.61(6)	848.14		
	$T = 323.15 \text{ K}$			$T = 333.15 \text{ K}$			$T = 343.15 \text{ K}$		
0.0000	752.71	1.82	2.42	745.79	1.54	2.06	738.9	1.31	1.78
0.1002	755.70	1.65	2.19	748.70	1.40	1.87	741.7	1.21	1.63
0.2000	759.11	1.49	1.96	752.00	1.27	1.69	744.9	1.10	1.48
0.3018	763.23	1.33	1.74	756.00	1.15	1.52	748.9	1.00	1.34
0.4001	767.89	1.18	1.54	760.53	1.03	1.35	753.2	0.89(9)	1.19
0.5000	773.64	1.04	1.34	766.10	0.90(7)	1.18	758.6	0.80(2)	1.06
0.6001	780.71	0.90(3)	1.16	772.93	0.79(2)	1.02	765.2	0.69(6)	0.91(0)
0.7005	789.60	0.77(1)	0.97(6)	781.29	0.67(7)	0.86(7)	773.6	0.60(0)	0.77(6)
0.8001	801.12	0.64(9)	0.81(0)	792.74	0.56(9)	0.71(8)	784.3	0.51(4)	0.65(5)
0.8999	816.60	0.52(7)	0.64(6)	807.75	0.47(7)	0.59(1)	798.8	0.43(4)	0.54(3)
1.0000	838.70	0.42(9)	0.51(1)	829.16	0.38(9)	0.46(9)	819.6	0.35(6)	0.43(4)
	$T = 353.15 \text{ K}$			$T = 363.15 \text{ K}$			$T = 373.15 \text{ K}$		
0.0000	731.8	1.13	1.55	724.7	0.99(2)	1.37	717.5	0.87(8)	1.22
0.1002	734.5	1.05	1.43	727.3	0.92(2)	1.27	720.0	0.81(9)	1.14
0.2000	737.7	0.96(3)	1.31	730.4	0.85(1)	1.17	722.9	0.76(0)	1.05
0.3018	741.4	0.87(7)	1.18	733.9	0.77(9)	1.06	726.3	0.69(9)	0.96(2)
0.4001	745.7	0.79(6)	1.07	738.0	0.70(2)	0.95(2)	730.3	0.64(2)	0.85(9)
0.5000	750.9	0.70(5)	0.93(9)	743.1	0.62(6)	0.84(3)	735.1	0.56(8)	0.77(2)
0.6001	757.2	0.61(4)	0.81(1)	749.2	0.55(7) ^b	0.74(4) ^c	741.0		
0.7005	765.3	0.54(1)	0.70(7)	756.9	0.48(7)	0.64(3)	748.5		
0.8001	775.7	0.46(7)	0.60(2) ^b	767.0	0.40(5) ^d	0.52(8) ^d	758.0		
0.8999	789.7	0.39(0)	0.49(3)	780.4	0.33(8)	0.43(3)			
1.0000	809.7	0.32(1)	0.39(6)	799.7	0.27(8)	0.34(7)			

^a X_1 is the mole fraction of toluene in the (toluene + *n*-hexadecane) mixture. Standard uncertainties u are $u(T) = 0.01 \text{ K}$, and combined expanded uncertainties U_c are $U_c(\rho) = 0.3 \text{ kg}\cdot\text{m}^{-3}$, $U_c(\mu) = 0.01 \text{ mPa}\cdot\text{s}$, $U_c(\nu) = 0.01 \text{ mm}^2\cdot\text{s}^{-1}$ (level of confidence = 0.95, $k \approx 2$) unless otherwise indicated with superscripts b to d. ^bCombined expanded uncertainty of 0.02 $\text{mPa}\cdot\text{s}$ or 0.02 $\text{mm}^2\cdot\text{s}^{-1}$; ^cCombined expanded uncertainty of 0.03 $\text{mm}^2\cdot\text{s}^{-1}$.

^dCombined expanded uncertainty of 0.07 $\text{mPa}\cdot\text{s}$ or 0.09 $\text{mm}^2\cdot\text{s}^{-1}$.

normal distribution is assumed, multiplying by a coverage factor of 2 produces a 95 % confidence interval. The purity of a sample also impacts the precision of the measurements, and this was taken into account when determining the combined expanded uncertainties.³⁸

4. RESULTS

4.1. Density. The density values of *n*-hexadecane, toluene, and their mixtures are given as a function of the mole fraction of toluene (X_1) in Table 2. At 373.15 K, density results were not reproducible for toluene mole fractions greater than $X = 0.8001$; therefore, only values up to $X = 0.8001$ are reported. The density values of *n*-hexadecane, ethylbenzene, and their mixtures are given as a function of the mole fraction of ethylbenzene (X_1) in Table 3. The measured density of the NIST-certified toluene standard (Table 4) matches the certified values within $0.02 \text{ kg}\cdot\text{m}^{-3}$ for the lower temperature data from

the DSA 500 and within $0.2 \text{ kg}\cdot\text{m}^{-3}$ for the higher temperature data from the SVM 3000. The densities of the pure components match reported values as shown in Table 4. The reported values for toluene and ethylbenzene were calculated using correlations from Marsh,³⁹ which are based on a compilation of over 100 values. Good agreement is also found between the mixture data reported herein and those data reported by Asfour et al.³⁴ at (293.15 and 313.15) K, as shown in Figures 1 and 2 for toluene and ethylbenzene mixtures, respectively.

For the mixtures, the density increased as the mole fraction of the aromatic compound increased, but the increases were not linear as shown in Figures 3 and 4 for toluene and ethylbenzene mixtures, respectively. A fourth-order polynomial was used to fit the density and mole fraction data:

$$\rho/\text{kg}\cdot\text{m}^{-3} = AX_1^4 + BX_1^3 + CX_1^2 + DX_1 + E \quad (1)$$

Table 3. Experimental Values of Density ρ ($\text{kg}\cdot\text{m}^{-3}$), Dynamic Viscosity μ ($\text{mPa}\cdot\text{s}$), and Kinematic Viscosity ν ($\text{mm}^2\cdot\text{s}^{-1}$) of Mixture of Ethylbenzene (1) + *n*-Hexadecane from $T = (293.15 \text{ to } 373.15) \text{ K}$ and 0.1 MPa^a

X_1	ρ kg·m ⁻³	μ mPa·s	ν mm ² ·s ⁻¹	ρ kg·m ⁻³	μ mPa·s	ν mm ² ·s ⁻¹	ρ kg·m ⁻³	μ mPa·s	ν mm ² ·s ⁻¹
	$T = 293.15\text{ K}$			$T = 303.15\text{ K}$			$T = 313.15\text{ K}$		
0.0000	773.49	3.44	4.45	766.55	2.72	3.55	759.63		
0.1007	777.15	3.01	3.88	770.16	2.42	3.14	763.17		
0.2000	781.37	2.63	3.36	774.31	2.14	2.76	767.24		
0.3002	786.28	2.28	2.90	779.13	1.88	2.41	771.97		
0.4013	792.08	1.96	2.48	784.83	1.64	2.09	777.56		
0.5002	798.81	1.69	2.11	791.42	1.42	1.80	784.01		
0.6001	806.86	1.43	1.78	799.32	1.23	1.54	791.75		
0.7002	816.95	1.21	1.48	809.21	1.05	1.29	801.42		
0.8001	829.46	1.01	1.22	821.46	0.88(5)	1.08	813.41		
0.9000	845.47	0.83(6)	0.98(9)	837.13	0.73(8)	0.88(2)	828.73		
1.0000	866.95	0.67(0)	0.77(3)	858.15	0.59(7)	0.69(6)	849.29		
	$T = 323.15\text{ K}$			$T = 333.15\text{ K}$			$T = 343.15\text{ K}$		
0.0000	752.71	1.82	2.42	745.79	1.53	2.05	738.9	1.31	1.77
0.1007	756.18	1.65	2.19	749.19	1.40	1.87	742.2	1.21	1.62
0.2000	760.17	1.49	1.96	753.09	1.28	1.69	746.0	1.10	1.48
0.3002	764.80	1.34	1.75	757.62	1.15	1.52	750.4	1.01	1.34
0.4013	770.27	1.19	1.54	762.96	1.03	1.35	755.6	0.90(8)	1.20
0.5002	776.58	1.05	1.36	769.13	0.92(3)	1.20	761.6	0.81(6)	1.07
0.6001	784.14	0.92(7)	1.18	776.51	0.81(7)	1.05	768.9	0.71(8)	0.93(5)
0.7002	793.60	0.80(5)	1.01	785.74	0.70(7)	0.90(0)	777.9	0.62(6)	0.80(5)
0.8001	805.42	0.68(6)	0.85(1)	797.18	0.60(7)	0.76(2)	789.0	0.54(8)	0.69(4)
0.9000	820.29	0.57(6)	0.70(3)	811.80	0.52(0)	0.64(1)	803.3	0.47(3)	0.58(9)
1.0000	840.38	0.48(5)	0.57(7)	831.40	0.44(0)	0.53(0)	822.3	0.40(2)	0.48(9)
	$T = 353.15\text{ K}$			$T = 363.15\text{ K}$			$T = 373.15\text{ K}$		
0.0000	731.8	1.13	1.55	724.7	0.99(0)	1.37	717.5	0.87(6)	1.22
0.1007	735.0	1.05	1.43	727.8	0.92(2)	1.27	720.6	0.82(0)	1.14
0.2000	738.7	0.96(6)	1.31	731.5	0.85(4)	1.17	724.1	0.76(2)	1.05
0.3002	743.0	0.88(4)	1.19	735.6	0.78(6)	1.07	728.1	0.69(7)	0.95(7)
0.4013	748.1	0.80(3)	1.07	740.6	0.70(9)	0.95(8)	732.9	0.63(3)	0.86(3)
0.5002	754.0	0.71(8)	0.95(2)	746.3	0.63(8)	0.85(5)	738.4	0.57(8)	0.78(3)
0.6001	761.1	0.64(0)	0.84(1)	753.1	0.58(3) ^b	0.77(4) ^b	745.1	0.52(4)	0.70(4)
0.7002	769.8	0.56(5)	0.73(4)	761.6	0.51(3)	0.67(4)	753.3	0.47(1)	0.62(5)
0.8001	780.7	0.49(7)	0.63(7)	772.2	0.45(4)	0.58(8)	763.6	0.41(7)	0.54(7)
0.9000	794.5	0.43(1)	0.54(3)	785.6	0.39(6)	0.50(5)	776.6	0.36(7)	0.47(3)
1.0000	813.1	0.36(8)	0.45(2)	803.7	0.33(9)	0.42(2)	794.2	0.31(4)	0.39(6)

^a X_1 is the mole fraction of ethylbenzene in (ethylbenzene + *n*-hexadecane). Standard uncertainties u are $u(T) = 0.01 \text{ K}$, and combined expanded uncertainties U_c are $U_c(\rho) = 0.3 \text{ kg}\cdot\text{m}^{-3}$, $U_c(\mu) = 0.01 \text{ mPa}\cdot\text{s}$, $U_c(\nu) = 0.01 \text{ mm}^2\cdot\text{s}^{-1}$ (level of confidence = 0.95, $k \approx 2$), unless indicated with superscript b. ^bCombined expanded uncertainty of $0.2 \text{ mPa}\cdot\text{s}$ or $0.3 \text{ mm}^2\cdot\text{s}^{-1}$.

as was done by Asfour et al.³⁴ In this equation X_1 is the mole fraction of the aromatic compound, and A , B , C , D , and E are fitting parameters, which are given in Table 5. Microsoft Excel 2010 was used to conduct the fitting operation. The standard error of the fit, as calculated by

$$\sigma = \sqrt{\frac{\sum (P_{\text{measured}} - P_{\text{m,cal}})^2}{N - n}} \quad (2)$$

is also given in Table 5. In this equation P_{measured} is the measured density and $P_{\text{m,cal}}$ is the fitted density, N is the number of experimental data, and n is the number of parameters in the fitting equation. The fits are good with $R^2 > 0.9999$ as shown in Figures 3 and 4. To fit the data at 373.15 K , the pure toluene density calculated using the correlation given by Marsh,³⁹ $798.8 \text{ kg}\cdot\text{m}^{-3}$, was used.

The excess molar volumes (V_m^E) of each aromatic compound in *n*-hexadecane were calculated using the following equation:

$$V_m^E = \frac{M_1 X_1 + M_2 X_2}{\rho_m} - \frac{M_1 X_1}{\rho_1} - \frac{M_2 X_2}{\rho_2} \quad (3)$$

where ρ_m is the density of the mixture, ρ_1 and ρ_2 are the densities, M_1 and M_2 are the molar masses, and X_1 and X_2 are the mole fractions of the aromatic compound as component 1 and *n*-hexadecane as component 2. The calculated excess molar volumes for a toluene and *n*-hexadecane mixture ($X_1 = 0.5000$) and for ethylbenzene and *n*-hexadecane mixture ($X_1 = 0.5002$) are given in Table 5. For both sets of mixtures, the excess molar volumes are negative and do not vary significantly with temperature. Additional excess molar volumes and their fitting using a Redlich–Kister type expression can be found in the

Table 4. Comparison of the Measured Density and Speed of Sound Values of Toluene, Ethylbenzene, and *n*-Hexadecane with Literature Values

compound	<i>T</i> /K	density/kg·m ⁻³		speed of sound/m·s ⁻¹	
		this study	literature	this study	literature
NIST certified toluene standard	293.15	866.84	866.828 ± 0.031 ^b	1326.3	
	303.15	857.52	857.507 ± 0.032 ^b	1283.3	
	313.15	848.14	848.131 ± 0.033 ^b	1240.6	
	323.15	838.69	838.684 ± 0.034 ^b	1198.6	
	333.15	829.16	829.152 ± 0.035 ^b	1157.2	
	343.15	819.5	819.516 ± 0.037 ^b		
	353.15	809.7	809.761 ± 0.038 ^b		
	363.15	799.7	799.867 ± 0.039 ^b		
toluene	293.15	866.84 ± 0.3	866.84 ± 0.05 ^a	1326.8	1326.9 ^e , 1324.3 ^f
	303.15	857.53 ± 0.3	857.54 ± 0.05 ^a	1283.7	1281.6 ^f
	313.15	848.14 ± 0.3	848.17 ± 0.05 ^a	1241.1	1240.9 ^e , 1239.7 ^f
	323.15	838.70 ± 0.3	838.73 ± 0.05 ^a	1199.0	1198.9 ^e , 1198.5 ^f
	333.15	829.16 ± 0.3	829.20 ± 0.05 ^a	1157.6	1157.7 ^e , 1158.0 ^f
	343.15	819.6 ± 0.3	819.56 ± 0.09 ^a		
	353.15	809.7 ± 0.3	809.80 ± 0.19 ^a		
	363.15	799.7 ± 0.3	799.90 ± 0.30 ^a		
ethylbenzene	293.15	866.95 ± 0.3	866.94 ± 0.22 ^a	1339.70	1340 ^g
	303.15	858.15 ± 0.3	858.15 ± 0.23 ^a	1298.05	
	313.15	849.29 ± 0.3	849.33 ± 0.24 ^a	1256.89	1257 ^g , 1256 ^h
	323.15	840.38 ± 0.3	840.44 ± 0.25 ^a	1216.35	
	333.15	831.40 ± 0.3	831.48 ± 0.26 ^a	1176.40	
	343.15	822.3 ± 0.3	822.43 ± 0.27 ^a		
	353.15	813.1 ± 0.3	813.28 ± 0.28 ^a		
	363.15	803.7 ± 0.3	804.02 ± 0.29 ^a		
	373.15	794.2 ± 0.3	794.63 ± 0.30 ^a		
<i>n</i> -hexadecane	293.15	773.49 ± 0.3	773.6 ± 0.3 ^c	1357.3 ± 0.3	1357.0 ± 0.3 ^d , 1357.7 ^g
	303.15	766.55 ± 0.3	766.7 ± 0.3 ^c	1320.0 ± 0.3	1319.5 ± 0.3 ^d , 1320.2 ^g
	313.15	759.63 ± 0.3	759.8 ± 0.3 ^c	1283.3 ± 0.3	1282.8 ± 0.3 ^d , 1283.4 ^g
	323.15	752.71 ± 0.3	752.9 ± 0.3 ^c	1247.3 ± 0.3	1246.8 ± 0.3 ^d , 1247.4 ^g
	333.15	745.79 ± 0.3	745.8 ± 0.3 ^c	1212.0 ± 0.3	1212.3 ^d
	343.15	738.9 ± 0.3	739.0 ± 0.2 ^c		
	353.15	731.8 ± 0.3	731.8 ± 0.3 ^c		
	363.15	724.7 ± 0.3	724.8 ± 0.2 ^c		
	373.15	717.5 ± 0.3	717.7 ± 0.2 ^c		

^aFrom equation fit by ref 39 to “reliable data” from over 15 sources. For toluene, the equation is $\rho = 1.18621 \cdot 10^3 - 1.47573T + 2.08566 \cdot 10^{-3} T^2 - 2.61945 \cdot 10^{-6} T^3$. For ethylbenzene, the equation is $\rho = 1.16628 \cdot 10^3 - 1.35889T + 1.81018 \cdot 10^{-3} T^2 - 2.24496 \cdot 10^{-6} T^3$. ^bNational Institute of Standards and Technology values for liquid density of SRM 211d “as shipped”. Error bars are the reported standard uncertainties.⁴⁴ ^cReferences 5 and 21. ^dReference 5. ^eReference 40. ^fReference 41. ^gReference 45. ^hReference 43.

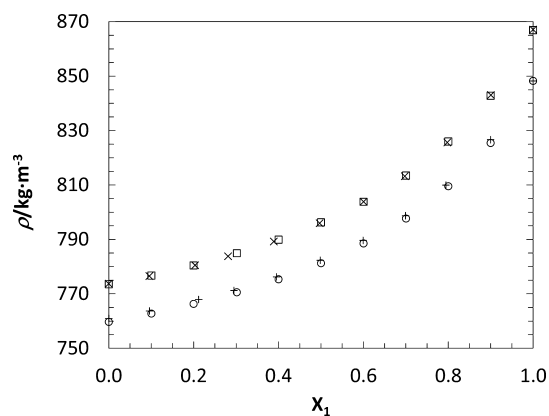


Figure 1. Comparison of the density of toluene (X_1) and *n*-hexadecane mixtures at □, 293.15 K and ○, 303.15 K with those given at ×, 293.15 K and +, 313.15 K by ref 34.

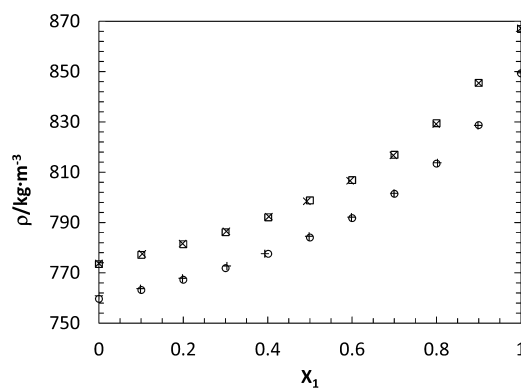


Figure 2. Comparison of the density of ethylbenzene (X_1) and *n*-hexadecane mixtures at □, 293.15 K and ○, 303.15 K with those given at ×, 293.15 and +, 313.15 K by ref 34

Supporting Information in Tables S1–S3. The density of the individual components depends on the attraction between

molecules, which in this case is London dispersion forces, as well as the shape and size. Individual toluene molecules contain the planar benzene ring, which allows for close spacing, and a

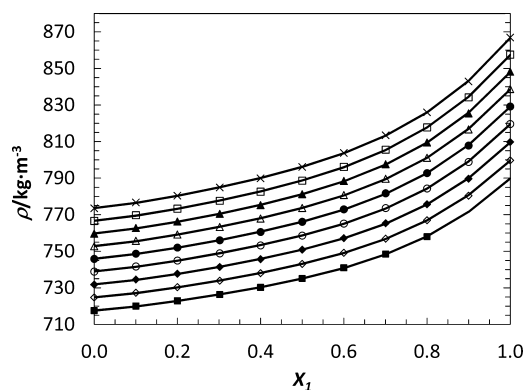


Figure 3. Density of toluene (X_1) + n -hexadecane mixtures at \times , 293.15 K; \square , 303.15 K; \blacktriangle , 313.15 K; \triangle , 323.15 K; \bullet , 333.15 K; \circ , 343.15 K; \blacklozenge , 353.15 K; \diamond , 363.15 K; \blacksquare , 373.15 K. Error bars, which are the combined expanded uncertainties with a 0.95 level of confidence ($k \approx 2$), are smaller than the symbols. Lines shown are second-order fits using eq 1 with the coefficients in Table 5.

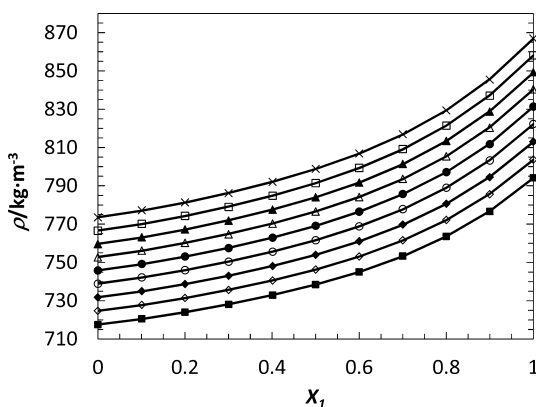


Figure 4. Density of ethylbenzene (X_1) + n -hexadecane mixtures at \times , 293.15 K; \square , 303.15 K; \blacktriangle , 313.15 K; \triangle , 323.15 K; \bullet , 333.15 K; \circ , 343.15 K; \blacklozenge , 353.15 K; \diamond , 363.15 K; \blacksquare , 373.15 K. Error bars, which are the combined expanded uncertainties with a 0.95 level of confidence ($k \approx 2$), are smaller than the symbols. Lines shown are fourth-order fits using eq 1 with the coefficients in Table 5.

methyl group, which reduced how closely spaced the benzene rings can be. The hexadecane is a longer molecule which can bend into more shapes and take up more space. When the two molecules are mixed, the smaller toluene molecules can fit within less compact n -hexadecane molecules, resulting in a negative excess molar volume.

Most of the two-component mixtures studied herein have a higher density than those of the hydrotreated renewable diesels algal HRD-76 and DSH-76. At 293.15 K, the density value of $769.8 \pm 0.2 \text{ kg}\cdot\text{m}^{-3}$ for DSH-76 is below that of pure n -hexadecane, $773.49 \text{ kg}\cdot\text{m}^{-3}$. For algal HRD-76 the density of $776.1 \pm 1.3 \text{ kg}\cdot\text{m}^{-3}$ falls between the density values for mole fraction of 0 and 0.1 for toluene ($776.71 \text{ kg}\cdot\text{m}^{-3}$ at $X_1 = 0.1$) and ethylbenzene mixtures ($777.15 \text{ kg}\cdot\text{m}^{-3}$ at $X_1 = 0.1$) at 293.15 K. The addition of toluene to hydrotreated renewable diesels will increase their density. In engines that deliver a constant volume of fuel into the reaction chamber, a higher density for hydrotreated fuels with the added aromatic compounds would mean a greater mass is available for combustion.

4.2. Viscosity. The dynamic and kinematic viscosity values of toluene, n -hexadecane, and their mixtures are given in Table 2 as a function of the mole fraction of toluene (X_1).

At 373.15 K, the viscosity results were not reproducible for toluene mole fractions greater than $X_1 = 0.5000$; therefore, only values up to $X_1 = 0.5000$ are reported. The viscosity values of ethylbenzene, n -hexadecane, and their mixtures are given in Table 3 as a function of the mole fraction of ethylbenzene (X_1). The viscosity values of the toluene and ethylbenzene agree with literature values within the error of the measurement as shown in Table 6. The viscosity values of n -hexadecane match exactly the values previously reported by our lab.²¹ Good agreement is also found between the mixture data reported herein and those data reported by Asfour et al.³³ at 293.15 K, as shown in Figures 5 and 6 for toluene and ethylbenzene mixtures, respectively.

The McAllister three-body model⁶⁵ was used to fit the kinematic viscosity data:

$$\begin{aligned} \ln \nu_m = & X_1^3 \ln \nu_1 + 3X_1^2 X_2 \ln \nu_{1,2} + 3X_1 X_2^2 \ln \nu_{2,1} \\ & + X_2^3 \ln \nu_2 - \ln \left(X_1 + X_2 \frac{M_2}{M_1} \right) \\ & + 3X_1^2 X_2 \ln \left(\frac{1}{3} \left(2 + \frac{M_2}{M_1} \right) \right) + 3X_1 X_2^2 \ln \left(\frac{1}{3} \left(1 + 2 \frac{M_2}{M_1} \right) \right) \\ & + X_2^3 \ln \left(\frac{M_2}{M_1} \right) \end{aligned} \quad (4)$$

Here ν_m is the kinematic viscosity of the binary mixture, X_1 and X_2 are the mole fractions, ν_1 and ν_2 are the kinematic viscosities of the pure components, and M_1 and M_2 are the molar masses of the aromatic compound as component 1 and n -hexadecane as component 2. The interaction parameters $\nu_{2,1}$ and $\nu_{1,2}$ were determined using the GRG nonlinear engine of the SOLVER function in Microsoft Excel 2010 to minimize the sum of the square of the difference between the value calculated by the model in eq 4, $\nu_{m,\text{calc}}$ and the measured kinematic viscosity of the binary mixture, $\nu_{m,\text{measured}}$:

$$\min \sum (\nu_{m,\text{calc}} - \nu_{m,\text{measured}})^2 \quad (5)$$

The standard error for the fit (σ) was determined by eq 2, where P_{measured} is the measured viscosity and $P_{m,\text{cal}}$ is the fitted viscosity. The fitted values of $\nu_{2,1}$ and $\nu_{1,2}$, and the standard errors of the fits are given in Table 7 for each temperature. The model fits the data well as shown in Figures 7 and 8.

The kinematic viscosity deviation (ν^E) in these two component systems was calculated using

$$\nu^E = \nu_m - (X_1 \nu_1) - (X_2 \nu_2) \quad (6)$$

ν_m is the kinematic viscosity of the binary mixture, ν_1 and ν_2 are the kinematic viscosities of the pure components, and X_1 and X_2 are the mole fractions of the aromatic compound as component 1 and n -hexadecane as component 2. The calculated values of the viscosity deviations for all two-component mixtures are given in Tables S4 and S5 of the Supporting Information. Figures 9 and 10 show that the viscosity deviations for the mixtures are negative and become less negative as temperature increases. The viscosity of the individual components depends on the attraction between molecules and shape of the molecules. Longer alkanes, such as n -hexadecane, can take a variety of shapes and individual molecules can become entangled with each other. Toluene and ethylbenzene molecules are more compact and are less likely to become entangled with each other. Mixing the toluene with the n -hexadecane will

Table 5. Parameters^a for eq 1, $\rho/\text{kg}\cdot\text{m}^{-3} = AX_1^4 + BX_1^3 + CX_1^2 + DX_1 + E$, that Correlate Density to Mole Fraction of Toluene (1) in (Toluene + *n*-Hexadecane) Mixtures or Density to Mole Fraction of Ethylbenzene (1) in (Ethylbenzene + *n*-Hexadecane) Mixtures, and the Excess Molar Volume^b (V_m^E) at $X_1 = 0.5000$ for Toluene and at $X_1 = 0.5002$ for Ethylbenzene, $T = (293.15 \text{ to } 373.15) \text{ K}$, and 0.1 MPa

T/K	A	B	C	D	E	R^2	standard error of fit	$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$
Ethylbenzene (1) + <i>n</i> -Hexadecane (2)								
293.15	79 ± 21	−77 ± 42	63 ± 27	28 ± 6	773.6 ± 0.4	0.9999	0.17	−0.23
303.15	77 ± 20	−75 ± 41	61 ± 27	28 ± 6	766.6 ± 0.4	0.9999	0.17	−0.24
313.15	76 ± 20	−74 ± 40	60 ± 26	27 ± 6	759.7 ± 0.4	0.9999	0.16	−0.25
323.15	72 ± 20	−69 ± 41	57 ± 26	27 ± 6	752.8 ± 0.4	0.9999	0.17	−0.25
333.15	72 ± 19	−70 ± 37	57 ± 24	27 ± 6	745.8 ± 0.4	0.9999	0.15	−0.25
343.15	68 ± 16	−64 ± 33	53 ± 21	26 ± 5	739.0 ± 0.3	0.9999	0.13	−0.22
353.15	69 ± 17	−68 ± 34	55 ± 22	25 ± 5	731.9 ± 0.3	0.9999	0.14	−0.23
363.15	67 ± 16	−66 ± 33	52 ± 21	25 ± 5	724.8 ± 0.3	0.9999	0.13	−0.22
373.15	63 ± 18	−60 ± 36	48 ± 23	25 ± 5	717.6 ± 0.3	0.9999	0.15	−0.20
Toluene (1) + <i>n</i> -Hexadecane (2)								
293.15	117 ± 33	−127 ± 67	82 ± 43	21 ± 10	773.6 ± 0.6	0.9999	0.27	−0.17
303.15	113 ± 32	−123 ± 64	79 ± 42	21 ± 10	776.7 ± 0.6	0.9999	0.26	−0.17
313.15	110 ± 31	−119 ± 62	77 ± 40	20 ± 9	759.8 ± 0.6	0.9999	0.26	−0.17
323.15	107 ± 29	−116 ± 60	75 ± 39	20 ± 9	752.8 ± 0.6	0.9999	0.25	−0.17
333.15	103 ± 30	−112 ± 61	73 ± 39	19 ± 9	745.9 ± 0.6	0.9999	0.25	−0.16
343.15	103 ± 29	−114 ± 59	74 ± 39	18 ± 8	739.0 ± 0.6	0.9999	0.24	−0.16
353.15	99 ± 27	−109 ± 54	69 ± 35	18 ± 8	731.9 ± 0.6	0.9999	0.22	−0.16
363.15	96 ± 28	−106 ± 56	68 ± 37	17 ± 8	724.8 ± 0.5	0.9999	0.23	−0.15
373.15	88 ± 25	−91 ± 51	58 ± 32	18 ± 7	717.6 ± 0.4	0.9999	0.57	−0.10

^aThe error for the coefficients A, B, C, D, and E represents a 95 % confidence interval. ^bThe standard deviations in the excess volume for toluene were calculated to be $0.03 \text{ cm}^3\cdot\text{mol}^{-1}$ by propagating the errors for the molar masses, masses, and densities. The combined expanded uncertainty calculated using a coverage factor of 2 (95 % confidence interval) was $0.06 \text{ cm}^3\cdot\text{mol}^{-1}$. The standard deviations in the excess volume for ethylbenzene was calculated to be $0.02 \text{ cm}^3\cdot\text{mol}^{-1}$ for $T \leq 333.15 \text{ K}$ and 0.03 for $T > 333.15 \text{ K}$ by propagating the errors for the molar masses, masses, and densities. The combined expanded uncertainties calculated using a coverage factor of 2 are $(0.04 \text{ and } 0.06) \text{ cm}^3\cdot\text{mol}^{-1}$ for $T \leq 333.15 \text{ K}$ and $T > 333.15 \text{ K}$, respectively.

reduce the entanglement of the *n*-hexadecane and allow the fluid to flow more easily than predicted by their individual viscosities. The net result is a negative viscosity deviation. Such entanglements should become smaller as the linear alkane becomes smaller, and such a result was found by Vavanellos et al.³⁵ in their work with mixtures of toluene and ethylbenzene with a linear alkanes ranging from 8 to 16 carbons. They found that the viscosity–composition curve relationship was virtually linear for octane mixed with toluene or ethylbenzene. For *n*-alkanes with larger carbon numbers and more likelihood of entanglement, the viscosity deviated in the negative direction from linearity. This deviation became greater as the number of carbons increased.

The kinematic viscosity deviations were fit to a Redlich–Kister type expression⁶⁶

$$\nu^E = X_1X_2 \sum_{j=1}^3 A_j(X_1 - X_2)^{j-1} \quad (7)$$

where A_j are adjustable parameters, j is the order of the polynomial, and X_1 and X_2 are the mole fraction of the aromatic compound and *n*-hexadecane, respectively. The standard error for the fit (σ) was determined by eq 2, where P_{measured} is the calculated kinematic viscosity deviation and $P_{\text{m,cal}}$ is the fitted kinematic viscosity deviation. The fitted values of A_1 , A_2 , and A_3 , and the standard errors of the fits are given in Table 8 for each temperature. The model fits the data well, as shown in Figures 9 and 10 and for toluene and ethylbenzene mixtures, respectively.

The viscosity values for the hydrotreated renewable fuels fall within the viscosity values of the mixtures measured herein. At 293.15 K, the viscosity of 3.40 mPa·s for algal HRD-76

is close to that of pure *n*-hexadecane, 3.44 mPa·s. For DSH-76, the viscosity of 2.74 mPa·s is between that of pure *n*-hexadecane and 2.64 mPa·s for toluene ($X_1 = 0.2000$) mixtures and 2.63 mPa·s for ethylbenzene ($X_1 = 0.2000$) mixtures. The addition of an aromatic compound lowers the viscosity, increasing the ease of pumping the fuel into the engine.

4.3. Speed of Sound and Bulk Modulus. The speed of sound values are given in Table 9 for the *n*-hexadecane, toluene, ethylbenzene, and their mixtures as a function of the mole fraction of the aromatic compound. The speed of sound measurements for the pure components agree with literature values within the error of the measurement as shown in Table 4. As the mole fraction of the aromatic compound increased, the speed of sound decreased before reaching a minimum and then increasing again to the value measured for the pure aromatic compound as shown in Figure 11. The mole fraction range over which the mixture values were lower than the pure components decreased as temperature increased. For example, the speed of sound for ethylbenzene mixtures was lower than both components for mole fractions between $X_1 = 0.5002$ and $X_1 = 0.9000$ at 293.15 K. At 333.15 K, only the values at $X_1 = 0.8001$ and $X_1 = 0.9000$ were lower than that of the pure components. Similar behavior has been found for binary mixtures of ethylbenzene with 1-nonanol or 2-decanol,⁴² toluene or ethylbenzene with ethoxyethanols,⁶⁷ and toluene or ethylbenzene mixed with cyclohexane where the range over which the minimum occurs declines with an increase in temperature.^{42,68} This behavior differs from mixtures of *n*-hexadecane and branched alkanes or *n*-dodecane and branched alkanes in

Table 6. Comparison of the Measured Viscosity Values of Toluene and Ethylbenzene with Literature Values

T/K	toluene				ethylbenzene			
	$\mu/\text{mPa}\cdot\text{s}$		$\nu/\text{mm}^2\cdot\text{s}^{-1}$		$\mu/\text{mPa}\cdot\text{s}$		$\nu/\text{mm}^2\cdot\text{s}^{-1}$	
	this work	reference	this work	reference	this work	reference	this work	reference
293.15	0.59(1) \pm 0.01	0.5859 ^a 0.5866 ^b 0.5887 ^c 0.5882 ^d	0.68(2) \pm 0.01	0.6767 ^b 0.6777 ^o 0.67774 ^p	0.67(0) \pm 0.01	0.673 ^b 0.6763 ^b 0.6783 ^b	0.77(3) \pm 0.01	0.7701 ^o 0.7823 ^b
303.15	0.52(8) \pm 0.01	0.517 ^e 0.519 ^f 0.5204 ^g 0.5203 ^b 0.521 ^h 0.5224 ⁱ 0.5226 ^c 0.524 ^j 0.5372 ^k	0.61(6) \pm 0.01	0.6066 ^b 0.6083 ^q 0.6196 ^r	0.59(8) \pm 0.01	0.584 ^h 0.5923 ^g 0.5976 ^t 0.598 ^b 0.5985 ^b 0.6003 ^b	0.69(6) \pm 0.01	0.6996 ^b
323.15	0.42(9) \pm 0.01	0.4189 ^b 0.420 ^f 0.4211 ⁱ 0.4215 ^m 0.4221 ^g 0.4222 ⁱ 0.4272 ^k	0.51(1) \pm 0.01	0.4991 ^b 0.5009 ^q 0.5028 ^r	0.48(5) \pm 0.01	0.474 ^b 0.4797 ^g 0.4814 ^b 0.483 ^b 0.4852 ^t	0.57(7) \pm 0.01	0.5725 ^b
333.15	0.38(9) \pm 0.01	0.380 ^b 0.381 ^f 0.390 ⁿ 0.3905 ^k	0.46(9) \pm 0.01	0.458 ^b 0.4608 ^r	0.44(0) \pm 0.01	0.436 ^b 0.437 ^b 0.4410 ^q	0.53(0) \pm 0.01	0.525 ^b
343.15	0.35(6) \pm 0.01	0.346 ^b 0.347 ^f	0.43(4) \pm 0.01	0.4075 ^q 0.422 ^b	0.40(2) \pm 0.01	0.387 ^b 0.397 ^b	0.48(9) \pm 0.01	0.483 ^b
353.15	0.32(1) \pm 0.01(3)	0.317 ^b 0.326 ⁿ	0.39(6) \pm 0.01(3)	0.391 ^b	0.36(8) \pm 0.01	0.364 ^{b,s}	0.45(2) \pm 0.01	0.447 ^b
363.15	0.27(8) \pm 0.01	0.291 ^b	0.34(7) \pm 0.01	0.363 ^b	0.34(0) \pm 0.01	0.334 ^b	0.42(2) \pm 0.01	0.416 ^b
373.15					0.31(4) \pm 0.01	0.308 ^b	0.39(6) \pm 0.01	0.388 ^b

^aReference 46. ^bReference 47. ^cReference 48. ^dReference 49. ^eReference 50. ^fReference 51. ^gReference 52. ^hReference 53. ⁱReference 54. ^jReference 55. ^kReference 56. ^lReference 57. ^mReference 58. ⁿReference 59. ^oReference 33. ^pReference 60. ^qReference 61. ^rReference 62. ^sReference 63. ^tReference 64.

which the lowest speed of sound value corresponds to a pure component value.^{3,21,23} The behavior was also not found in binary mixtures of toluene or ethylbenzene with hexane, heptane, or nonane.⁶⁹

The speed of sound of all mixtures decreased as temperature increased (Table 9), and the decline was linear over the temperature range measured as illustrated for ethylbenzene in Figure 12. Speed of sound and temperature data were fit to

$$c/\text{m}\cdot\text{s}^{-1} = AT/K + B \quad (8)$$

using the Microsoft Excel linear regression software in its Analysis Toolpak, and the standard error of the fit was calculated using eq 2. The fitting parameters are given in Table 10. All fits are good ($R^2 \geq 0.9999$) as illustrated in Figure 12 for ethylbenzene and hexadecane mixtures.

For ethylbenzene the relationship

$$c/\text{m}\cdot\text{s}^{-1} = -4.084T/K + 2536 \quad (9)$$

can be used to predict the speed of sound value at 298.15 K. The predicted value of 1318 $\text{m}\cdot\text{s}^{-1}$ matches the value 1318 $\text{m}\cdot\text{s}^{-1}$ reported by George and Sastry⁶⁷ but is higher than 1297 $\text{m}\cdot\text{s}^{-1}$ reported by Vitall and Lobbia.⁷⁰

Table 7. Values of the Coefficients for the McAllister Equation (eq 4) and Associated Standard Deviations (eq 2) for Binary Mixtures of *n*-Hexadecane with Toluene or Ethylbenzene from $T = (293.15 \text{ to } 373.15) \text{ K}$

T	$\nu_{1,2}$	$\nu_{2,1}$	σ
K	$\text{mm}^2\cdot\text{s}^{-1}$	$\text{mm}^2\cdot\text{s}^{-1}$	$\text{mm}^2\cdot\text{s}^{-1}$
Ethylbenzene			
293.15	1.82	2.85	0.0075
303.15	1.60	2.37	0.0066
323.15	1.24	1.75	0.0030
333.15	1.09	1.54	0.0030
343.15	0.970	1.36	0.0035
353.15	0.873	1.22	0.0030
363.15	0.801	1.08	0.0057
373.15	0.743	0.966	0.0060
Toluene			
293.15	1.87	2.90	0.0090
303.15	1.64	2.41	0.0077
323.15	1.28	1.75	0.0049
333.15	1.14	1.53	0.0040
343.15	1.01	1.36	0.0036
353.15	0.900	1.21	0.0058
363.15	0.839	1.09	0.0051

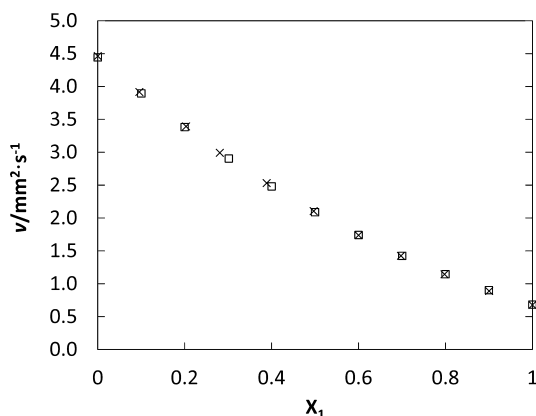


Figure 5. Comparison of the kinematic viscosity of toluene (X_1) and n -hexadecane mixtures, \square , with those given by ref 33, \times , at 293.15 K.

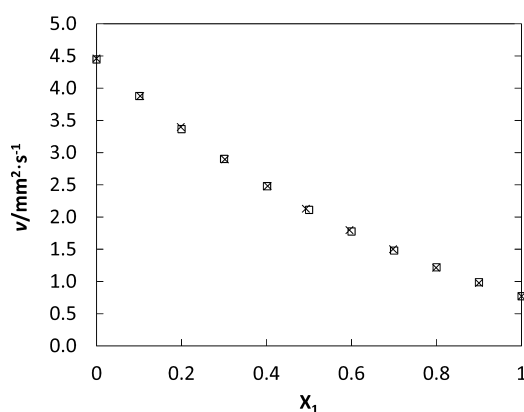


Figure 6. Comparison of the kinematic viscosity of ethylbenzene (X_1) and n -hexadecane mixtures, \square , with those given by ref 33, \times , at 293.15 K.

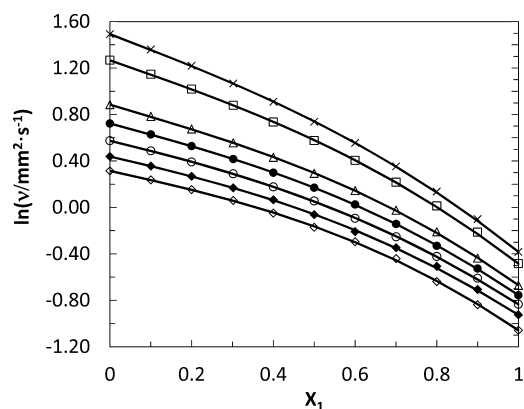


Figure 7. Kinematic viscosity of toluene (X_1) + n -hexadecane mixtures at \times , 293.15 K; \square , 303.15 K; \triangle , 323.15 K; \bullet , 333.15 K; \circ , 343.15 K; \blacklozenge , 353.15 K; \diamond , 363.15 K. Error bars, which are the combined expanded uncertainties with a 0.95 level of confidence ($k \approx 2$), are smaller than symbols. Lines shown are fits to eq 4 with the coefficients in Table 7.

The isentropic bulk modulus, E_v , was calculated at each temperature and ambient pressure from the speed of sound (c) and density (ρ) by⁷¹

$$E_v/\text{Pa} = (c^2/\text{m}^2\cdot\text{s}^{-2})(\rho/\text{kg}\cdot\text{m}^{-3}) \quad (10)$$

These values for the mixtures of n -hexadecane and with either toluene or ethylbenzene are given in Table 11. The bulk modulus

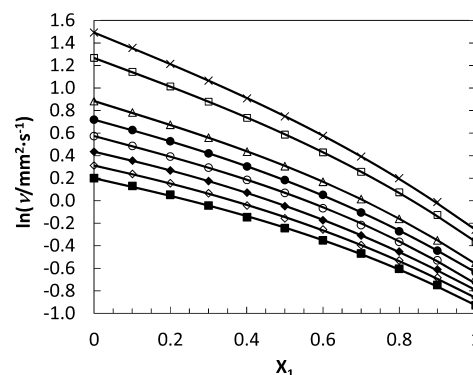


Figure 8. Kinematic viscosity of ethylbenzene (X_1) + n -hexadecane mixtures at \times , 293.15 K; \square , 303.15 K; \triangle , 323.15 K; \bullet , 333.15 K; \circ , 343.15 K; \blacklozenge , 353.15 K; \diamond , 363.15 K; \blacksquare , 373.15 K. Error bars, which are the combined expanded uncertainties with a 0.95 level of confidence ($k \approx 2$), are smaller than symbols. Lines shown are fits to eq 4 with the coefficients in Table 7.

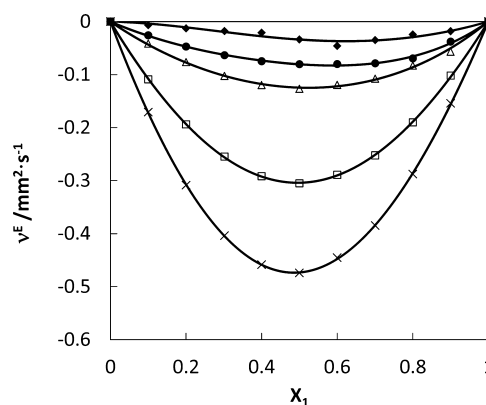


Figure 9. Kinematic viscosity deviation of toluene (X_1) + n -hexadecane mixtures as calculated by eq 6 at: \times , 293.15 K; \square , 303.15 K; \triangle , 323.15 K; \bullet , 333.15 K; and \blacklozenge , 353.15 K. Lines shown are fits to eq 7 with the coefficients in Table 8.

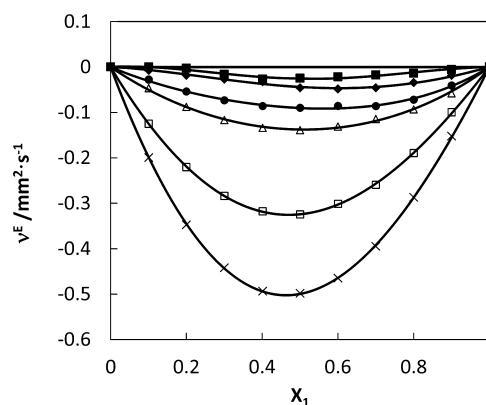


Figure 10. Kinematic viscosity deviation of ethylbenzene (X_1) + n -hexadecane mixtures as calculated by eq 6 at: \times , 293.15 K; \square , 303.15 K; \triangle , 323.15 K; \bullet , 333.15 K; \blacklozenge , 353.15 K; \blacksquare , 373.15 K. Lines shown are fits to eq 7 with the coefficients in Table 8.

decreases with increasing temperature. As the mole fraction of the aromatic compound increases, the bulk modulus initially decreases and then increases to a value higher than that of the pure n -hexadecane. Such behavior is caused by the nonlinear behavior of the speed of sound shown in Figure 11 and the fact

Table 8. Parameters for the Redlich–Kister Equation, eq 7, for Excess Viscosity of Mixtures of *n*-Hexadecane with Toluene or Ethylbenzene and the Standard Errors at 0.1 MPa

<i>T</i> K	<i>A</i> ₁ mm ² ·s ^{−1}	<i>A</i> ₂ mm ² ·s ^{−1}	<i>A</i> ₃ mm ² ·s ^{−1}	$\sigma \cdot 10^3$ mm ² ·s ^{−1}
Ethylbenzene				
293.15	−1.998	0.304	0.060	1.8
303.15	−1.297	0.159	0.060	1.5
323.15	−0.550	−0.022	−0.038	3.2
333.15	−0.361	−0.079	−0.066	2.9
343.15	−0.254	−0.092	−0.052	3.5
353.15	−0.176	−0.099	0.040	2.5
363.15	−0.130	−0.065	0.080	4.4
373.15	−0.102	−0.029	0.126	2.8
Toluene				
293.15	−1.893	0.111	0.109	1.7
303.15	−1.216	0.023	−0.116	1.5
323.15	−0.498	−0.046	−0.035	3.3
333.15	−0.322	−0.096	−0.084	2.2
343.15	−0.213	−0.113	−0.043	3.6
353.15	−0.135	−0.096	0.027	4.9
363.15	−0.042	−0.097	−0.057	4.8

that, as the mole fraction of the aromatic compounds increase, the density increases but the speed of sound decreases.

Most of the two-component mixtures studied herein have a higher speed of sound and bulk moduli than those of the hydrotreated renewable diesels algal HRD-76 and DSH-76. At 293.15 K, the speed of sound of $1308.5 \pm 0.3 \text{ m} \cdot \text{s}^{-1}$ for DSH-76 is below that of any of the mixtures. For algal HRD-76, the speed of sound of $1340.9 \pm 0.6 \text{ m} \cdot \text{s}^{-1}$ falls between those

values for mole fractions of 0.3 and 0.4 for both toluene and ethylbenzene mixtures with *n*-hexadecane. At 293.15 K, the bulk moduli of $(1317 \pm 0.3 \text{ and } 1395 \pm 2) \text{ MPa}$ for DSH-76 and Algal HRD-76, respectively, are lower than the bulk moduli measured herein for the toluene in *n*-hexadecane mixtures $[(1412 \text{ to } 1526) \text{ MPa}]$ and the ethylbenzene in *n*-hexadecane mixtures $[(1423 \text{ to } 1556) \text{ MPa}]$.^{7,23} The addition of the toluene or ethylbenzene at low mass percentages decreases the speed of sound very little and has minimal impact on the bulk modulus. Since the bulk modulus changes very little, then the fuel injection time should not be impacted significantly by the addition of small amounts of an aromatic compound.

4.4. Flash Point and Surface Tension. The surface tension values are given in Table 12 for the mixtures studied herein as a function of the mole fraction of the aromatic compound. A linear regression of surface tension versus temperature data found in the literature^{72–76} for *n*-hexadecane yields the following relationship

$$\text{surface tension (mN} \cdot \text{m}^{-1}) = -0.085T/\text{K} + 52.4539 \quad (11)$$

that was presented graphically in Luning Prak et al.⁵ This equation predicts that the value of surface tension at 294.3 K should be $27.4 \text{ mN} \cdot \text{m}^{-2}$, which agrees with the data reported herein of $27.3 \pm 0.2 \text{ mN} \cdot \text{m}^{-2}$. The linear regression of toluene surface tension data with temperature reported by Jasper⁷⁷ predicts a surface tension of $28.4 \text{ mN} \cdot \text{m}^{-2}$ at 294.4 K, which agrees with the data reported herein of $28.4 \pm 0.2 \text{ mN} \cdot \text{m}^{-2}$. For ethylbenzene, the value predicted by the correlation in Jasper⁷⁷ of $29.1 \text{ mN} \cdot \text{m}^{-2}$ at 295.3 K agrees with the data reported herein of $29.2 \pm 0.2 \text{ mN} \cdot \text{m}^{-2}$. As can be seen from the data in Table 12, the surface tension increases as the mole fraction of the branched component increases, but the trend is not linear.

Table 9. Experimental Values of Speed of Sound c ($\text{m} \cdot \text{s}^{-1}$) of Mixtures of Toluene + *n*-Hexadecane and Ethylbenzene + *n*-Hexadecane from $T = (293.15 \text{ to } 333.15) \text{ K}$ and 0.1 MPa^a

<i>X</i> ₁	<i>T</i> = 293.15 K	<i>T</i> = 303.15 K	<i>T</i> = 313.15 K	<i>T</i> = 323.15 K	<i>T</i> = 333.15 K
Ethylbenzene (1) + <i>n</i> -Hexadecane (2)					
0.0000	1357.3	1320.0	1283.3	1247.3	1212.0
0.1007	1353.4	1316.0	1279.2	1243.2	1207.7
0.2000	1349.4	1312.0	1275.1	1239.0	1203.4
0.3002	1345.2	1307.8	1270.8	1234.5	1198.8
0.4013	1340.7	1303.1	1266.0	1229.4	1193.6
0.5002	1336.7	1298.9	1261.6	1224.8	1188.6
0.6001	1333.1	1295.0	1257.4	1220.3	1183.8
0.7002	1330.4	1291.9	1253.8	1216.2	1179.2
0.8001	1329.3	1291.1	1251.3	1213.1	1175.5
0.9000	1331.5	1291.3	1251.6	1212.5	1173.9
1.0000	1339.7	1298.1	1256.9	1216.4	1176.4
Toluene (1) + <i>n</i> -Hexadecane (2)					
0.0000	1357.3	1320.0	1283.3	1247.3	1212.0
0.1002	1352.9	1315.5	1278.7	1242.6	1207.1
0.2000	1348.1	1310.6	1273.6	1237.4	1201.7
0.3018	1343.1	1305.5	1268.4	1231.9	1196.0
0.4001	1337.2	1299.4	1262.1	1225.4	1189.2
0.5000	1332.0	1293.9	1256.2	1219.2	1182.7
0.6001	1326.5	1288.0	1250.0	1212.5	1175.6
0.7005	1321.5	1282.4	1243.8	1205.7	1168.2
0.8001	1318.0	1278.2	1238.8	1199.9	1161.7
0.8999	1318.0	1277.0	1236.4	1196.3	1156.7
1.0000	1326.8	1283.7	1241.1	1199.0	1157.6

^aStandard uncertainties u are $u(T) = 0.01 \text{ K}$, and combined expanded uncertainties U_c are $U_c(c) = 0.3 \text{ m} \cdot \text{s}^{-1}$.

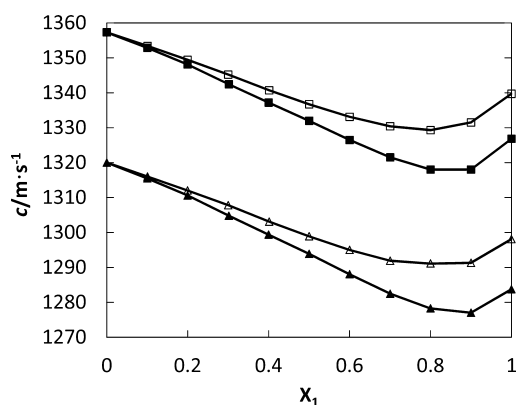


Figure 11. Speed of sound of *n*-hexadecane mixtures with toluene at ■, 293.15 K and ▲, 303.15 K and with ethylbenzene at □, 293.15 K and △, 303.15 K. X_1 is the mole fraction of the aromatic compound in the *n*-hexadecane mixture.

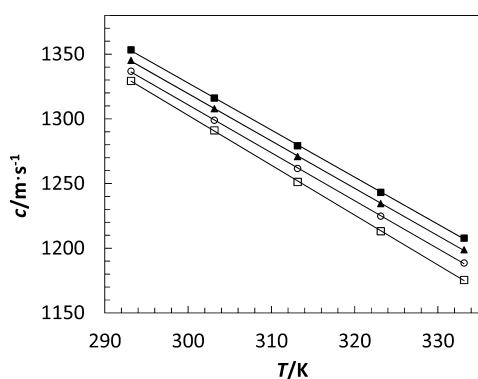


Figure 12. Speed of sound of ethylbenzene (X_1) + *n*-hexadecane mixtures at mole fractions: ■, $X_1 = 0.1002$; ▲, $X_1 = 0.3018$; ○, $X_1 = 0.5000$; and □, $X_1 = 0.8001$. Error bars, which are the combined expanded uncertainties with a 0.95 level of confidence ($k \approx 2$), are smaller than symbols. Lines shown are linear fits using eq 8 with the coefficients in Table 10.

Similar nonlinear trends have been found for *n*-hexadecane and branched alkanes.^{5,21} The lack of linearity between surface tension and mole fraction in the bulk mixture is not surprising because surface tension depends on the concentration of each compound at the interface, which may differ from that in the bulk solution.⁸²

For flash point, increasing the concentration of the aromatic compound in *n*-hexadecane decreases the flash point (Table 12), but the trend is not linear. Nonlinear behavior has been found for *n*-hexadecane with branched alkanes^{5,21} and with aromatic compounds with *n*-heptane.⁷⁸ The flash point is sensitive to the presence of components with a low flash point, since they are the first to combust. Since the aromatic compounds have a lower flashpoint than *n*-hexadecane, there is a large drop in flashpoint when they are added at low concentrations. As their concentrations are further increased, the flashpoint decreases steadily. The measured flash point of toluene, 278.5 ± 2 K, falls within the reported values of (277 and 280) K,^{79–81} while the measured flash point of ethylbenzene, 295 ± 2 K, is slightly higher than the reported value of 291 K⁸¹ but agrees within the error with the reported values of (294.15 and 293) K.^{79,80} The flash point of *n*-hexadecane was taken from Luning Prak et al.⁵

The flash points for some of the hydrotreated renewable fuels are matched by values in these mixtures, but the surface

Table 10. Parameters for eq 8: $c = AT/K + B$, that Relates Speed of Sound, c ($\text{m}\cdot\text{s}^{-1}$), to Temperature for Toluene in (Toluene + *n*-Hexadecane) Mixtures and for Ethylbenzene in the (Ethylbenzene + *n*-Hexadecane) Mixtures over the Temperature Range $T = (293.15 \text{ to } 333.15) \text{ K}^a$

X_1	A/K^{-1}	$B/\text{m}\cdot\text{s}^{-1}$	R^2	σ
Ethylbenzene (1) + <i>n</i> -Hexadecane (2)				
0.0000	-3.63 ± 0.07	2422 ± 23	0.9999	0.73
0.1007	-3.64 ± 0.07	2420 ± 22	0.9999	0.70
0.2000	-3.65 ± 0.07	2418 ± 21	0.9999	0.67
0.3002	-3.66 ± 0.06	2418 ± 19	0.9999	0.61
0.4013	-3.68 ± 0.06	2418 ± 20	0.9999	0.62
0.5002	-3.70 ± 0.06	2422 ± 18	0.9999	0.58
0.6001	-3.73 ± 0.07	2427 ± 17	0.9999	0.55
0.7002	-3.78 ± 0.05	2437 ± 17	0.9999	0.55
0.8001	-3.86 ± 0.06	2460 ± 20	0.9999	0.62
0.9000	-3.94 ± 0.06	2486 ± 18	0.9999	0.58
1.0000	-4.08 ± 0.06	2536 ± 20	0.9999	0.63
Toluene (1) + <i>n</i> -Hexadecane (2)				
0.0000	-3.63 ± 0.07	2422 ± 23	0.9999	0.73
0.1002	-3.65 ± 0.07	2421 ± 22	0.9999	0.67
0.2000	-3.66 ± 0.07	2420 ± 21	0.9999	0.67
0.3018	-3.68 ± 0.06	2420 ± 20	0.9999	0.64
0.4001	-3.70 ± 0.06	2421 ± 19	0.9999	0.60
0.5000	-3.73 ± 0.06	2426 ± 18	0.9999	0.58
0.6001	-3.77 ± 0.06	2432 ± 17	0.9999	0.55
0.7005	-3.83 ± 0.05	2445 ± 17	0.9999	0.54
0.8001	-3.91 ± 0.06	2463 ± 18	0.9999	0.57
0.8999	-4.03 ± 0.05	2500 ± 17	0.9999	0.53
1.0000	-4.23 ± 0.06	2567 ± 20	0.9999	0.61

^aError bars are the 95 % confidence interval.

tension values are not. The surface tensions of $25.0 \text{ mN}\cdot\text{m}^{-1}$ for DSH-76²³ and $26.0 \text{ mN}\cdot\text{m}^{-1}$ for algal HRD-76⁷ are lower than the surface tensions measured herein for either the toluene in *n*-hexadecane mixtures (27.3 to 28.4) $\text{mN}\cdot\text{m}^{-2}$ or the ethylbenzene in *n*-hexadecane mixtures (27.3 to 29.2) $\text{mN}\cdot\text{m}^{-1}$. The flash point values of (360 and 378) K for algal HRD-76⁷ and DSH-76,²³ respectively, fall within the range of flash point measured herein for the toluene in *n*-hexadecane mixtures, (278.5 to 408) K, and for the ethylbenzene in *n*-hexadecane mixtures, (295 to 408) K. The addition of the aromatic compounds to hydrotreated fuels will increase the surface tension of the mixture, which will alter the shape of the droplets formed in the combustion chamber and change the combustion characteristics. The addition of the aromatic compounds will also lower the flash point. The amount added cannot be too great or the fuel will drop below the lower limit of 333 K set by military specifications.⁸³

5. CONCLUSIONS

In this work, the physical properties of mixtures of *n*-hexadecane with toluene or ethylbenzene were measured. Many of the pure component measurements fell within values reported in the literature. Several correlations were developed that can be used in computer simulations that model the transport and reaction of these surrogate mixtures in engines. The densities of the mixtures at each temperature were well fit using a fourth-order polynomial function, and the viscosity values of the mixtures at each temperature were well fit using the McAllister three-body model. A linear relationship was found between the speed of sound and temperature. The speed of sound and bulk modulus

Table 11. Calculated Isentropic Bulk Modulus, E_v (MPa), of Mixtures of Toluene + *n*-Hexadecane and Ethylbenzene + *n*-Hexadecane from $T = (293 \text{ to } 333) \text{ K}$ and 0.1 MPa^a

	$T = 293.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 313.15 \text{ K}$	$T = 323.15 \text{ K}$	$T = 333.15 \text{ K}$
Ethylbenzene (1) + <i>n</i> -Hexadecane (2)					
0.0000	1425	1336	1251	1171	1096
0.1007	1423	1334	1249	1169	1093
0.2000	1423	1333	1248	1167	1091
0.3002	1423	1333	1247	1166	1089
0.4013	1424	1333	1246	1164	1087
0.5002	1427	1335	1248	1165	1087
0.6001	1434	1341	1252	1168	1088
0.7002	1446	1351	1260	1174	1093
0.8001	1466	1369	1274	1185	1101
0.9000	1499	1396	1298	1206	1119
1.0000	1556	1446	1342	1243	1151
Toluene (1) + <i>n</i> -Hexadecane (2)					
0.0000	1425	1336	1251	1171	1096
0.1002	1422	1332	1247	1167	1091
0.2000	1418	1328	1243	1162	1086
0.3018	1416	1325	1239	1158	1081
0.4001	1412	1321	1235	1153	1076
0.5000	1412	1320	1233	1150	1072
0.6001	1414	1321	1232	1148	1068
0.7005	1421	1325	1234	1148	1066
0.8001	1435	1336	1242	1153	1070
0.8999	1464	1360	1262	1169	1081
1.0000	1526	1413	1306	1206	1111

^aStandard uncertainties u are $u(T) = 0.01 \text{ K}$, and combined expanded uncertainties U_{E_v} are $U_c(E_v) = 0.4 \text{ MPa}$.

Table 12. Experimental Values of Flash Point and Surface Tension of Toluene + *n*-Hexadecane Mixtures and Ethylbenzene + *n*-Hexadecane Mixtures at Room Temperature, $294.4 \pm 1 \text{ K}^a$

X_1	surface tension/ $\text{mN}\cdot\text{m}^{-1}$	flash point/K
Ethylbenzene (1) + <i>n</i> -Hexadecane (2)		
0.0000	27.3	408 ^b
0.1007	NA	346
0.2000	27.4	328
0.3002	NA	319
0.4013	27.5	313
0.5002	27.5	308
0.6001	27.8	305
0.7002	28.0	302
0.8001	28.2	299
0.9000	28.5	297
1.0000	29.2	295
Toluene (1) + <i>n</i> -Hexadecane (2)		
0.0000	27.3	408 ^b
0.1002	NA	330
0.2000	NA	313
0.3018	NA	303
0.4001	27.3(3)	295
0.5000	27.5 \pm 0.3	292
0.6001	27.6	289
0.7006	27.7	286
0.8001	27.8	284
0.8999	28.0	281
1.0000	28.4	278.5

^a X_1 is the mole fraction of the aromatic compound in the mixture. Combined expanded uncertainties U_c are $U_c(X_1) = 0.0001$ and $U_c(\text{surface tension}) = 0.25 \text{ mN}\cdot\text{m}^{-1}$ and $U_c(\text{flash point}) = 2 \text{ K}$, (level of confidence = 0.95, $k \approx 2$). NA, not measured. ^bReference 5.

values of some of the mixtures were lower than those of the pure components. Neither flash point nor surface tension values were linearly related to mole fraction of the aromatic compound. With these two measurements, the bulk concentration does not dominate these chemical properties. For flash point, the more volatile substance dominates the behavior because it will volatilize and combust first; while for surface tension, the surface concentrations of each compound do not necessarily match those in the bulk. When predicting the impact of adding aromatic compounds to hydrotreated renewable diesel fuels, the addition will cause an increase in density, speed of sound, and surface tension and a decrease in viscosity and flash point and will have minimal impact on the bulk modulus.

■ ASSOCIATED CONTENT

📄 Supporting Information

Values of the excess molar volume and viscosity deviation for the mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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