

Densities and Viscosities of Ternary Mixtures of Heptane, Octane, Nonane, and Hexyl Benzene from 293.15 K to 313.15 K

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Densities and viscosities of four ternary mixtures made from heptane, octane, nonane, and hexyl benzene were measured. The temperature ranged from 293.15 K to 313.15 K. The experimental viscosities of the four pure hydrocarbons and their ternary mixtures vs temperature were fitted to the Andrade equation with an average absolute deviation of 0.13 %. On the basis of these data, the excess molar volumes and viscosity deviations were calculated. The prediction results based on the Przedziecki–Sridhar method and the Sastri–Rao method for low-temperature liquid viscosity estimation, the Dymond–Assael hard sphere model, and an equation of state based viscosity model proposed by Fan and Wang were compared with the experimental data.

Introduction

Alkyl benzene is an important intermediate which is widely used in the surfactant and plasticizer industries. Alkyl benzene is synthesized via a Friedel–Crafts alkylation of benzene with olefins. To design such a process, knowledge of thermophysical properties of a hydrocarbon mixture (containing alkyl benzene) is essential. In the petroleum industry, accurate viscosity and density prediction models for the pure hydrocarbons as well as for their mixtures are required for the reservoir simulation. Most of the industrial applicable mathematic models were based primarily on the empirical correlations that were frequently applied beyond their range. The experimental data reported in the literatures have been used for model development.^{1–5}

The density and viscosity data of many binary systems have been reported. Boned et al.^{6,7} determined dynamic viscosities and densities of the heptylbenzene, heptylcyclohexane, and methylcyclohexane + *cis*-decalin + 2,2,4,4,6,8,8-heptamethylnone ternary system. Nevertheless, for the alkane + alkyl benzene ternary systems, to the best of our knowledge, such data have not been reported in the literature.

In this work, the densities and viscosities for heptane + octane + nonane, heptane + octane + hexyl benzene, heptane + nonane + hexyl benzene, and octane + nonane + hexyl benzene from 293.15 K to 313.15 K are measured. On the basis of these experimental data, the excess molar volumes V^E and viscosity deviations $\Delta\eta$ were calculated. The prediction results based on the Przedziecki–Sridhar method and the Sastri–Rao method for low-temperature liquid viscosity estimation, the Dymond–Assael hard sphere model,⁵ and an equation of state based viscosity model proposed by Fan and Wang⁴ were compared with the experimental data.

Experimental Section

Materials. Heptane, octane, and nonane were obtained from Bodi and Guoyao Chemical Reagent Companies in Tianjin. Hexyl benzene was obtained from Fluka. All the chemicals used were of analytical grade and were used without further purification.

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Table 1. Comparison of Measured Densities and Viscosities of Heptane and Nonane with the Literature

substance	<i>T</i> /K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
		exptl	lit.	exptl	lit.
heptane	293.15	0.6828	0.6839 ⁹	0.4142	0.4051 ⁹
			0.6848 ¹¹		0.4170 ¹¹
			0.6836 ¹²		0.4140 ¹²
	298.15	0.6786	0.6796 ^{9,10}	0.3928	0.3959 ⁹
			0.6794 ¹³		0.3950 ¹⁰
			0.6754 ⁹		0.3880 ¹³
303.15	0.6747	0.6751 ¹²	0.3728	0.3696 ⁹	
308.15	0.6707		0.3541		
313.15	0.6656	0.6674 ¹¹	0.3374	0.3420 ¹¹	
nonane	293.15	0.7179	0.6665 ¹²	0.7091	0.7200 ⁹
			0.7179 ⁹		0.7140 ¹¹
			0.7213 ¹¹		0.7140 ¹²
	298.15	0.7140	0.7140 ^{9,11,13}	0.6640	0.6682 ⁹
			0.7176 ¹²		0.6650 ¹⁰
			0.7101 ⁹		0.6620 ¹³
	303.15	0.7108	0.7098 ¹²	0.6217	0.6213 ⁹
	308.15	0.7067		0.5849	0.6280 ¹²
	313.15	0.7028	0.7098 ⁹	0.5500	0.5550 ^{9,11,12}
0.7056 ¹¹					
0.7018 ¹²					

tion. The purity of all chemicals was checked by gas chromatography. The gas chromatographic analysis of pure components showed that the major peak area exceeded 99.98 % (mass fraction purity) for heptane, 99.99 % for octane, 99.00 % for nonane, and 97.00 % for hexyl benzene.

Apparatus and Procedure. The hydrocarbon mixtures were prepared as follows: The reagents were injected into a beaker and mixed uniformly. The mass fractions of the mixtures were measured by a SHIMADZU GC-14B station equipped with a thermal conductivity detector. Dry helium was used as the carrier gas, and the GC capillary column, with crossbond 5 % diphenyl and 95 % dimethyl polysiloxane, was 30 m in length and 0.53 mm in inner diameter.

The densities of the pure hydrocarbons and their mixtures were measured with a pycnometer (10 mL), and its volume over the experimental temperature range from 293.15 K to 313.15 K was calibrated with pure water. The temperature was

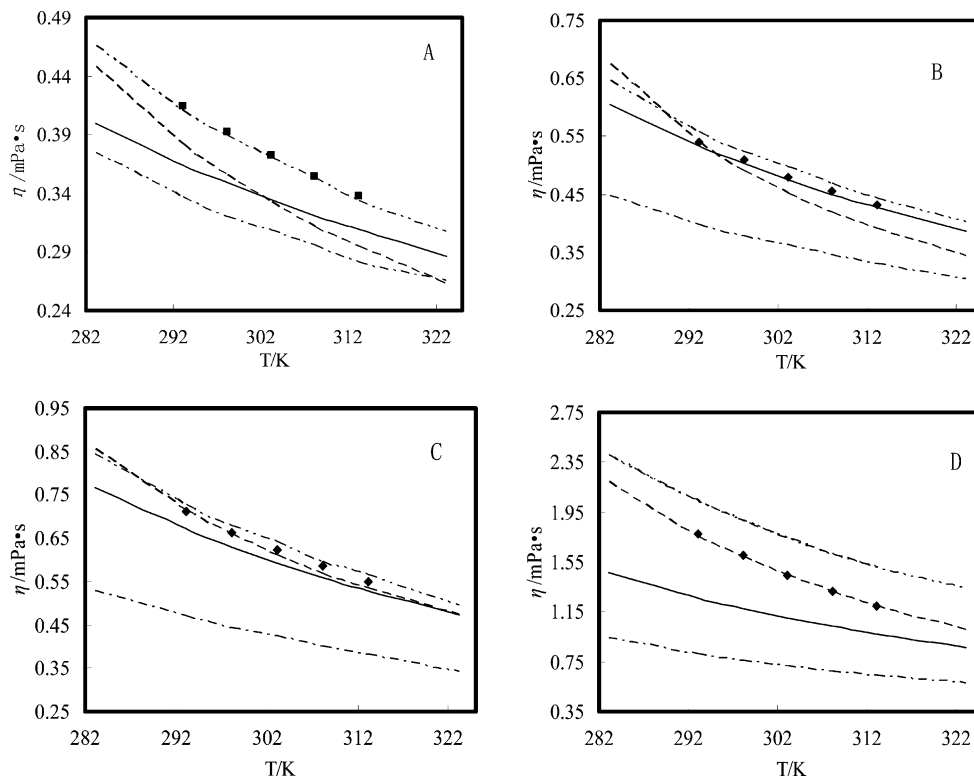


Figure 1. Plot of η vs T for pure liquids: A, heptane; B, nonane; C, octane; D, hexyl benzene; —, Sastri-Rao;⁵ - - - -, Przedziecki-Sridhar;⁵ - · - · -, PR μ ;⁴ - - - -, Dymond-Assael hard sphere model;^{5,19} ◆, experimental data.

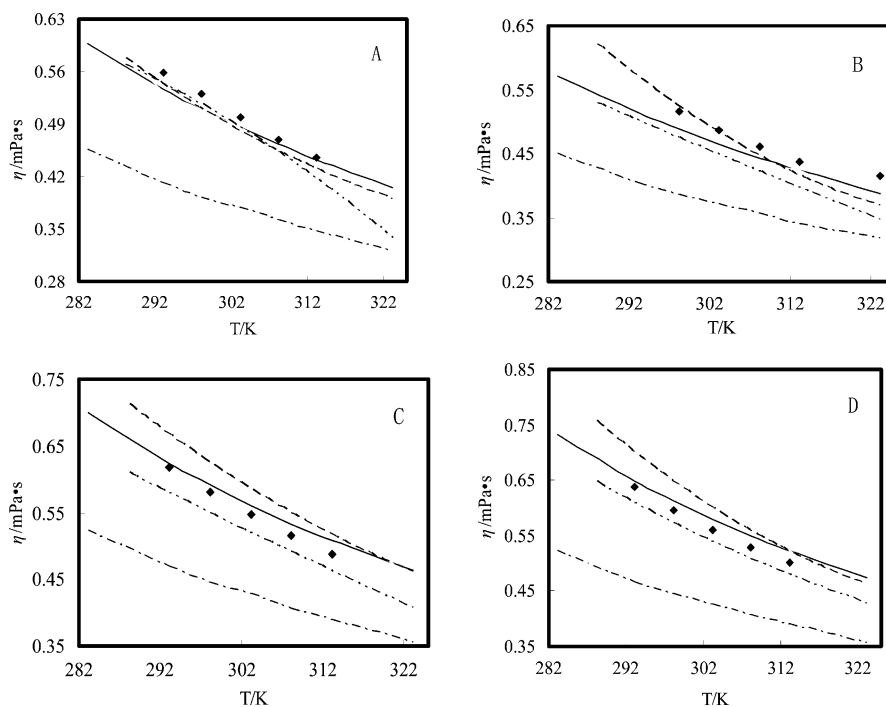


Figure 2. Plot of η vs T for mixtures: A, heptane + octane + nonane; B, heptane + octane + hexyl benzene; C, heptane + nonane + hexyl benzene; D, octane + nonane + hexyl benzene; —, Sastri-Rao;⁵ - - - -, Przedziecki-Sridhar;⁵ - · - · -, PR μ ;⁴ - - - -, Dymond-Assael hard sphere model;^{5,19} ◆, experimental data.

controlled by a constant water bath with an accuracy of ± 0.05 K.

Measurements of viscosities and densities of the pure hydrocarbons and their mixtures were carried out in the same water bath. The viscosities were measured using an Ubbelohde capillary viscometer. The capillary was calibrated for kinetic energy correction with double-distilled water at the experimental

temperature range from 293.15 K to 313.15 K according to the following equation

$$v = \frac{\eta}{\rho} = k_1 t - k_2/t \quad (1)$$

where k_1 and k_2 are the viscometer constants and t , η , and ρ are the efflux time, experimental viscosity, and density, respectively.

Table 2. Measured Densities ρ , Viscosities η_{exptl} , Calculated Excess Molar Volumes V^E , and the Viscosity Deviations $\Delta\eta$ for Mixtures at 101.325 Pa and Prediction Results for Viscosities Based on the PR μ Viscosity Model (PR μ),⁴ the Sastri–Rao Method (S–R),⁵ the Przedziecki–Sridhar Method (P–S),⁵ and the Dymond–Assael Hard Sphere Model (D–A)^{5,19}

mixtures	T	ρ	η_{exptl}	RE/% ^a				V^E	$\Delta\eta$
	K	g·cm ⁻³	mPa·s	PR μ	S–R	P–S	D–A	cm ³ ·mol ⁻¹	mPa·s
heptane (1) + octane (2) + nonane (3) $x_1 = 0.2872, x_2 = 0.2077, x_3 = 0.5051$	293.15	0.7036	0.5590	-4.60	-4.08	-26.42	1.55	0.4672	-0.03093
	298.15	0.6994	0.5299	-3.84	-3.85	-26.00	2.65	0.5394	-0.02406
	303.15	0.6958	0.4985	-2.51	-2.69	-24.13	5.51	0.5756	-0.02290
	308.15	0.6917	0.4687	-3.14	-1.28	-22.91	1.10	0.5594	-0.02294
	313.15	0.6878	0.4448	-3.09	-0.61	-22.12	2.92	0.5135	-0.01992
heptane (1) + octane (2) + hexyl benzene (3) $x_1 = 0.3026, x_2 = 0.6402, x_3 = 0.0571$	293.15	0.7049	0.5163	9.59	-0.54	-21.71	1.37	0.3697	-0.05681
	298.15	0.7012	0.4870	6.36	0.21	-20.80	3.70	0.3124	-0.04938
	303.15	0.6973	0.4604	4.93	0.93	-19.35	5.80	0.3651	-0.04271
	308.15	0.6936	0.4368	2.45	1.51	-18.45	0.85	0.3838	-0.03688
	313.15	0.6888	0.4144	2.42	2.22	-17.81	1.84	0.4100	-0.03207
heptane (1) + nonane (2) + hexyl benzene (3) $x_1 = 0.2762, x_2 = 0.6386, x_3 = 0.0852$	293.15	0.7173	0.6188	6.83	0.89	-24.34	1.14	1.2440	-0.10051
	298.15	0.7138	0.5811	6.15	1.74	-23.49	-3.04	1.7890	-0.08769
	303.15	0.7098	0.5470	7.71	2.56	-21.90	-1.00	1.3220	-0.07683
	308.15	0.7054	0.5162	6.86	3.29	-21.35	0.61	1.3494	-0.06696
	313.15	0.7014	0.4871	7.40	4.27	-20.28	2.61	1.3955	-0.05980
octane (1) + nonane (2) + hexyl benzene (3) $x_1 = 0.5638, x_2 = 0.3448, x_3 = 0.0914$	293.15	0.7194	0.6375	11.18	1.71	-26.90	0.13	0.8007	-0.07451
	298.15	0.7157	0.5966	7.89	2.65	-25.63	2.92	0.7760	-0.06564
	303.15	0.7118	0.5611	7.42	3.33	-24.08	5.18	0.8918	-0.05667
	308.15	0.7074	0.5294	5.13	3.89	-23.27	-0.39	0.9830	-0.04883
	313.15	0.7048	0.5006	4.32	4.41	-22.27	3.06	0.6680	-0.04175

$$^a \text{RE} = (\eta_{\text{calcd}} - \eta_{\text{exptl}})/\eta_{\text{exptl}}$$

Table 3. Fitted Coefficients of the Andrade Equation and Standard Deviations for Pure Substances and Mixtures from 293.15 K to 313.15 K

system	coefficients		σ^a
	A	B	
heptane	-4.0991	943.42	0.0005
octane	-4.1542	1037.41	0.0007
nonane	-4.3168	1165.03	0.0003
hexyl benzene	-4.3471	1463.06	0.0062
heptane + octane + nonane	-4.2080	1064.05	0.0036
octane + nonane + hexyl benzene	-4.2305	1107.70	0.0016
heptane + octane + hexyl benzene	-4.0962	1006.85	0.0006
heptane + nonane + hexyl benzene	-4.2180	1095.80	0.0005

$$^a \sigma = \sqrt{\sum_{i=1}^m (\eta_i - \eta_i^{\text{calcd}})^2 / (m-n)}$$

The values of the absolute viscosity and density for calibration were taken from the literature.⁸ The viscometer was suspended in a thermostated water bath maintained to ± 0.05 K. An electronic digital stopwatch with an uncertainty of ± 0.01 s was used for flow time measurement. Measurements were repeated four times at each temperature for all mixtures, and the results were averaged.

The overall uncertainty of density measurements depends on equilibrium temperature, composition, and calibration fluid. The uncertainty of viscosity measurements depends on temperature, flow time, composition, and calibration fluid. So, according to the precision of all experimental instruments, the experimental average uncertainties of density and viscosity were estimated to be $(\Delta\rho/\rho \text{ or } \Delta\eta/\eta) = \pm 0.001$. The densities and viscosities of heptane and nonane from 293.15 K to 313.15 K were measured in this work, and the results agreed well with the literature values^{9–13} as shown in Table 1.

Results, Viscosity Prediction, and Discussion

Results and Correlation. The experimental densities and viscosities for heptane + octane + nonane, heptane + octane

+ hexyl benzene, heptane + nonane + hexyl benzene, and octane + nonane + hexyl benzene systems from 293.15 K to 313.15 K were listed in Table 2. The experimental viscosities as a function of temperature were fitted to the following Andrade equation

$$\ln(\eta/\text{mPa}\cdot\text{s}) = A + B/(T/\text{K}) \quad (2)$$

where η is viscosity; T is temperature; and A and B are coefficients. The A , B , and standard deviation σ of pure hydrocarbons and mixtures are listed in Table 3. The standard deviation σ is calculated by the following equation

$$\sigma = \sqrt{\frac{\sum_{i=1}^m (\eta_i - \eta_i^{\text{calcd}})^2}{m-n}} \quad (3)$$

where η_i and η_i^{calcd} are the experimental data and calculated results, respectively; m is the number of data points; and n is the number of equation parameters.

The excess molar volumes V^E were calculated from these measured density data according to the following equations^{14–16}

$$V^E = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} - \frac{x_3 M_3}{\rho_3} \quad (4)$$

where ρ is the density of the mixture; x_1 , x_2 , and x_3 are the mole fractions of components 1, 2, and 3; M_1 , M_2 , and M_3 are the molar masses; and ρ_1 , ρ_2 , and ρ_3 are the densities of the pure hydrocarbons, respectively.

The viscosity deviations $\Delta\eta$ were calculated from the following relation^{14–16}

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2 + x_3\eta_3) \quad (5)$$

Table 4. Parameters of the PR μ Model for the Substances Measured in This Work and Average Absolute Deviations (AAD) of the Calculation Results for Liquid (L) and Gas (G) Viscosities to Experimental Data^a

substance	T range	P range	phase/state	NP	coefficients					AAD
	K	bar			$e_1/10^{-7}\text{Pa}\cdot\text{s}$	$e_2/10^{-7}\text{Pa}\cdot\text{s}$	$e_3/10^{-7}\text{Pa}\cdot\text{s}$	m	n	%
heptane	300–620	1–500	G/L	425	976.9	–120.4	712.3	0.02018	–0.02793	7.87
octane	320–670	1–500	G/L	330	995.4	–96.87	740.4	0.02277	–0.02663	8.41
nonane	300–470	1–500	L	281	2190	–181.9	2541	0.02477	0	5.02
hexyl benzene	270–340	1	L	70	9366	17.13	22090	0.09369	0	0.94

^a Data source: Stephen¹⁷ and Yaws.¹⁸

where η is the viscosity of mixtures and η_1 , η_2 , and η_3 are the viscosities of components 1, 2, and 3, respectively. The obtained excess molar volumes and viscosity deviations were listed in Table 2.

Viscosity Prediction Model. The viscosity models based on the similarity of PvT and $T\eta P$ relationships and the equation of state were developed by Lawal² and Guo et al.³ Recently, a viscosity model for calculation of the viscosity of both gas and liquid phases was proposed by Fan and Wang based on the Peng–Robinson equation of state (hereafter named as the PR μ model)⁴

$$T^r = \frac{R'P}{\eta - b} - \frac{a}{\mu^2 + 2\eta b - b^2} \quad (T^r/\text{K} = T - T_d; T_d/\text{K} = \delta T_c) \quad (6)$$

where δ equals 0.45 for normal alkanes and equals 0.35 for hexyl benzene; η is viscosity (10^{-7} Pa·s); P denotes pressure (bar); T is temperature (K); and the subscript c refers to the critical value. Similar to the Peng–Robinson equation of state, the three equation parameters a , b , and r_c can be obtained at the critical point due to the critical isobar on the $T\eta P$ diagram shown as a horizontal inflection point; thus

$$a = 0.45724r_c^2 P_c^2 / T_c^r \quad (7)$$

$$b = 0.0778r_c P_c / T_c^r \quad (8)$$

$$r_c = \frac{T_c^r \eta_c}{0.3074P_c} \quad (9)$$

where the critical viscosity η_c is calculated from the Uyehara–Watson correlation

$$\eta_c / 10^{-7} \text{ Pa}\cdot\text{s} = 7.7(T_c/\text{K})^{-1/6} M^{1/2} (P_c/\text{bar})^{2/3} \quad (10)$$

For the viscosity calculation at the pressures outside of the critical isobar, the following correction is proposed

$$R' = \beta(P)r_c \quad (11)$$

$$\beta = m(1 - P_r^{-1}) + nP_r^{-1}[(P_r + 0.25)^{-1} - 0.8] + P_r^{-1} \quad (12)$$

where $P_r = P/P_c$ and the specific parameters m and n for the substances measured in this work are listed in Table 4. With a , b , and R' known, at the specified temperature and pressure, three real roots can be solved from eq 6. The smallest root represents the viscosity of vapor, and the maximum root represents the viscosity of liquid. In this paper, the results of predicted liquid viscosity from the above model are

named as η^{PR} , and it is further corrected with the following correlations

$$\eta / 10^{-7} \text{ Pa}\cdot\text{s} = \eta^{\text{PR}} + c_0 + c \quad (13)$$

$$c_0 / 10^{-7} \text{ Pa}\cdot\text{s} = 6.714(P_r - 1) - 127.8[(P_r + 1)^{-1} - 0.5] \quad (14)$$

$$c / 10^{-7} \text{ Pa}\cdot\text{s} = e_1 \ln \eta_r + e_2(\eta_r - 1) + e_3(\eta_r^{-1} - 1) - 0.5(\eta_r^2 - 1) \quad (15)$$

where $\eta_r = \eta^{\text{PR}}/\eta_c$, the parameters in eq 16 for the pure substances used in this work, and the average absolute deviations (AADs) of the calculation results for the liquid and gas viscosities to the experimental data^{17,18} over a wide range of temperatures and pressures are listed in Table 4. For mixture viscosity prediction, the following simple mixing rule for parameters of the PR μ model can be applied

$$z_m = \sum_i x_i z_i \quad (z = a, b, c, r_c, T_d, \text{ and } \beta) \quad (16)$$

The Przedziecki–Sridhar and Sastry–Rao estimation methods⁵ for low-temperature liquid viscosity were applied in this paper to make parallel calculations. The obtained results for pure substances were extended to the viscosities of the mixture based on the method of Grunberg and Nissan⁵

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n x_i x_j G_{ij} \quad (17)$$

Isdal et al. proposed a group contribution method to estimate the binary interaction parameter G_{ij} at 298 K.⁵ At other temperatures, the following equation was applied

$$G_{ij} = 1 - (1 - G_{ij}^{298}) \frac{573 - (T/\text{K})}{275} \quad (18)$$

The Dymond–Assael hard sphere model^{5,19} for the prediction of dense-fluid viscosity was developed on the basis of hard sphere theory over wide temperature and pressure ranges. According to this model, a reduced viscosity is defined as follows

$$\eta^* = 6.053 \cdot 10^8 \left(\frac{1}{MRT} \right)^{1/2} \frac{\eta V^{2/3}}{R_\eta} \quad (19)$$

where V is the molar volume ($\text{m}^3 \cdot \text{mol}^{-1}$); M is the molar mass; R is the universal gas constant; and R_η is a roughness factor introduced to account for nonspherical shape effects. This reduced viscosity can be expressed as a function only of the volume ratio V_r ($V_r = V/V_0$), where V_0 is a characteristic volume, which corresponds in a hard sphere system to the volume of close packing. A universal curve is expressed by the equation

$$\log \eta^* = 1.0945 - 9.26324V_r^{-1} + 71.0385V_r^{-2} - 301.9012V_r^{-3} + 797.690V_r^{-4} - 1221.977V_r^{-5} + 987.5574V_r^{-6} - 319.4636V_r^{-7} \quad (20)$$

in which V_o was derived for n -alkanes²⁰ at first and later for aromatic hydrocarbons²¹ and alcohols.²² In this paper, the characteristic volume V_o (10^{-6} m³·mol⁻¹) and R_η of heptane, octane, nonane, and hexyl benzene were calculated according to the literature.^{5,19}

To predict the viscosity of mixtures from pure components, it was assumed that the mixture behaves as a single-component liquid with molecular parameters given by the mole-fraction average of the individual components i ²³

$$V_{0,\text{mix}} = \sum_i x_i V_{0,i} \quad \text{and} \quad R_\eta = \sum_i x_i R_{\eta,i} \quad (21)$$

A comparison of the calculated T - η curves based on the above three models with the experimental data of the four pure substances is graphically shown in Figure 1. The results of the four ternary mixtures measured in this work are graphically shown in Figure 2 and listed in Table 2. The relative errors (RE) of the predicted viscosities are calculated according to the following equation

$$\text{RE} = |\eta_{\text{exptl}} - \eta_{\text{calcd}}|/\eta_{\text{exptl}} \quad (22)$$

From these figures and Table 2, it can be seen that the Dymond–Assael hard sphere model gives the best predictions, and the AAD for the ternary mixtures tested is 2.4 %; the Sastri–Rao model gives accurate predictions, and the AAD is 2.9 %; the PR μ model gives reasonable predictions, and the AAD is 7.1 %; and the prediction results of the Przedziecki–Sridhar model are not satisfactory. An example of step by step calculation with the PR μ model is shown in Appendix A.

Conclusion

This work presents new experimental density and viscosity data of four ternary hydrocarbon mixtures (heptane + octane + nonane, heptane + octane + hexyl benzene, heptane + nonane + hexyl benzene, and octane + nonane + hexyl benzene systems) from 293.15 K to 313.15 K. From these data, the excess molar volumes V^E and viscosity deviations $\Delta\eta$ were calculated, and the viscosities of pure liquids and mixtures from 293.15 K to 313.15 K were fitted to the Andrade equation.

Four viscosity models were applied in this paper to make parallel viscosity calculations. One of them was an equation of state based model (PR μ) proposed by Fan and Wang, which is applicable to the viscosity prediction of both gas and liquid phases. The other three models were the Przedziecki–Sridhar method, the Sastri–Rao method, and the Dymond–Assael hard sphere model. Both the Przedziecki–Sridhar and the Sastri–Rao methods were applicable only for low-temperature liquid viscosity predictions, and the Dymond–Assael hard sphere model is applicable for liquid viscosity prediction with wide temperature and pressure ranges. The prediction results based on the Dymond–Assael hard sphere model, the Sastri–Rao model, and the PR μ model were satisfactory, whereas the accuracy of the Przedziecki–Sridhar model was inadequate.

Appendix A

Calculation of Viscosity of Heptane at 1 bar and 293.15 K with the PR μ Model. Step 1. For heptane: $T_c = 540.20$ K; $P_c = 27.4$ bar; $\omega = 0.35$; $M = 100.204$ g·mol⁻¹.

Step 2. Calculate the parameters of the PR μ model

$$\eta_c = 7.7T_c^{-1/6}M^{0.5}P_c^{2/3} = 7.7 \cdot 540.20^{-1/6} \cdot 100.204^{0.5} \cdot 27.4^{2/3} = 245.47 \text{ (} 10^{-7} \text{ Pa}\cdot\text{s)}$$

$$T_d = 0.45T_c = 0.45 \cdot 540.20 = 243.09 \text{ K}$$

$$T'_c = T_c - T_d = 540.20 - 243.09 = 297.11 \text{ K}$$

$$r_c = \eta_c T'_c / 0.3074 P_c = 245.47 \cdot 297.11 / (0.3074 \cdot 27.4) = 8.66 \cdot 10^3 \text{ (} 10^{-7} \text{ Pa}\cdot\text{s}\cdot\text{K}\cdot\text{bar}^{-1}\text{)}$$

$$a = 0.457235 r_c^2 P_c^2 / T'_c = 0.457235 \cdot 8660^2 \cdot 27.4^2 / 297.11 = 8.66 \cdot 10^7 \text{ (} 10^{-7} \text{ Pa}\cdot\text{s})^2 \cdot \text{K}$$

$$b = 0.0778 r_c P_c / T'_c = 0.0778 \cdot 8.66 \cdot 10^3 \cdot 27.4 / 297.11 = 62.13 \text{ (} 10^{-7} \text{ Pa}\cdot\text{s)}$$

$$T' = T - T_d = 293.15 - 243.09 = 50.06 \text{ K}$$

$$P_r = \frac{P}{P_c} = \frac{1}{27.4} = 0.03650$$

$$\beta = m(1 - P_r^{-1}) + nP_r^{-1}[(P_r + 0.25)^{-1} - 0.8] + P_r^{-1} = 0.02018 \left(1 - \frac{1}{0.03650} \right) - 0.02793 \cdot \frac{1}{0.03650} \left[\frac{1}{0.03650 + 0.25} - 0.8 \right] + \frac{1}{0.03650} = 24.8083$$

Step 3. Solving eq 6: $T' = R'P/(\eta - b) - a/(\eta^2 + 2\eta b - b^2)$ for η , eq 6 is transformed to following cubic equation

$$\eta^3 + \eta^2 \left(b - \frac{R'P}{T'} \right) + \eta \left(\frac{a}{T'} - \frac{2R'Pb}{T'} - 3b^2 \right) + b^3 + \frac{R'Pb}{T'} - \frac{ab}{T'} = 0$$

with $\eta^3 + p\eta^2 + q\eta + \gamma = 0$, where

$$p = b - \frac{R'P}{T'} = 62.12746 - 214816.5 \cdot 1/50.06 = -4229.05$$

$$q = \frac{a}{T'} - \frac{2R'Pb}{T'} - 3b^2 = 86630234.8/50.06 - 2 \cdot 214816.5 \cdot 1 \cdot 62.12746/50.06 - 3 \cdot 62.12746^2 = 1.1858 \cdot 10^6$$

$$\gamma = b^3 + \frac{R'Pb^2}{T'} - \frac{ab}{T'} = 62.12746^3 + 214816.5 \cdot 1 \cdot 62.12746^2/50.06 - 86630234.8 \cdot 62.12746/50.06 = -9.0710 \cdot 10^7$$

$$\eta^{\text{PR}} = 3933.465 \text{ (} 10^{-7} \text{ Pa}\cdot\text{s)}$$

Step 4. Correction of η^{PR}

$$c_0 = 6.714(P_r - 1) - 127.8[(P_r + 1)^{-1} - 0.5] = 6.714(0.03650 - 1) - 127.8((0.03650 + 1)^{-1} - 0.5) = -65.869 \text{ (} 10^{-7} \text{ Pa}\cdot\text{s)}$$

$$\eta_r = \frac{\eta^{\text{PR}}}{\eta_c} = \frac{3933.465}{245.4753} = 16.0240$$

$$c = e_1 \ln \eta_r + e_2(\eta_r - 1) + e_3(\eta_r^{-1} - 1) - 0.5(\eta_r^2 - 1) = \\ 976.9 \ln 16.02387 - 120.4(16.02387 - 1) + \\ 712.3(16.02387^{-1} - 1) - 0.5(16.02387^2 - 1) = \\ 105.3945 (10^{-7} \text{ Pa}\cdot\text{s})$$

A real root can be then obtained

$$\eta = \eta^{\text{PR}} + c_0 + c = 3933.465 - 65.869 + 105.3945 = \\ 3972.991 (10^{-7} \text{ Pa}\cdot\text{s})$$

Calculation of Viscosity of Heptane at 373.15 K and Saturated Pressure (1.0606 bar). Similarly, the viscosity of heptane at 293.15 K and 1.0606 bar can be calculated with the PR μ model, and the following cubic equation can be obtained

$$\eta^3 - 1.5910 \cdot 10^3 \eta^2 + 4.4909 \cdot 10^5 \eta - 3.4761 \cdot 10^7 = 0$$

Three real roots can be obtained

$$\eta_1^{\text{PR}} = 1255.0067 (10^{-7} \text{ Pa}\cdot\text{s})$$

$$\eta_2^{\text{PR}} = 146.0049 (10^{-7} \text{ Pa}\cdot\text{s})$$

$$\eta_3^{\text{PR}} = 189.9786 (10^{-7} \text{ Pa}\cdot\text{s})$$

The largest root is the viscosity of the saturated liquid phase, 1255.0067 (10⁻⁷ Pa·s), and the smallest root is the viscosity of the vapor phase, 146.0049 (10⁻⁷ Pa·s).

The viscosities μ_1^{PR} and μ_2^{PR} are corrected as follows

$$c_0 = 6.714(P_r - 1) - 127.8[(P_r + 1)^{-1} - 0.5] = 6.714 \\ (0.038708 - 1) - 127.8((0.038708 + 1)^{-1} - 0.5) = \\ -65.869 (10^{-7} \text{ Pa}\cdot\text{s})$$

$$\eta_{1r} = \frac{\eta_1^{\text{PR}}}{\eta_c} = \frac{1255.0067}{245.4753} = 5.11256$$

$$\eta_{2r} = \frac{\eta_2^{\text{PR}}}{\eta_c} = \frac{146.0049}{245.4753} = 0.594784$$

$$c_1 = 976.9 \ln 15.11256 - 120.4(15.11256 - 1) + 712.3 \\ (15.11256^{-1} - 1) - 0.5(15.11256^2 - 1) = 513.3101$$

$$c_2 = 976.9 \ln 0.594784 - 120.4(0.594784 - 1) + 712.3 \\ (0.594784^{-1} - 1) - 0.5(0.594784^2 - 1) = 26.83334$$

$$\eta_1 = \eta_1^{\text{PR}} + c_0 + c_1 = 1255.0067 - 65.869 + 513.3101 = \\ 1702.448 (10^{-7} \text{ Pa}\cdot\text{s})$$

$$\eta_2 = \eta_2^{\text{PR}} + c_0 + c_2 = 146.0046 - 65.869 + 26.83334 = \\ 106.9693 (10^{-7} \text{ Pa}\cdot\text{s})$$

The experimental data is 0.0074 (mPa·s) for gas and 0.1980 (mPa·s) for liquid.

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