Liquid Viscosities of Cyclohexane, Cyclohexane + Tetradecane, and Cyclohexane + Benzene from (313 to 393) K and Pressures Up to 60 MPa

Miguel A. Hernández-Galván,[†] Fernando García-Sánchez,*,[†] Blanca E. García-Flores,[†] and Javier Castro-Arellano[‡]

Laboratorio de Termodinámica, Programa de Investigación en Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México, D.F., México, and Departamento de Ingeniería Química, SEPI-ESIQIE, Instituto Politécnico Nacional, Unidad Profesional Adolfo López Mateos, Zacatenco, 07738 México, D.F., México

Liquid viscosities of pure cyclohexane and of the cyclohexane + tetradecane and cyclohexane + benzene systems at four different compositions were measured using a rolling-ball viscometer from (313.2 to 393.2) K and pressures up to 60 MPa with an estimated experimental uncertainty in the measured viscosity data of 2 %. A comparison between our measured viscosities and those reported by others authors for cyclohexane was established with the hard-sphere scheme given by Assael et al. [*Int. J. Thermophys*. **1992**, *13*, 269−281]. The comparison showed an average relative deviation of 2.3 %. The measured mixture viscosity data were regressed with the correlations of Grunberg−Nissan (GN) and Katti−Chaudhri (KC), and a liquid viscosity model based on Eyring's theory coupled with a cubic equation of state (ET-EoS), all of them using a single temperature-independent binary interaction parameter to describe the whole η, T, p, x surface of study. Results of the representation with the GN, KC, and ET-EoS viscosity models yielded, respectively, average relative deviations of (3.4, 3.8, and 3.5) % for the cyclohexane + tetradecane system and of (3.1, 3.0, and 4.0) % for the cyclohexane + benzene system, showing that these viscosity models are capable of representing satisfactorily the experimental viscosity behavior of these systems over the whole temperature, pressure, and composition range studied. Furthermore, two viscosity approaches with a physical and theoretical background (the hard-sphere scheme and the free-volume model) were used for modeling the viscosities of the two binary systems studied. Results of the modeling with the hard-sphere and free-volume viscosity models yielded, respectively, average relative deviations of (4.0 and 26.1) % for the cyclohexane + tetradecane and of (7.3 and 4.8) % for the cyclohexane + benzene system.

Introduction

Experimental high-pressure liquid viscosities of pure hydrocarbons and their mixtures are important to simulate the behavior of petroleum fluids at oil field conditions. To extend the database of viscosities for pure hydrocarbons and their mixtures over a wide range of temperature and pressure, we have undertaken a systematic study of liquid viscosities of mixtures containing paraffin, aromatic, and naphthenic compounds. This study is part of an ongoing research program on viscosity measurements of hydrocarbons at high pressures.

In this work, we report liquid viscosity measurements of pure cyclohexane and of the cyclohexane + tetradecane and cyclohexane + benzene systems from (313.2 to 393.2) K and pressures up to 60 MPa over the entire composition range. All of the dynamic viscosity data reported here were determined in a high-pressure rolling-ball viscometer using a density Tait-type correlation reported by Assael et al.[1] for tetradecane and by Cibulka and Takagi[2,3] for benzene and cyclohexane. This viscosity measurement technique has been used by us in a previous work[4] in the measurement of liquid viscosities of benzene, tetradecane, and the benzene + tetradecane system from (313.2 to 393.2) K and pressures up to 60 MPa, and by several authors[5−9] in the measurement of high-pressure viscosity data of pure *n*-alkanes, binary and ternary mixtures of *n*-alkanes, and CO_2 + *n*-alkanes.

The measured mixture viscosity data of the cyclohexane + tetradecane and cyclohexane + benzene systems were represented with the GN[10] and KC[11] correlations, and the ET-EoS[4] viscosity model, all of them using a single temperature-independent binary interaction parameter to describe the whole η, T, p, x surface of study. For comparison, these mixture viscosity data were also modeled with the hard-sphere scheme[12] and the free-volume model,[13,14] which are based on a physical and theoretical background and do not use any adjustable parameter for determining the dynamic viscosity of a binary system.

Experimental Section

Materials. Cyclohexane, linear tetradecane, and benzene were acquired from Aldrich (USA) with a minimum mole fraction purity of 99.9 %, 99 %, and 99.9 %, respectively. All of these chemicals were used without further purification.

Apparatus and Procedure. The experimental apparatus used in this study has been previously described[4] and will not be repeated in detail here. Briefly, the apparatus consists of a commercial rolling-ball viscometer (Ruska, model 1602-828), a pressure line, and a high-pressure cell for storing the sample at high pressure before transferring it to the viscometer.

The rolling-ball viscometer, designed to operate in the viscosity range of (0.1 to 3000) mPa·s, consists of a mechanical test assembly and a control unit with a digital watch. The

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* To whom correspondence should be addressed. Tel.: +52 55 9175 6574. E-mail: fgarcias@imp.mx.
[†] Instituto Mexicano del Petróleo.
[‡] Instituto Politécnico Nacional.

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mechanical assembly is a stainless steel high-pressure housing, which can be fixed at an angle of 23°, 45°, or 70° with the horizontal to carry out the measurements. Inside the housing, there is a cylindrical barrel in which a steel ball rolls on a perfectly polished surface. The upper end of the housing is closed by means of a plug that contains the barrel seal and a solenoid, while another plug that contains the bottom contact closes the lower end of the housing. When the barrel seal is closed, both ends of the barrel are closed so the sphere falls through the fluid inside the barrel. The solenoid holds the steel sphere in the upper part of the measuring barrel, and it will not fall through the fluid until the solenoid current is interrupted in the control unit. The temperature is measured by means of a thermocouple with an uncertainty of 0.1 K over the temperature range from (303 to 423) K. The pressure circuit connected to the viscometer consists of a set of valves, tubing, a high-pressure stainless steel cell, a syringe high-pressure pump (ISCO, model 100DM) with an uncertainty of 0.02 MPa, and a vacuum pump.

The experimental procedure starts with a comprehensive cleaning of the whole system to remove any trace of dust or grease that prevents the steel ball from rolling freely through the liquid inside the barrel of the viscometer; the system is then evacuated using the vacuum pump. Afterward, the high-pressure cell is loaded with about 200 mL of the fluid (the viscometer requires about 80 mL for complete filling, and the rest of the liquid is used to pressurize the system). The fluid is then introduced into the viscometer through the high-pressure cell by means of the ISCO syringe pump with a pressure rating of 69 MPa. Finally, the experimental temperature and pressure are fixed. Once the equilibrium conditions are reached and stabilized, measurements of the fall times are performed.

In the rolling-ball viscometer, a stainless steel sphere rolls through a fluid of unknown viscosity at given conditions of temperature and pressure for a precise distance. The viscosity is then a function of the rolling time and the density difference between the sphere and fluid, which can be expressed as

$$\eta = K(T,p,t)(\rho_{\text{ball}} - \rho_{\text{fluid}}) \tag{1}$$

where η is the absolute viscosity, t is the roll time, ρ_{ball} is the density of the sphere, ρ_{fluid} is the density of the fluid, and $K(T, p, t)$ is a function of temperature, pressure, and the rolling time of the ball, which is obtained by calibrating the viscometer with different substances of known viscosity and density. Further details involving the calibration of the viscometer are given in a previous work.[4] Once the calibration of the viscometer is completed and after carrying out an error analysis to eq 1, the experimental uncertainty in the measured viscosity data is estimated to be 2 % on the whole temperature and pressure range studied.

Results

Liquid viscosities of pure cyclohexane and of the binary systems cyclohexane + tetradecane and cyclohexane + benzene were experimentally measured over the temperature range from (313.2 to 393.2) K and pressures up to 60 MPa. All of the measurements were performed using a sphere of 6.22 mm diameter and an inclination angle of 23°. For each viscosity value, an average value of 10 measurements of all the rolling times was used. The viscometer was rotated during 15 min to obtain a uniform temperature and mixing in the barrel. Thermal and mechanical equilibrium was reached in the viscometer before the time was recorded. The binary mixtures of cyclohexane + tetradecane and cyclohexane + benzene were made up gravimetrically by using an analytical balance with a precision of 0.1 mg at room temperature and atmospheric pressure. The uncertainty in the preparation of the mixture is estimated to be better than 0.01 mass %.

To apply eq 1 for determining the value of the viscosity, it is necessary to know the density of the fluid, ρ_{fluid}, and that of the ball, ρ_{ball}, at the pressure and temperature conditions of the fall times measurements. The density of the ball (here, $\rho_{\text{ball}} = 7.6185$ $\text{g}\cdot\text{cm}^{-3}$) is assumed to be constant, so that the effects of pressure and temperature upon the density of the ball are neglected. Fluid densities of tetradecane are determined using the following Tait-like equation suggested by Assael et al.[1] for *n*-alkane compounds (from ethane to hexadecane)

$$\rho_{\text{fluid}}(T,p) = \rho_0(T,p_0)\left[1 - 0.2\log\left(\frac{B(T) + p}{B(T) + p_0}\right)\right]^{-1} \tag{2}$$

where ρ_{fluid} and ρ_0 are the densities of the fluid at pressures p and p_0, respectively, and $B(T)$ is a temperature-dependent parameter. The density of the fluid at $p_0 = 0.101325$ MPa is determined from the correlation proposed by Cibulka and Hnědkovský[15]

$$\rho_0 = \rho_c[1 + \sum_{i=1}^{5} a_i(1 - T_r)^{1/3}] \tag{3}$$

where ρ_c is the critical density of the fluid, T_r is the reduced temperature ($T_r = T/T_c$), and coefficients a_i ($i = 1,..., 5$) are parameters that depend on the type of fluid under study.

Fluid densities for benzene and cyclohexane are determined using the following Tait-like equation proposed by Cibulka and Takagi[2,3] for aromatic and nonhydrocarbon compounds

$$\rho_{\text{fluid}}(T,p) = \rho_0(T,p_0)\left[1 - C(T)\ln\left(\frac{B(T) + p}{B(T) + p_0}\right)\right]^{-1} \tag{4}$$

where $B(T)$ and $C(T)$ are temperature-dependent parameters, and the reference density $\rho_0(T, p_0)$ is evaluated at $p_0 = 0.101325$ MPa by using the correlations also reported by Cibulka and Takagi.[2,3]

For mixtures, fluid densities can be calculated from the pure-component density, ρ_{fluid}, assuming that no volume change takes place during mixing, as suggested by Assael et al.[1] Therefore, the density of the binary mixtures was calculated from

$$\rho_{\text{mix}} = \frac{\sum_{i=1}^{2} m_i}{\sum_{i=1}^{2} V_i} = \left(\sum_{i=1}^{2} \frac{w_i}{\rho_{\text{fluid},i}}\right)^{-1} \tag{5}$$

where m_i, V_i, and w_i are the mass, the volume, and the mass fraction of component i, respectively. Although eq 5 assumes that the mixing is ideal, this can be used for nonideal mixtures taking into account that an error of 10 $\text{kg}\cdot\text{m}^{-3}$ in liquid density generates a relative error of 0.001 for viscosity, as showed by Et-Tahir et al.[16] These authors, based on the fact that extrapolation to 100 MPa of measurements of ρ_{fluid} carried out between (0.1 and 40) MPa yielded an error less than 10 $\text{kg}\cdot\text{m}^{-3}$, reported that the principal cause of uncertainty for viscosity is the accuracy of the apparatus and not the value of ρ_{fluid}. For tetradecane, the density average deviation reported by Assael et al.[1] is 0.06 %, obtained from the fit of 117 data points to eq 2 over the temperature range from (298 to 358) K and pressures up to 370 MPa. For benzene, Cibulka and Takagi[2] reported an absolute root-mean-square deviation (rmsd) of 0.603 $\text{kg}\cdot\text{m}^{-3}$, obtained from the fit of 718 data points to eq 4 over the temperature range from (283 to 499) K and pressures up to 278 MPa, whereas for cyclohexane, Cibulka and Takagi[3] reported an absolute rmsd of 0.654 $\text{kg}\cdot\text{m}^{-3}$, obtained from the fit of 708

Table 1. Experimental Dynamic Viscosities as a Function of Temperature and Pressure for Cyclohexane

	η/mPa·s				
p/MPa	T/K = 313.2	T/K = 333.2	T/K = 353.2	T/K = 373.2	T/K = 393.2
0.69	0.723	0.540	0.424	0.323	0.248
5	0.772	0.576	0.450	0.349	0.262
10	0.825	0.616	0.480	0.371	0.284
20	0.926	0.692	0.540	0.420	0.329
30	1.018	0.762	0.597	0.461	0.369
40	1.111	0.837	0.651	0.504	0.414
50	1.240	0.912	0.703	0.557	0.453
60	1.347	0.994	0.752	0.608	0.492

Table 2. Experimental Dynamic Viscosities as a Function of Temperature, Pressure, and Mole Fraction for the Cyclohexane (1) + Tetradecane (2) System

	η/mPa·s			
p/MPa	T/K = 313.2	T/K = 333.2	T/K = 353.2	T/K = 393.2
		$x_1 = 0.204$		
0.69	1.412	1.049	0.828	0.496
5	1.494	1.114	0.877	0.526
10	1.589	1.186	0.931	0.565
20	1.782	1.326	1.029	0.639
30	1.982	1.462	1.125	0.710
40	2.195	1.599	1.216	0.786
50	2.424	1.740	1.311	0.855
60	2.672	1.888	1.403	0.925
		$x_1 = 0.405$		
0.69	1.303	0.968	0.760	0.447
5	1.365	1.018	0.803	0.481
10	1.447	1.077	0.854	0.515
20	1.612	1.199	0.950	0.591
30	1.787	1.315	1.043	0.661
40	1.981	1.435	1.129	0.731
50	2.185	1.563	1.219	0.793
60	2.422	1.698	1.305	0.855
		$x_1 = 0.600$		
0.69	1.123	0.878	0.661	0.404
5	1.182	0.924	0.703	0.429
10	1.256	0.981	0.749	0.461
20	1.397	1.092	0.840	0.521
30	1.545	1.194	0.932	0.585
40	1.701	1.301	1.025	0.644
50	1.860	1.408	1.113	0.703
60	2.038	1.517	1.203	0.761
		$x_1 = 0.800$		
0.69	0.935	0.711	0.540	0.339
5	0.986	0.754	0.580	0.359
10	1.044	0.805	0.621	0.386
20	1.164	0.905	0.705	0.439
30	1.291	1.005	0.789	0.496
40	1.424	1.102	0.870	0.549
50	1.569	1.201	0.952	0.604
60	1.720	1.298	1.030	0.666

Table 3. Experimental Dynamic Viscosities as a Function of Temperature, Pressure, and Mole Fraction for the Cyclohexane (1) + Benzene (2) System

	η/mPa·s				
p/MPa	T/K = 313.2	T/K = 333.2	T/K = 353.2	T/K = 373.2	T/K = 393.2
			$x_1 = 0.195$		
0.69	0.500	0.400	0.328	0.282	0.254
5	0.521	0.418	0.342	0.293	0.262
10	0.547	0.439	0.358	0.305	0.272
20	0.600	0.483	0.393	0.332	0.293
30	0.654	0.529	0.430	0.362	0.315
40	0.710	0.577	0.469	0.393	0.339
50	0.767	0.626	0.509	0.425	0.365
60	0.824	0.676	0.551	0.460	0.393
			$x_1 = 0.405$		
0.69	0.499	0.405	0.333	0.284	0.252
5	0.522	0.423	0.346	0.294	0.258
10	0.550	0.445	0.363	0.306	0.267
20	0.609	0.493	0.399	0.333	0.285
30	0.670	0.544	0.439	0.363	0.307
40	0.735	0.598	0.482	0.397	0.332
50	0.802	0.656	0.530	0.434	0.360
60	0.869	0.715	0.579	0.474	0.392
			$x_1 = 0.600$		
0.69	0.527	0.417	0.338	0.288	0.258
5	0.557	0.441	0.355	0.301	0.267
10	0.593	0.470	0.377	0.316	0.278
20	0.665	0.528	0.422	0.349	0.300
30	0.738	0.589	0.468	0.384	0.325
40	0.810	0.651	0.517	0.420	0.350
50	0.882	0.713	0.567	0.458	0.378
60	0.951	0.774	0.617	0.498	0.407
			$x_1 = 0.797$		
0.69	0.602	0.449	0.346	0.289	0.262
5	0.642	0.480	0.368	0.304	0.271
10	0.689	0.518	0.395	0.323	0.283
20	0.782	0.594	0.452	0.361	0.307
30	0.874	0.673	0.511	0.403	0.333
40	0.962	0.751	0.573	0.447	0.362
50	1.047	0.828	0.635	0.493	0.391
60	1.127	0.901	0.696	0.539	0.424

data points to eq 4 over the temperature range from (286 to 523) K and pressures up to 250 MPa. These values suggest that eq 5 can be used to calculate the density of the mixtures, ρ_{mix}, for the systems cyclohexane + tetradecane and cyclohexane + benzene without affecting the experimentally measured viscosity value.

Table 1 presents the experimental viscosity values of pure cyclohexane at different temperatures and pressures. Viscosity data of pure tetradecane and benzene, measured at the same temperatures and pressures studied for cyclohexane, were reported previously.[4]

Table 2 presents the experimental viscosity values of the cyclohexane + tetradecane system determined at different temperatures, pressures, and mole fraction compositions. Viscosities of binary mixtures for this system were determined by Awwad and Salman[17] at 298.15 K and atmospheric pressure. These data are, to our knowledge, the only viscosity data reported in the open literature for this binary system.

Four different mole fractions of cyclohexane were selected in this study for determining their viscosities at several pressures and temperatures. These viscosities along with those obtained for pure components allow one to follow the behavior of the viscosities for the cyclohexane (1) + tetradecane (2) system over the whole concentration range. For instance, Figure 1 shows the behavior of the viscosity as a function of pressure at different temperatures for a $x_1 = 0.405$ mol fraction, whereas Figure 2 shows the variation of the viscosity as a function of the mole fraction of cyclohexane at 393.2 K for the different pressures investigated.

Figure 1 shows that viscosity increases as pressure is increased for all isotherms investigated, but it decreases as temperature increases for a given pressure, while Figure 2 shows that viscosity decreases smoothly as the mole fraction of cyclohexane increases. Similar trends of the viscosity as a

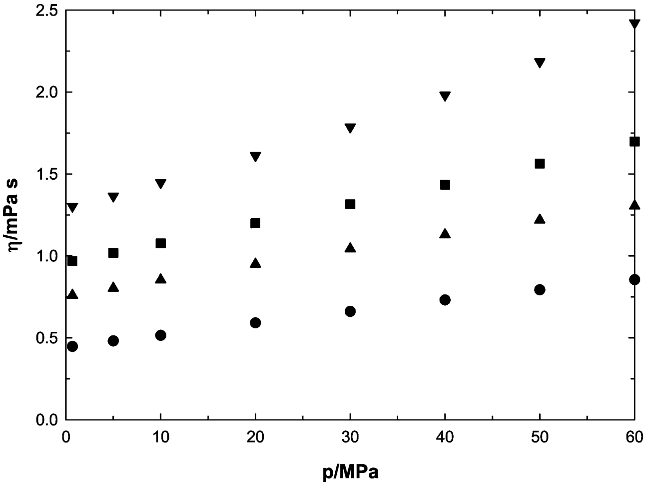

Figure 1. Experimental dynamic viscosity as a function of pressure for the system cyclohexane (1) + tetradecane (2) at the composition of $x_1 = 0.405$: ▼, 313.2 K; ■, 333.2 K; ▲, 353.2 K; ●, 393.2 K.

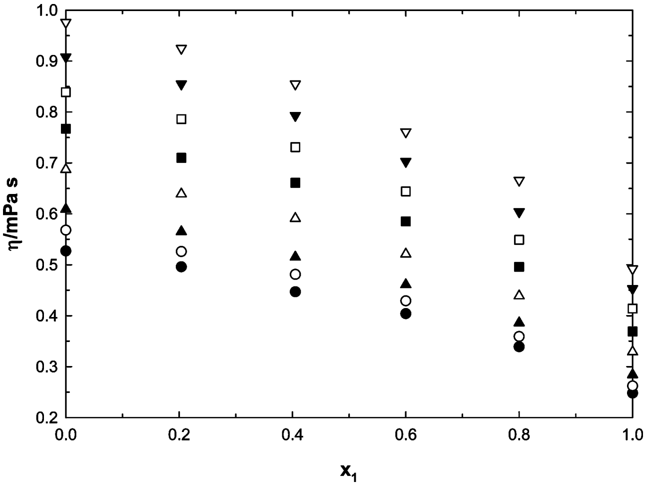

Figure 2. Experimental dynamic viscosity as a function of composition for the system cyclohexane (1) + tetradecane (2) at 393.2 K: ●, 0.69 MPa; ○, 5 MPa; ▲, 10 MPa; △, 20 MPa; ■, 30 MPa; □, 40 MPa; ▼, 50 MPa; ▽, 60 MPa.

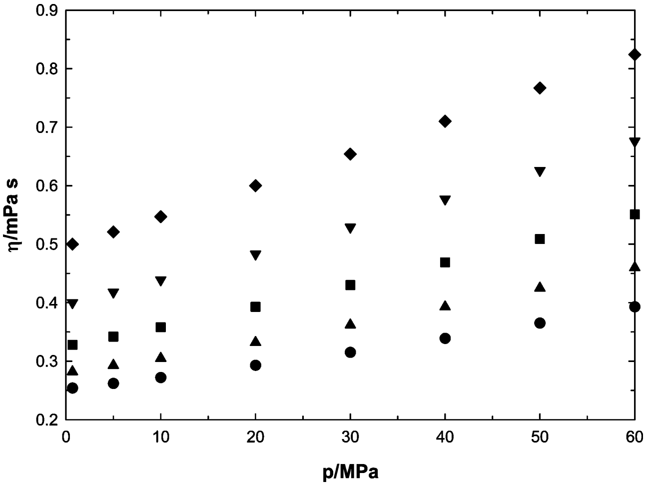

Figure 3. Experimental dynamic viscosity as a function of pressure for the system cyclohexane (1) + benzene (2) at the composition of $x_1 = 0.195$: ◆, 313.2 K; ▼, 333.2 K; ■, 353.2 K; ▲, 373.2 K; ●, 393.2 K.

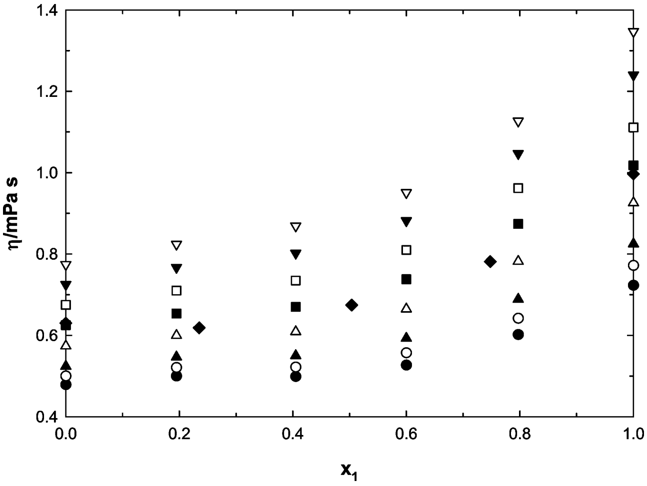

Figure 4. Experimental dynamic viscosity as a function of composition for the system cyclohexane (1) + benzene (2) at 313.2 K. This work: ●, 0.69 MPa; ○, 5 MPa; ▲, 10 MPa; △, 20 MPa; ■, 30 MPa; □, 40 MPa; ▼, 50 MPa; ▽, 60 MPa. Reference 19: ◆, 30 MPa.

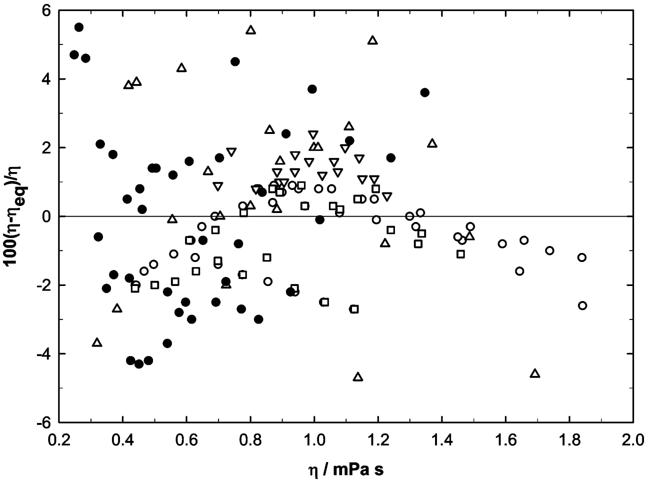

Figure 5. Relative deviation of measured viscosities from the correlation of Assael et al.[12] with those reported by other authors. ●, this work; ▽, ref 19; ○, ref 20; □, ref 21; △, ref 22.

function of pressure were observed for the other three mixtures. Analogously, similar behaviors of viscosity as a function of cyclohexane composition were observed for the other temperatures investigated.

On the other hand, Table 3 presents the experimental values of the binary mixture cyclohexane + benzene at different pressures, temperatures, and mole fraction compositions. Liquid viscosities of this system have been previously measured over the entire range of cyclohexane mole fraction by Papaioannou et al.[18] at 298.15 K and atmospheric pressure and by Matsuo and Makita[19] at (298.15 and 313.15) K and at pressures up to 49 MPa using a capillary viscometer.

As shown in Table 3, four different compositions in terms of mole fraction of cyclohexane were selected for determining their viscosities at several pressures and temperatures. Again, to illustrate the behavior of the viscosities for the system cyclohexane (1) + benzene (2), Figure 3 presents the behavior of the viscosity as a function of pressure at different temperatures for a $x_1 = 0.195$ mol fraction. This figure shows that viscosity increases as pressure is increased for all isotherms investigated, but it decreases as temperature increases for a given pressure.

Figure 4 shows the variation of the viscosity as a function of the mole fraction of cyclohexane at 313.2 K for the different pressures investigated. This figure shows a regular monotonic behavior of viscosity as a function of the composition at several pressures; that is, the viscosity increases smoothly as the mole fraction of cyclohexane increases for all isobars studied. Similar behaviors of viscosity as a function of cyclohexane composition were observed for the other temperatures investigated.

Figure 4 also presents the experimental viscosities determined for this system by Matsuo and Makita[19] at 313.15 K and 30 MPa over the entire range of cyclohexane mole fraction. As can been in this figure, our results are, on the whole, slightly higher than those reported by these authors for the different cyclohexane concentrations; however, they agree closely with their reported viscosity values for pure cyclohexane and benzene. We believe that these discrepancies can be due to the different apparatuses used in these works for determining liquid viscosities.

To compare our experimental data of pure cyclohexane with those reported by other authors,[19−22] the hard-sphere scheme proposed by Assael et al.[12] was used for comparison. These authors expressed the viscosity as

$$\eta = (0.1657 \cdot 10^{-8}) \frac{\eta^*_{\text{expl}}}{V^{2/3}} \left(\frac{1}{MRT} \right)^{-1/2} \tag{6}$$

where V is the molar volume, M is the molecular weight, T is the absolute temperature, and η^*_{expl} is the reduced experimental viscosity calculated from

$$\log\left(\frac{\eta^*_{\text{expl}}}{R_\eta} \right) = \sum_{i=0}^{7} a_i \left(\frac{V_0}{V} \right)^i \tag{7}$$

with $a_0 = 1.0945$, $a_1 = -9.26324$, $a_2 = 71.0385$, $a_3 = -301.9012$, $a_4 = 797.69$, $a_5 = -1221.9770$, $a_6 = 987.5574$, and $a_7 = -319.4636$. In eq 7, R_η is the roughness factor, which includes the effects caused by the nonsphericity of the molecules. For cyclohexane, Assael et al.[23] reported a value of R_η equal to 1.0, whereas the characteristic volume V_0 for this component is calculated from the expression

$$10^6 V_0 = 82.89 - 5.909 T_{\text{r}} - 10.047 T_{\text{r}}^2 \tag{8}$$

also reported by these authors.

For cyclohexane, Figure 5 shows that our experimental results agree with the values predicted by the Assael et al. correlation within 3 % with an average relative deviation of 2.3 % and maximum deviation of 5.4 % based on 40 experimental points. This figure also shows that our results agree reasonably well with values given by Matsuo and Makita,[19] Jonas et al.,[20] Kashiwagi and Makita,[21] and Tanaka et al.[22]

Data Correlation

The results obtained for dynamic viscosities of binary mixtures for the cyclohexane + tetradecane and cyclohexane + benzene systems were used to test the semiempirical relations of GN[10] and KC,[11] and a viscosity model based on the Eyring's theory coupled with a cubic equation of state (ET-EoS) proposed by Hernández-Galván et al.[4] These viscosity models were selected here because they are capable of representing satisfactorily the η, T, p, x surface from low to elevated pressures of binary systems containing hydrocarbon compounds. These models were applied to the representation of the viscosity data for the systems cyclohexane + tetradecane and cyclohexane + benzene, over the whole temperature, pressure, and composition ranges studied by using a single temperature-independent binary interaction parameter.

For a binary mixture, the GN equation is expressed as

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 g_{12}^{\text{GN}} \tag{9}$$

while the KC equation is given by

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 g_{12}^{\text{KC}} \tag{10}$$

where η_i is the viscosity of component i, η is the viscosity of the mixture, x_i is the mole fraction of component i, and g_{12}^{GN} and g_{12}^{KC} are the interaction parameters that characterize the binary formed by components 1 and 2 for the GN and KC correlations, respectively.

The form of the ET-EoS viscosity model for a binary mixture can be written as

$$\eta = \frac{(\eta V)^{\text{id}}}{V_{\text{m}}} \exp\left[\sum_{i=1}^{2} x_i (\ln \phi_i - \ln \phi_i^0) + x_1 x_2 g_{12}^{\text{EE}} \right] \tag{11}$$

where $(\eta V)^{\text{id}}$ is the kinematic viscosity of an ideal solution given by

$$(\eta V)^{\text{id}} = \exp\left[\sum_{i=1}^{2} x_i \ln(\eta_i^0 V_i^0) \right] \tag{12}$$

and g_{12}^{EE} is the interaction parameter for this viscosity model, whose value can be optimized from binary viscosity data by matching the experimental viscosity data with those predicted from eq 11.

The calculation of the kinematic viscosity of an ideal solution $(\eta V)^{\text{id}}$ requires the values of the viscosities of the pure components η_i^0 at the temperature and pressure of interest. For cyclohexane, the experimental viscosities are given in Table 1, whereas for tetradecane and benzene, the experimental viscosities are reported elsewhere.[4]

The use of an equation of state in eq 11 is advantageous because it allows the simultaneous determination of the fugacity coefficient of component i in the mixture $\phi_i(T,p,x)$, the molar volume of the liquid mixture $V_{\text{m}}(T,p,x)$, the fugacity coefficient of the pure fluid $\phi_i^0(T,p)$, and the molar volume of the pure liquid $V_i^0(T,p)$. In this work, the prediction of these properties was performed using the Peng−Robinson equation of state.[24]

Equations 9, 10, and 11 were applied to the modeling of the experimental liquid viscosity data given in Tables 2 and 3 for the systems cyclohexane + tetradecane and cyclohexane + benzene, respectively. The mixture interaction parameter in these equations was obtained by searching the minimum of the following objective function:

$$f = \sum_{i=1}^{N_{\text{p}}} \left(\frac{\eta_i^{\text{expl}} - \eta_i^{\text{calc}}}{\eta_i^{\text{expl}}} \right)^2 \tag{13}$$

where the summation is over the whole composition range, N_{p} is the number of experimental points, and η^{expl} and η^{calc} are the experimental and calculated viscosities of the binary mixture, respectively.

The overall performance of the viscosity models was established through the average relative deviation,

$$ARD = \frac{1}{N_{\text{p}}} \sum_{i=1}^{N_{\text{p}}} \left| \frac{\eta_i^{\text{expl}} - \eta_i^{\text{calc}}}{\eta_i^{\text{expl}}} \right| \tag{14}$$

with maximum deviation obtained from

$$MD = \max\left|\frac{\eta_i^{\text{expl}} - \eta_i^{\text{calc}}}{\eta_i^{\text{expl}}}\right| \tag{15}$$

The interaction parameters obtained from the regression of the viscosity data with the GN, KC, and ET-EoS viscosity models are given in Table 4. An examination of the average relative deviation (*ARD*) and maximum deviation (*MD*) values for the different viscosity models shows that the three models yielded essentially the same results. Notwithstanding, it should be mentioned that the GN correlation is slightly superior to the ET-EoS viscosity model in correlating the viscosity data of the cyclohexane + tetradecane and cyclohexane + benzene systems.

For comparison, two viscosity models with a physical and theoretical background, the hard-sphere scheme[12] and the free-volume model,[13,14] were also applied to the modeling of the viscosity data for the systems cyclohexane + tetradecane and cyclohexane + benzene.

The hard-sphere model, given by eq 6, was applied to mixtures by using the following mixing rules for the roughness factor, R_η, and the characteristic volume, V_0, of the mixture

$$R_\eta = \sum_{i=1}^{\text{nc}} x_i R_{\eta,i} \tag{16}$$

$$V_0 = \sum_{i=1}^{\text{nc}} x_i V_{0,i} \tag{17}$$

where $R_{\eta,i}$ and $V_{0,i}$ are the roughness factor and characteristic volume of component i, respectively, x_i is the mole fraction of component i, and nc is the number of components. For n-alkanes, the roughness factor R_η is calculated from the correlation[12]

$$R_\eta = 0.995 - 8.944 \cdot 10^{-4} C + 5.427 \cdot 10^{-3} C^2 \tag{18}$$

where C is the number of carbon atoms in the molecule. From eq 18, R_η is 2.046 for tetradecane, whereas for benzene a value of R_η equal to 0.960 is reported by Assael et al.[25] For n-alkanes, the characteristic volume V_0 is calculated from the correlation[26]

$$10^6 V_0 = 117.874 + 0.15(-1)^C - 0.25275T + 5.48 \cdot 10^{-4} T^2 - 4.246 \cdot 10^{-7} T^3 + (C - 6)(1.27 - 9 \cdot 10^{-4} T)(13.27 + 0.025C) \tag{19}$$

whereas for benzene, this value is calculated from the correlation[25]

$$10^6 V_0 = -3324.7C^{-2} + 529.47C^{-1} + (9.48786C^{-2} - 8.55176 \cdot 10^{-2} C + 6.03463 \cdot 10^{-3} C^2)T + (-1.5797 \cdot 10^{-3} + 3.9901 \cdot 10^{-4} C - 2.2309 \cdot 10^{-5} C^2)T^2 \tag{20}$$

where T is the absolute temperature.

The free-volume viscosity model, proposed by Allal et al.[13] for the modeling of the viscosity of Newtonian fluids in the dense phase ($\rho_{\text{fluid}} > 200\ \text{kg} \cdot \text{m}^{-3}$) with small molecules, can be expressed as

$$\eta = \frac{\rho_{\text{fluid}} l (E_0 + pM/\rho_{\text{fluid}})}{\sqrt{3RTM}} \exp\left[B\left(\frac{E_0 + pM/\rho_{\text{fluid}}}{2RT}\right)^{3/2}\right] \tag{21}$$

where l is analogous with a length, E_0 is the energy within the molecule, p is the pressure, T is the temperature, M is the molecular weight, and R is the gas constant. This model, which connects the dynamic viscosity η to the molecular structure through a representation of the free-volume fraction, involves three physical parameters l, E_0, and B that are characteristic of the molecule. Although this model was conceived originally for modeling dense fluids, it was later extended to the dilute gas limit by Allal et al.[14]

For each of the studied fluids, the three characteristic parameters in eq 21 were adjusted and are reported in Table 5 along with the average relative deviation (*ARD*) and maximum deviation (*MD*). As can be seen in this table, the obtained *ARD*s for benzene and cyclohexane are within the experimental uncertainty, whereas for tetradecane it is higher than the experimental one, which can be attributed to the fact that the free-volume model was originally developed for the modeling of the viscosity of small molecules.

Equation 21 was applied to the studied mixtures by using the following mixing rules suggested by Zéberg-Mikkelsen et al.[27]

$$M = \sum_{i=1}^{\text{nc}} x_i M_i \tag{22}$$

$$E_0 = \sum_{i=1}^{\text{nc}} \sum_{j=1}^{\text{nc}} x_i x_j \sqrt{E_{0,i} E_{0,j}} \tag{23}$$

$$\frac{1}{B} = \sum_{i=1}^{\text{nc}} x_i \frac{1}{B_i} \tag{24}$$

$$l = \sum_{i=1}^{\text{nc}} x_i l_i \tag{25}$$

where x_i is the mole fraction of component i.

Table 4. Results of the Viscosity Data Correlation for the Cyclohexane (1) + Benzene (2) and Cyclohexane (1) + Tetradecane (2) Systems with the GN, KC, and ET-EoS Models

binary system	g_{12}	100 *ARD*	100 *MD*
GN Model			
cyclohexane + benzene	−0.365	3.1	11.0
cyclohexane + tetradecane	0.441	3.4	8.9
KC Model			
cyclohexane + benzene	−0.293	3.0	9.8
cyclohexane + tetradecane	0.803	3.8	11.3
ET-EoS Model			
cyclohexane + benzene	−0.336	4.0	12.6
cyclohexane + tetradecane	0.897	3.5	9.1

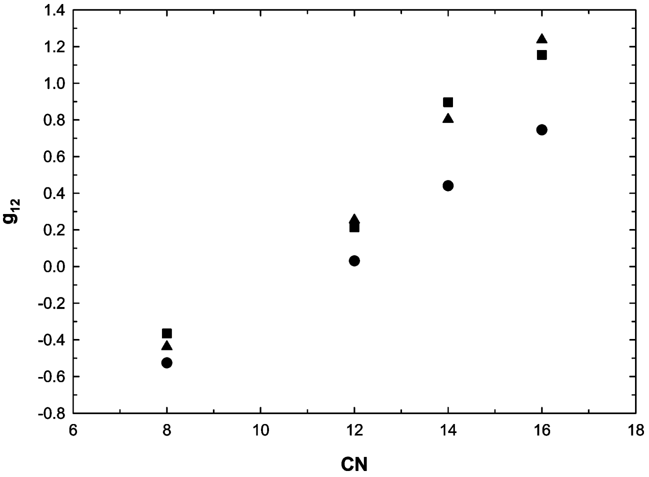

Figure 6. Interaction parameter g_{12} as a function of the n-alkane carbon number (CN) for the systems cyclohexane (1) + n-alkane (2): ●, GN model; ▲, KC model; ■, ET-EoS model.

Table 5. Pure Component Parameters *B*, E_0, and *l* of the Free-Volume Model for Benzene, Cyclohexane, and Tetradecane

component	*M*	E_0/J·mol^{-1}	*B*	l/Å	100 *ARD*	100 *MD*
benzene	78.11	49 995.7	0.06483	0.417466	1.1	2.8
cyclohexane	84.17	52 940.2	0.08175	0.324922	2.0	6.3
tetradecane	198.39	154 572.9	0.01869	0.261883	2.7	8.2

Table 6. Results of the Viscosity Data Modeling for the Cyclohexane + Benzene and Cyclohexane + Tetradecane Systems with the Hard-Sphere and Free-Volume Models

binary system	100 *ARD*	100 *MD*
Hard-Sphere Model		
cyclohexane + benzene	7.3	18.3
cyclohexane + tetradecane	4.0	8.9
Free-Volume Model		
cyclohexane + benzene	4.8	14.1
cyclohexane + tetradecane	26.1	41.8

Table 7. Results of the Viscosity Data Correlation for Cyclohexane (1) + *n*-Alkane (2) Binary Systems with the GN, KC, and ET-EoS Viscosity Models

binary system	g_{12}	100 *ARD*	100 *MD*
GN Model			
cyclohexane + octane	−0.525	3.3	7.4
cyclohexane + dodecane	0.031	2.2	6.6
cyclohexane + hexadecane	0.746	1.8	5.2
KC Model			
cyclohexane + octane	−0.437	3.3	7.2
cyclohexane + dodecane	0.254	2.9	7.8
cyclohexane + hexadecane	1.237	2.8	8.4
ET-EoS Model			
cyclohexane + octane	−0.365	3.3	8.0
cyclohexane + dodecane	0.215	2.3	7.6
cyclohexane + hexadecane	1.155	2.7	8.5

Results of the modeling obtained with the hard-sphere and free-volume models for the cyclohexane + tetradecane and cyclohexane + benzene systems are presented in Table 6. This table shows that, according to the average relative deviation (*ARD*) and maximum deviation (*MD*) values, the hard-sphere model is superior to the free-volume model in modeling the viscosity data of the two binary systems studied over the whole temperature, pressure, and composition range studied; however, the results of the modeling were not better than those obtained with the GN and KC equations or the ET-EoS viscosity model. Nonetheless, it is worth mentioning that although the hard-sphere and free-volume models yield *ARD*s higher than those obtained with the other viscosity models considered, they use no adjustable parameter for determining the dynamic viscosity of a binary system, so that the prediction performance of the hard-sphere and free-volume models should be regarded to be acceptable.

On the other hand, the GN, KC, and ET-EoS models were also used for the representation of the viscosity data for the systems cyclohexane + octane, cyclohexane + dodecane, and cyclohexane + hexadecane reported by Tanaka et al.[22] These viscosity data were measured at (298, 323, and 348) K and pressures up to 150 MPa or freezing pressures. However, the regression of these data was limited to the conditions of pressure presented in Table 2 for the cyclohexane + tetradecane system, to follow the behavior of the interaction parameters for these viscosity models up to 60 MPa.

The results of the regression for these binary systems for the GN, KC, and ET-EoS models are given in Table 7. In this table, the interaction parameter, the average relative deviation (*ARD*), and the maximum deviation (*MD*) for each viscosity model are presented. An examination of this table shows that the interaction parameters obtained for the three models are negative for the cyclohexane + octane system and positive for the cyclohexane + dodecane and cyclohexane + hexadecane systems. In this case, the interaction parameter value increases as the carbon number of the *n*-alkane increases. This table also shows that the GN equation yielded the best results of the viscosity data regression for the three binary systems; however, the results of the regression with the ET-EoS and KC models are very close to those obtained with the GN equation. Figure 6 presents the variation of the interaction parameter g_{12} as a function of the *n*-alkane carbon number for the systems cyclohexane (1) + *n*-alkane (2) studied. This figure shows that the interaction parameter g_{12}, for the three models considered, goes from negative to positive values and that it increases as the carbon number of the *n*-alkane increases.

Conclusions

A rolling-ball viscometer has been used to experimentally determine liquid viscosities of pure cyclohexane and of the systems cyclohexane + tetradecane and cyclohexane + benzene, over the temperature range from (313.2 to 393.2) K and pressures up to 60 MPa with an experimental uncertainty in the measured viscosity data of 2 %.

The GN and KC semiempirical relations and a liquid viscosity model based on Eyring's theory coupled with a cubic equation of state (ET-EoS) were used to represent the measured viscosity data of the cyclohexane + tetradecane and cyclohexane + benzene systems using a single temperature-independent binary interaction parameter. Results of the representation showed that these viscosity models are able to represent satisfactorily the viscosity data of these systems over the whole temperature, pressure, and composition range studied.

The hard-sphere and free-volume models were also used for modeling the viscosity data of these two binary systems. Results of the modeling effort with these models yielded higher average deviations than those obtained with the GN, KC, and ET-EoS models; however, due to that both models do not use any adjustable parameter for determining the dynamic viscosity of a binary system, the prediction performance of these models should be regarded to be acceptable.

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