

Liquid viscosities of benzene, *n*-tetradecane, and benzene + *n*-tetradecane from 313 to 393 K and pressures up to 60 MPa: Experiment and modeling

Miguel A. Hernández-Galván^{a,b}, Fernando García-Sánchez^{a,*}, Ricardo Macías-Salinas^c

^a *Laboratorio de Termodinámica, Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México, D.F., Mexico*

^b *Facultad de Química, Universidad Nacional Autónoma de México, Av. Universidad 3000, 04510 México, D.F., Mexico*

^c *Departamento de Ingeniería Química, SEPI-ESIQIE, Instituto Politécnico Nacional, Unidad Profesional Adolfo López Mateos, Zacatenco, 07738 México, D.F., Mexico*

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Abstract

In this work, kinematic viscosities of benzene, *n*-tetradecane, and of the mixture benzene + *n*-tetradecane at four different compositions were measured using a rolling-ball viscometer from 313.2 to 393.2 K and pressures up to 60 MPa. Kinematic viscosities were converted to dynamic viscosities through the use of a density Tait-like equation for pure components and a single density mixing rule for the mixtures. A comparison between our measured viscosities and those reported by other authors for benzene and *n*-tetradecane was established with the correlation given by Assael et al. [M.J. Assael, J.H. Dymond, M. Papadaki, P.M. Patterson, Correlation and prediction of dense fluid transport coefficients. I. *n*-alkanes, *Int. J. Thermophys.* 13 (1992) 269–281]. The comparison showed an average absolute deviation of 1.5% for benzene and 2.7% for *n*-tetradecane. The measured mixture viscosity data were modeled with a proposed liquid viscosity model based on the Eyring's theory coupled with a cubic equation of state and using a single temperature-independent binary interaction parameter to describe the whole $\eta - T - p - x$ surface of study. Results of the modeling effort yielded an average absolute deviation of 2.0%, which is within the experimental uncertainty.

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1. 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. Also, high-pressure viscosity data over a wide range of temperature and pressure for a given composition can be used to test the capability of semi theoretical and empirical viscosity models. Unfortunately, experimental studies of viscosity for a wide range of compositions at different pressures and temperatures are costly and time consuming. An alternative to overcome this problem is to use predictive models; however, the reliability of these methods depends greatly on the accuracy and availability of the experimental data.

In order to extend the database of viscosities for pure hydrocarbon 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 a research program on viscosity measurements of hydrocarbons at oil reservoir conditions.

In this work, we report liquid viscosity measurements for the binary system benzene + *n*-tetradecane from 313.2 to 393.2 K and at pressures up to 60 MPa over the entire composition range. Kinematic viscosity data for this system were determined in a high-pressure rolling-ball viscometer (Ruska, model 1602–716). This viscosity measurement technique has been used by several authors (Barrufet et al. [1,2], Estrada-Baltazar et al. [3,4], Iglesias-Silva [5]) in the measurement of high-pressure viscosity data of pure *n*-alkanes, binary and ternary mixtures of *n*-alkanes, and CO₂ + *n*-alkanes. More recently, Pensado et al. [6] used the

* Corresponding author. Tel.: +52 55 9175 6574; fax: +52 55 9175 6380.
E-mail address: fgarcias@imp.mx (F. García-Sánchez).

same technique for determining viscosity measurements of pure 2-3-dimethylpentane at pressures up to 60 MPa.

Dynamic viscosities were obtained through the use of a density Tait-type correlation reported by Assael et al. [7]. The measured viscosity data for pure benzene and *n*-tetradecane are compared with those values obtained from the correlation published by Assael et al. [8] while a proposed liquid viscosity model is used in the modeling of measured mixture viscosities data.

2. Experimental

2.1. Materials

Benzene and *n*-tetradecane were acquired from Aldrich (USA) with a minimum purity of 99.9 mol% and 99 mol%, respectively. Octane and dodecane, used to calibrate the apparatus, were purchased from Aldrich (USA) both with a certified purity greater than 99 mol%. All these chemicals were used without any further purification.

2.2. Apparatus

The experimental apparatus used in this work is shown schematically in Fig. 1. It is based on the high-pressure viscosity technique, which 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 Ruska rolling-ball viscometer has been designed to operate in the viscosity range of 0.1–3000 mPa s. This viscometer consists of a mechanical test assembly and a control unit (Chro-

malox 2140) with a digital watch. The mechanical assembly is a stainless steel high-pressure housing fixed to a base allowing circular movements. The housing 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. That is, the watch in the unit control is activated when the current is interrupted and it is stopped automatically when the sphere reaches the end of its travel thus eliminating the human error when measuring the sphere roll time. Hence, repeatability of the roll time measurements is $\pm 0.1\%$. The angle at which the sphere is rolling and the sphere diameter should be selected by taking into account the viscosity of the fluid. Thus, for instance, higher angles with lower diameters should be used for high viscosities.

The viscometer is heated with an electronic heating jacket control system and the temperature can be controlled within ± 0.2 K. The temperature is measured by means of a thermocouple with a precision of ± 0.1 K over the temperature range of 303–423 K. The pressure circuit (see Fig. 1) connected to the viscometer consists a set of valves (Ruska), 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 (Edwards).

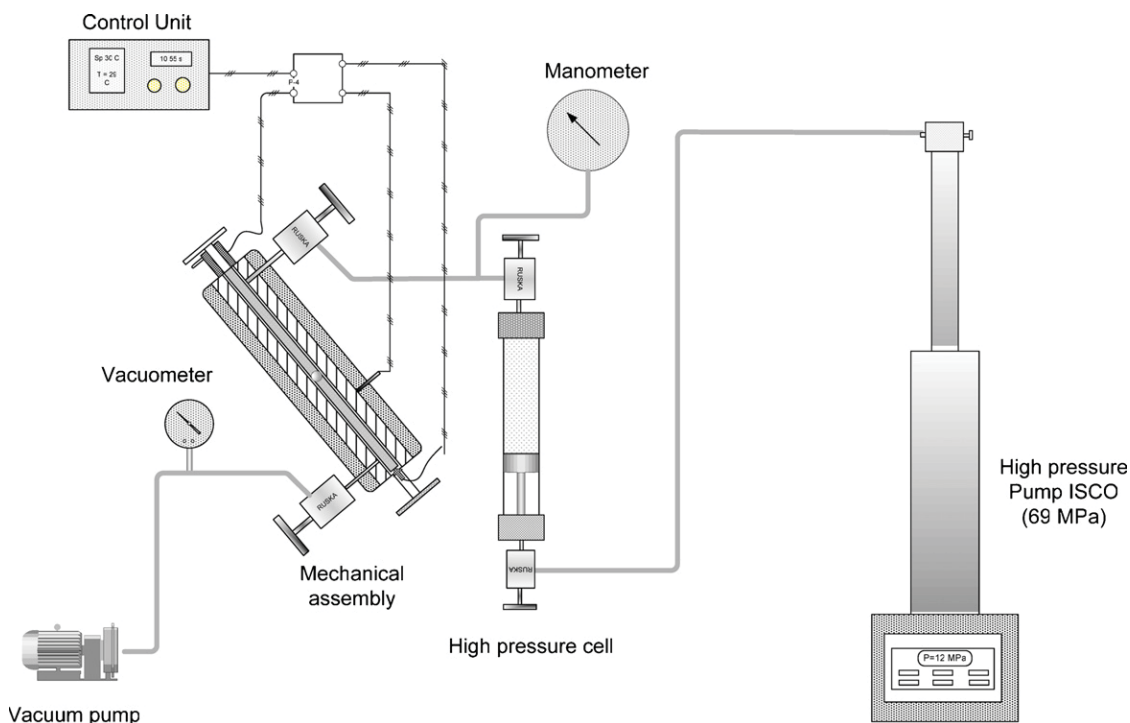


Fig. 1. Schematic diagram of the rolling-ball viscometer and the charging system.

2.3. Preparation of mixtures

The binary mixtures of benzene + *n*-tetradecane were made up gravimetrically by using an analytical balance (Sartorius, model BP301S) with a precision of ± 0.1 mg at room temperature and at atmospheric pressure. The quantity of the mixture required to perform the viscosity measurements in our apparatus is about 200 mL. This is because more than 100 mL of the mixture remains inside the high-pressure equilibrium cell (see Fig. 1) after transferring the mixture to the viscometer. The precision in the preparation of the mixture is estimated to be better than ± 0.01 mass%.

2.4. Procedure

The procedure used to perform viscosity measurements is as follows: a comprehensive cleaning of the whole system is first carried out in order to remove any trace of dust or grease that avoids the steel ball to roll freely through the liquid inside the barrel of the viscometer. The system is then evacuated using the vacuum pump. Second, 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 syringe pump ISCO, with a maximum capacity 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.

2.5. Calibration

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:

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

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 pressure, temperature, and the rolling time of the ball, which is obtained by calibrating the viscometer with different substances of known viscosity and density. In this work, we have used a Cannon certified viscosity standard, octane, and dodecane as calibrating fluids at 0.1 MPa and 303.2 K. For all time measurements, the sphere selected has a diameter of 6.22 mm along with an inclination angle of 23° .

According to Estrada-Baltazar et al. [3], function $K(t, p, T)$ can be written as:

$$K(t, p, T) = \frac{\kappa(t)}{X(t, p, T)} \quad (2)$$

where $\kappa(t)$ is considered, under laminar conditions, a linear function of t . The functionality of this constant at 0.101325 MPa and

303.2 K obtained here is:

$$\kappa(t) = -0.027431 + 0.0070455(t, s) \quad (3)$$

In order to obtain the correction function $X(t, p, T)$, the roll times of octane and dodecane were measured at temperatures from 303.2 to 393.2 K and pressures up to 60 MPa. The best polynomial form selected for the correction function $X(t, p, T)$ is:

$$\begin{aligned} X(t, p, T) = & 11.83758 + 0.00463(p, \text{MPa}) + 0.11976(t, s) \\ & - 0.57156(T, \text{K})^{0.5} + 8.493 \times 10^{-3}(p, \text{MPa})^{0.5} \\ & - 1.26562(t, s)^{0.5} - 1.9498 \times 10^{-5}(T, \text{K})(p, \text{MPa}) \\ & + 1.4622 \times 10^{-4}(T, \text{K})(t, s) - 7.2276 \times 10^{-4}(t, s)^2 \\ & + 1.8372 \times 10^{-5}(T, \text{K}) \end{aligned} \quad (4)$$

This correction function was determined using the roll times of octane and dodecane measured at the different conditions of temperature and pressure. They were converted to viscosity values using Eq. (1) with $X(t, p, T) = 1$. The ratio of the calculated viscosities to the literature values, $\eta_{\text{calc}}/\eta_{\text{lit}}$, were then correlated as a function of time, pressure and temperature to yield Eq. (4). In this case, the literature viscosity data for octane and dodecane were taken from Kashiwagi and Makita [9] and from Caudwell et al. [10], respectively. The uncertainty of the viscosity estimated for these two alkanes is $\pm 2\%$ on the whole temperature and pressure range studied. More details of the calibration procedure can be found elsewhere [11].

In order to determine the value of the viscosity using the rolling-ball viscometer, 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 is assumed to be constant and equal to 7.6185 g cm^{-3} ; i.e., the effects of pressure and temperature upon the density of the ball are neglected. Fluid densities of *n*-alkanes (from ethane to *n*-hexadecane) are determined by using the following Tait-like equation suggested by Assael et al. [7].

$$\rho_{\text{fluid}}(T, p) = \rho_0(T, p_0) \left[1 - 0.2 \log \left(\frac{B(T) + p}{B(T) + p_0} \right) \right]^{-1} \quad (5)$$

where ρ_{fluid} and ρ_0 are the densities of the fluid and that of the ball at pressures p and p_0 , respectively, and $B(T)$ is a temperature-dependent parameter. By selecting p_0 equal to the atmospheric pressure (0.101325 MPa), the density of the liquid at this pressure is determined from the correlation proposed by Cibulka and Hnědkovský [12],

$$\rho_0 = \rho_c \left[1 + \sum_{i=1}^5 a_i (1 - T_r)^{1/3} \right] \quad (6)$$

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 ($i = 1, \dots, 5$) are parameters that depend on the type of fluid under study.

For *n*-alkanes (from ethane to *n*-hexadecane), Assael et al. [7] found that the average percent deviation of Eq. (5) with respect to the experimental data is 0.5%.

For aromatic hydrocarbons, Cibulka and Takagi [13] fitted available data on the compressed liquid density to a Tait equation written in the form:

$$\rho_{\text{fluid}}(T, p) = \rho_0(T, p_0) \left[1 - C(T) \ln \left(\frac{B(T) + p}{B(T) + p_0} \right) \right]^{-1} \quad (7)$$

where $B(T)$ and $C(T)$ are temperature-dependent parameters. For benzene, the average percent deviation reported by these authors using Eq. (7) with respect to the experimental density data is 0.1%.

For a mixture of N -components, its density can be calculated from the expression:

$$\rho_{\text{mix}} = \left(\sum_{i=1}^N \frac{w_i}{\rho_i} \right)^{-1} \quad (8)$$

where w_i and ρ_i are the weight fraction and density for the pure component i , respectively. Although Eq. (8) assumes that the mixing is ideal, this can be used for non-ideal mixtures taking into account that 10 kg/m³ in liquid density generates a relative error of 0.001 for viscosity [14].

Once the calibration of the viscometer is completed and after applying Eq. (1), viscosities are determined with an overall uncertainty of about $\pm 2\%$, which is comparable to that obtained by other authors using the same experimental technique [1–6].

3. Experimental results

Viscosities of the system benzene + n -tetradecane have been previously measured at atmospheric pressure over the entire range of mole fraction by Awwad et al. [15] at 298.15 K and by Mutalik et al. [16] at temperatures from 298.15 to 308.15. However, viscosity data at high pressures for this system have not been previously studied.

In this work, liquid viscosities of pure benzene and n -tetradecane and of the binary mixture benzene + n -tetradecane were experimentally measured over the temperature range from 313.2 to 393.2 K and pressures up to 60 MPa. All the measurements used 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 roll time 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. Fluid densities of n -tetradecane and benzene were calculated with the correlations given by Eqs. (5) and (7), respectively.

Table 1 shows the experimental viscosity values of pure benzene and n -tetradecane at different temperature and pressures, while Table 2 presents the experimental values of the binary mixture benzene + n -tetradecane at different pressures, temperatures and mole fraction compositions. As can be seen in Table 2, four different compositions in terms of mole fraction of benzene were selected in this study for determining their viscosities at several pressures and temperatures. These viscosities along with those obtained for pure components allow us to follow the behavior of the viscosities for the mixture benzene + n -tetradecane over the whole concentration range. As an example of this behav-

Table 1

Experimental dynamic viscosities, η (mPa s), as a function of temperature and pressure for benzene and n -tetradecane

p (MPa)	T (K)				
	313.2	333.2	353.2	373.2	393.2
Benzene					
0.69	0.479	0.387	0.317	0.269	0.239
5	0.500	0.404	0.331	0.279	0.246
10	0.524	0.424	0.347	0.291	0.255
20	0.574	0.466	0.380	0.316	0.273
30	0.625	0.509	0.415	0.344	0.294
40	0.675	0.553	0.451	0.372	0.315
50	0.725	0.597	0.489	0.402	0.339
60	0.774	0.641	0.526	0.434	0.364
n-Tetradecane					
0.69	1.653	1.218	0.896	0.660	0.527
5	1.738	1.283	0.957	0.708	0.568
10	1.831	1.345	1.017	0.757	0.609
20	2.025	1.473	1.128	0.852	0.687
30	2.241	1.607	1.229	0.943	0.767
40	2.483	1.740	1.325	1.031	0.839
50	2.767	1.886	1.423	1.117	0.908
60	3.093	2.043	1.518	1.202	0.976

ior, Fig. 2 presents the behavior of the viscosity as a function of pressure at different temperatures for a specific composition of 0.602 mole fraction. Fig. 3 shows the behavior of the viscosity as a function of temperature at different pressures for the same composition. In these figures, solid lines are used to better identify the trends of the experimental results.

An examination of Fig. 2 shows that viscosity increases linearly as pressure is increased for all isotherms investigated, but it decreases as temperature increases for a given pressure. This effect can be seen in more detail in Fig. 3. In this figure, it is observed that viscosity decreases as temperature increases for all isobars studied, following a regular trend. This figure also

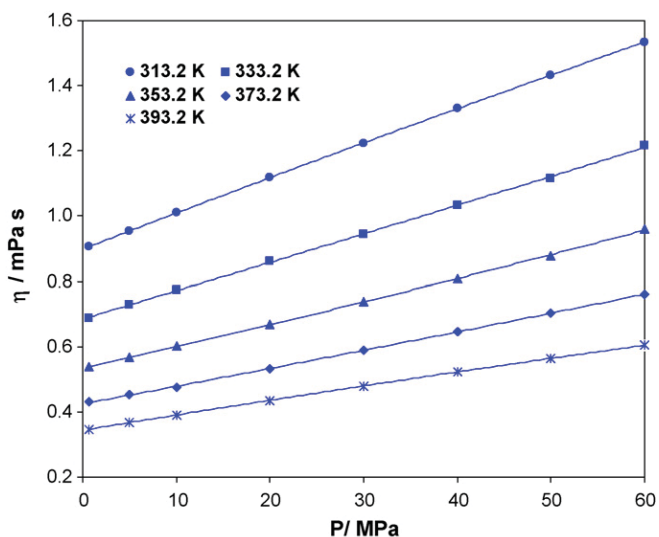


Fig. 2. Experimental dynamic viscosity as a function of pressure for benzene + n -tetradecane at the composition of 0.602 benzene mole fraction. Solid lines used to better identify the experimental data.

Table 2

Experimental dynamic viscosities, η (mPa s), as a function of temperature and pressure for the binary mixture benzene (1) + *n*-tetradecane (2)

p (MPa)	T (K)				
	313.2	333.2	353.2	373.2	393.2
$x_1 = 0.179$					
0.69	1.393	1.045	0.819	0.596	0.466
5	1.461	1.098	0.855	0.635	0.495
10	1.538	1.157	0.904	0.678	0.531
20	1.695	1.273	0.996	0.765	0.601
30	1.860	1.389	1.080	0.849	0.670
40	2.036	1.515	1.168	0.926	0.738
50	2.224	1.657	1.278	1.001	0.804
60	2.434	1.846	1.391	1.070	0.868
$x_1 = 0.436$					
0.69	1.103	0.838	0.614	0.485	0.394
5	1.159	0.884	0.662	0.515	0.419
10	1.223	0.935	0.705	0.549	0.445
20	1.347	1.037	0.793	0.620	0.496
30	1.473	1.135	0.883	0.688	0.554
40	1.600	1.228	0.956	0.753	0.610
50	1.729	1.319	1.032	0.819	0.662
60	1.866	1.421	1.116	0.879	0.717
$x_1 = 0.602$					
0.69	0.905	0.688	0.537	0.430	0.347
5	0.955	0.728	0.566	0.452	0.368
10	1.011	0.775	0.601	0.477	0.390
20	1.118	0.862	0.668	0.533	0.436
30	1.225	0.946	0.739	0.590	0.479
40	1.329	1.032	0.809	0.646	0.524
50	1.432	1.115	0.878	0.704	0.565
60	1.535	1.216	0.959	0.761	0.604
$x_1 = 0.798$					
0.69	0.679	0.528	0.421	0.356	0.307
5	0.712	0.557	0.443	0.371	0.320
10	0.753	0.592	0.469	0.389	0.336
20	0.835	0.661	0.523	0.427	0.367
30	0.916	0.730	0.578	0.467	0.398
40	1.000	0.797	0.634	0.509	0.432
50	1.081	0.863	0.690	0.553	0.466
60	1.160	0.927	0.745	0.598	0.499

shows that the viscosity is larger at high pressures and low temperatures than at low pressures and high temperatures. Similar trends of the viscosity as a function of either pressure or temperature were observed for the other three mixtures under study having different compositions.

Fig. 4 shows the variation of the viscosity as a function of the mole fraction of benzene at 333.2 K for the different pressures investigated. This figure shows a regular monotonic behavior of viscosity as a function of the composition at several pressures; i.e., the viscosity decreases almost linearly as the mole fraction of benzene increases for all isobars studied. It can also be noted in this figure that the viscosity is larger at high pressures and low benzene concentrations than at low pressures and high benzene concentrations. Finally, Fig. 5 shows the variation of viscosity as a function of the mole fraction of benzene at 60 MPa for the different temperatures investigated. This figure depicts a decreasing linear-like behavior of viscosity as benzene concentration increases for all isotherms studied. It

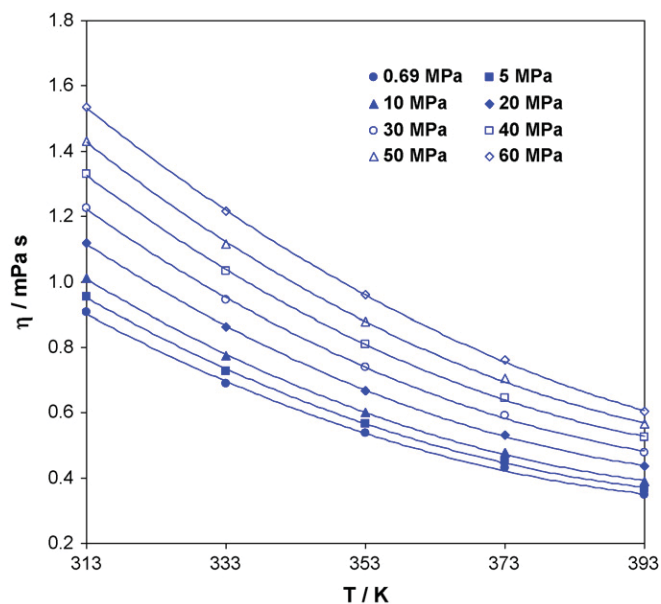


Fig. 3. Experimental dynamic viscosity as a function of temperature for benzene + *n*-tetradecane at the composition of 0.602 benzene mole fraction.

can be also deduced from this figure that viscosity is larger at low temperatures and low benzene concentrations than at high temperatures and high benzene concentrations. Similar behaviors of viscosity as a function of benzene composition were observed for the other pressures or/and temperatures investigated.

In order to compare our experimental data of pure benzene and *n*-tetradecane components with those reported by other authors [9,17–20], the correlation proposed by Assael et al. [8] was used for comparison. These authors express the

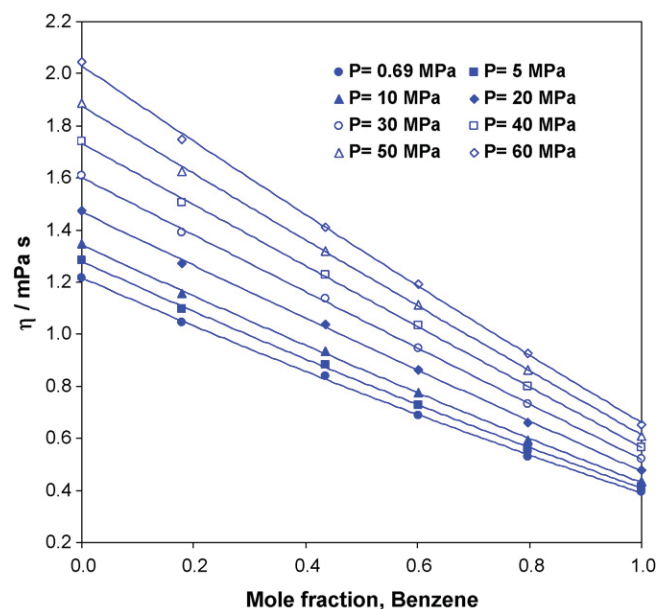


Fig. 4. Experimental dynamic viscosity as a function of composition for benzene + *n*-tetradecane at 333.2 K.

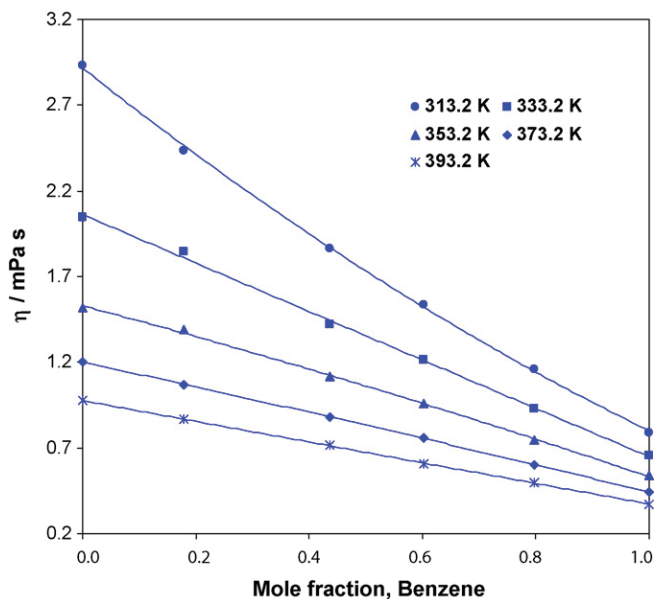


Fig. 5. Experimental dynamic viscosity as a function of composition for benzene + *n*-tetradecane at 60 MPa.

viscosity as:

$$\eta = (0.1657 \times 10^{-8}) \frac{\eta_{\text{expl}}^*}{V^{2/3}} \left(\frac{1}{MRT} \right)^{-1/2} \quad (9)$$

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:

$$\log \left(\frac{\eta_{\text{expl}}^*}{R_\eta} \right) = \sum_{i=0}^7 a_i \left(\frac{V_0}{V} \right)^i \quad (10)$$

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. (9), R_η is the roughness factor, which includes the effects caused by the nonsphericity of the molecules as [8]:

$$R_\eta = 0.995 - 8.944 \times 10^{-4}C + 5.427 \times 10^{-3}C^2 \quad (11)$$

where C is the number of carbon atoms in the molecule. From Eq. (11) R_η is 2.046 for *n*-tetradecane [8] whereas for benzene a value of R_η equal to 0.960 is reported by Assael et al. [21]. For *n*-alkanes (*n*-pentane to *n*-hexadecane), the characteristic volume V_0 are calculated from the correlation [7,22]:

$$10^6 V_0 = 117.874 + 0.15(-1)^C - 0.25275T + 5.48 \times 10^{-4}T^2 - 4.246 \times 10^{-7}T^3 + (C - 6)(1.27 - 9 \times 10^{-4}T)(13.27 + 0.025C) \quad (12)$$

As for the case of aromatic compounds such as benzene, toluene, xylenes, ethyl benzene, and mesitylene, these values can be calculated from the correlation [21]:

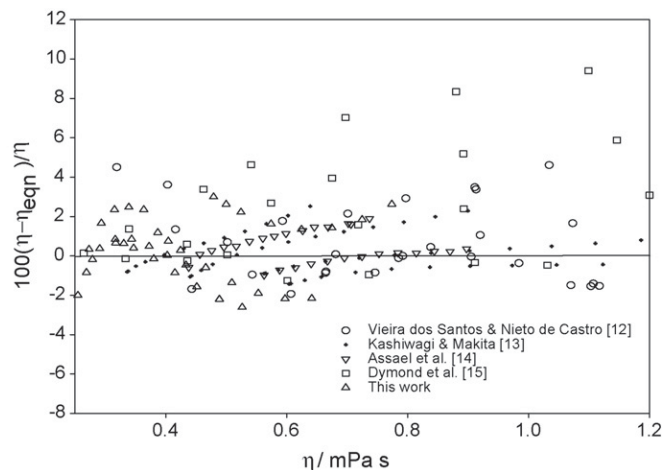


Fig. 6. Relative deviation of measured benzene viscosities from the correlation of Assael et al. [8].

$$10^6 V_0 = -3324.7C^{-2} + 529.47C^{-1} + (9.48786C^{-2} - 8.55176 \times 10^{-2}C + 6.03463 \times 10^{-3}C^2)T + (-1.5797 \times 10^{-3} + 3.9901 \times 10^{-4}C - 2.2309 \times 10^{-5}C^2)T^2 \quad (13)$$

For benzene, Fig. 6 shows that our experimental results agree with the values predicted by the Assael et al. correlation within 3% with an average absolute deviation (AAD) of 1.5% and maximum deviation (DM) of 5.4% based on 40 experimental points. Our results agree reasonably well with values given by Vieira dos Santos and Nieto de Castro [17], Kashiwagi and Makita [9], and Assael et al. [18], but for viscosities greater than 0.7 mPa s the discrepancies between our viscosity values and those of Dymond et al. [19] are as high as 7%.

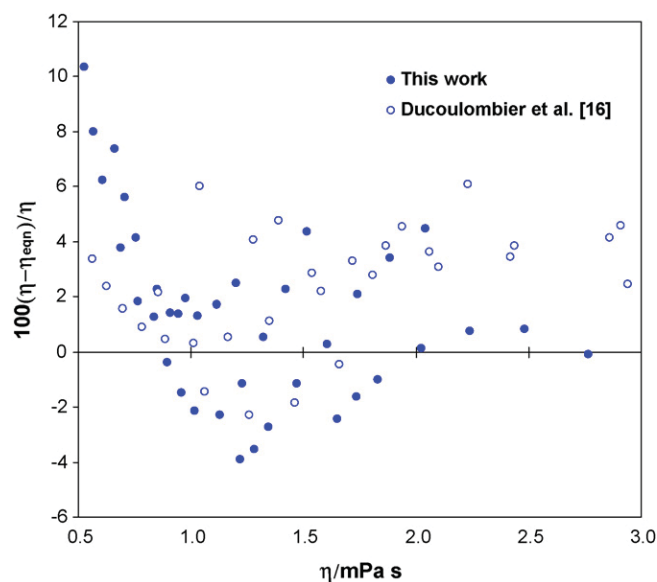


Fig. 7. Relative deviation of measured *n*-tetradecane viscosities from the correlation of Assael et al. [8].

Fig. 7 shows the relative deviation between our measured *n*-tetradecane viscosities and those viscosities obtained from Eq. (9). An examination of this figure indicates that the predictive capability of the Assael et al. correlation is within 8% with an AAD of 2.7% and DM of 10.4% based on 40 experimental points. In this case, the correlation underestimates most of the experimental data at low viscosities. This figure also shows that our results agree satisfactorily with the values given by Ducoulombier et al. [20].

4. Modeling

As mentioned above, the correlation proposed by Assael et al. [8] can either underpredicts or overpredicts the behavior of pure components and their mixtures over wide ranges of temperature and pressure. In a study based upon the viscosity of five liquid hydrocarbons at pressures up to 250 MPa, Oliveira and Wakeham [23] reported that the accuracy of Assael et al.'s correlation is estimated to be no better than $\pm 5\%$. In an attempt to obtain accurate modeling of pure fluids and mixtures from low to elevated pressures, Quiñones-Cisneros et al. [24,25] proposed a new model named as friction-theory (*f-theory*) model, which is based on friction concepts of classical mechanics and the van der Waals theory of fluids. This *f-theory* model was applied to the prediction of pure *n*-alkanes and binary to quaternary *n*-alkane mixtures. A theory based on the free-volume concept to model the viscosity of Newtonian fluids in the gaseous and dense states was subsequently proposed by Allal et al. [26–28]. This model was tested on several binary and ternary systems [29,30]. Alternatively, Macías-Salinas et al. [31] extended a one-fluid viscosity model for saturated liquids [32] to the representation of experimental liquid viscosities of binary and ternary *n*-alkane mixtures within a wide range of temperature, pressure, and composition. Later, Macías-Salinas et al. [33] developed an Eyring-theory-based model coupled with a cubic equation of state to properly correlate and/or predict liquid viscosity of highly non-ideal binary solutions over a wide range of temperature, pressure, and composition. Following the ideas of Macías-Salinas et al. [33], we propose an Eyring-theory-based model coupled with a cubic equation of state to represent the measured liquid viscosities of the benzene + *n*-tetradecane system. A feature of the model is that it uses a single temperature-independent binary interaction parameter to describe the whole $\eta - T - p - x$ surface of interest.

The model is based on the following Eyring's viscosity expression for liquid mixtures:

$$\eta = \frac{(\eta V)^{\text{id}}}{V_m} \exp\left(\frac{G^{\neq, \text{EX}}}{RT}\right) \quad (14)$$

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

$$(\eta V)^{\text{id}} = \exp\left[\sum_{i=1}^N x_i \ln(\eta_i^0 V_i^0)\right] \quad (15)$$

The excess activation free energy of flow $G^{\neq, \text{EX}}$ in Eq. (14) depends on temperature, pressure, and composition, which can be expressed as:

$$\frac{G^{\neq, \text{EX}}}{RT} = \frac{G^{\text{EX}}}{RT} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N x_i x_j g_{ij} \quad g_{ii} = 0, \quad g_{ij} = g_{ji} \quad (16)$$

which for a binary mixture yields:

$$\frac{G^{\neq, \text{EX}}}{RT} = \frac{G^{\text{EX}}}{RT} + x_1 x_2 g_{12} \quad (17)$$

where g_{12} is an interaction parameter characterizing the binary mixture formed by components 1 and 2. Its value can be optimized from binary viscosity data by matching the experimental viscosity data with those predicted from Eq. (14).

The value of G^{EX} in Eq. (17) can be directly calculated from an equation of state as follows:

$$\frac{G^{\text{EX}}}{RT} = \frac{G^{\text{EX}, \text{EoS}}}{RT} = \sum_{i=1}^N x_i (\ln \phi_i - \ln \phi_i^0) \quad (18)$$

In this case, the use of an equation of state is advantageous since it allows the simultaneous determination of the fugacity coefficient of component i in the mixture $\phi_i(T, p, \mathbf{x})$, the molar volume of the liquid mixture $V_m(T, p, \mathbf{x})$, 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 PR equation of state [34], which can be written as:

$$p = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \quad (19)$$

where constants a and b for pure-components are related to:

$$a = 0.45724 \frac{RT_c}{p_c} \alpha(T_r) \quad (20)$$

$$b = 0.07780 \frac{RT_c}{p_c} \quad (21)$$

and $\alpha(T_r)$ is expressed in terms of the acentric factor ω as:

$$\alpha(T_r) = \left[1 + (0.37464 + 1.5422\omega - 0.26992\omega^2)(1 - T_r^{1/2}) \right]^2 \quad (22)$$

For mixtures, constants a and b are given by:

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (23)$$

$$b = \sum_{i=1}^N x_i b_i \quad (24)$$

and a_{ij} is defined as:

$$a_{ij} = \sqrt{a_i a_j} \quad (25)$$

Eq. (19) can be written in terms of the compressibility factor Z , as:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (26)$$

where $A = ap/(RT)^2$ and $B = bp/(RT)$.

The expression for the fugacity coefficient of component i is given by:

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left(\frac{2\sum_{j=1}^N x_j a_{ij}}{a} - \frac{b_i}{b} \right) \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (27)$$

The final form of the viscosity model is thus obtained by combining Eqs. (14)–(16) and Eq. (18).

$$\eta = \frac{(\eta V)^{\text{id}}}{V_m} \exp \left[\sum_{i=1}^N x_i (\ln \phi_i - \ln \phi_i^0) + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N x_i x_j g_{ij} \right] \quad (28)$$

$$g_{ii} = 0, \quad g_{ij} = g_{ji}$$

The calculation of the kinematic viscosity of an ideal solution $(\eta V)^{\text{id}}$, Eq. (15), requires the values of the viscosities of the pure components η_i^0 at the temperature and pressure of interest. For pure benzene and n -tetradecane, the experimental viscosities are given in Table 1.

Eq. (28) was applied to the modeling of the experimental liquid viscosity data given in Table 2 for the system benzene + n -tetradecane. In order to obtain the mixture interaction parameter g_{12} a non-linear regression analysis was performed by searching the minimum of the following objective function.

$$f = \sum_{i=1}^{N_p} \left(\frac{\eta_i^{\text{expl}} - \eta_i^{\text{calc}}}{\eta_i^{\text{expl}}} \right)^2 \quad (29)$$

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 correlating result obtained for this mixture gave an optimized interaction parameter $g_{12} = 0.8794$. The overall performance of the model yielded an average absolute deviation:

$$\text{AAD}(\%) = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{\eta_i^{\text{expl}} - \eta_i^{\text{calc}}}{\eta_i^{\text{expl}}} \right| \quad (30)$$

of 2.0% with a maximum deviation.

$$\text{DM}(\%) = \text{Max} \left(100 \times \left| \frac{\eta_i^{\text{expl}} - \eta_i^{\text{calc}}}{\eta_i^{\text{expl}}} \right| \right) \quad (31)$$

of 7.1% based on 160 experimental points over the temperature range from 313.2 to 393.2 K and pressures up to 60 MPa. The AAD value falls within the experimental uncertainty reported

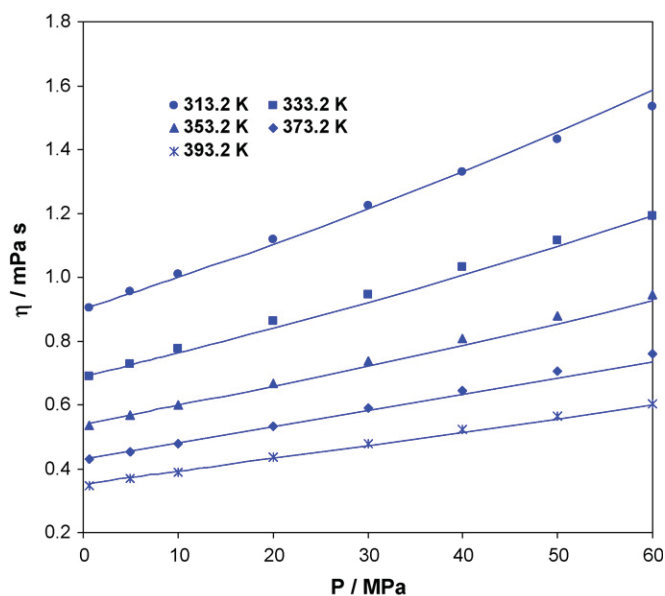


Fig. 8. Experimental and calculated viscosities as a function of pressure for benzene + n -tetradecane at the composition of 0.602 benzene mole fraction. Solid lines: proposed model with $g_{12} = 0.8794$ fitted to the mixture viscosity data of this work.

in this work. Calculations were also carried out using $g_{12} = 0$. In this case, the average absolute deviation and maximum deviation were 14.5% and 26.5%, respectively. These results show the strong effect of the interaction parameter g_{12} on the representation of the viscosity data for this system. To illustrate the goodness of the regression, we have plotted in Fig. 8 the calculated and experimental values of the mixture viscosity for a composition of 0.602 benzene mole fraction. In this figure, the symbols are the experimental pressure and temperature data while the solid lines are those calculated with the model. This figure shows that the present approach provides a good fit to experimental results for most cases. Similar plots were prepared for the other three compositions reported in Table 2 yielding similar results.

In order to compare the results obtained using Eq. (28) with others viscosity models, we have used the Grunberg–Nissan [35] and Katti–Chaudhri [36] one-parameter equations to represent the viscosity data of the benzene + n -tetradecane system over the whole temperature range under study.

For a binary mixture, the Grunberg–Nissan (GN) equation is expressed as:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 g_{12}^{\text{GN}} \quad (32)$$

while the Katti–Chaudhri (KC) equation is given by:

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2 g_{12}^{\text{KC}} \quad (33)$$

The interaction parameters obtained from the correlation of the viscosity data were $g_{12}^{\text{GN}} = 0.509$ and $g_{12}^{\text{KC}} = 1.035$ for the GN and KC equations, respectively. The average absolute deviation and maximum deviation obtained for these equations are the following: AAD = 2.4% and DM = 7.4% for the Grunberg–Nissan equation, and AAD = 3.5% and DM = 8.3% for the Katti–Chaudhri equation. When the interactions param-

eters g_{12}^{GN} and g_{12}^{KC} were set equal to zero, the average absolute deviation and maximum deviation obtained for these equations are the following: AAD = 9.8% and DM = 15.4% for the GN equation, and AAD = 19.0% and DM = 26.4% for the KC equation.

The Assael et al.'s correlation for mixtures [22] was also used to calculate the viscosities for this system. The resulting AAD and DM obtained using this correlation were 2.9% and 11.3%, respectively.

An examination of the values of AAD and DM obtained for the different viscosity models, shows that the model proposed in this work is superior to the Grunberg–Nissan and Katti–Chaudhri equations in correlating the viscosity data of the system benzene + *n*-tetradecane, and that the results obtained with this model are better than those obtained with the Assael et al.'s correlation.

5. Conclusions

A rolling-ball viscometer has been successfully used to experimentally determine kinematic viscosities of benzene, *n*-tetradecane, and the binary mixture of benzene + *n*-tetradecane over the temperature range from 313.2 to 393.2 K and pressures up to 60 MPa, with an estimated uncertainty of $\pm 2\%$.

The experimental viscosities results for benzene and *n*-tetradecane were compared with the correlation of Assael et al. [8]. For benzene they agree within 3% of the values predicted by this correlation with average absolute deviation of 1.5%, but for *n*-tetradecane the correlation underestimated the viscosity up to 10% with an average absolute deviation of 2.7%.

A new proposed liquid viscosity model based on the Eyring's theory coupled with a cubic equation of state and using a single temperature-independent binary interaction was used to represent the measured viscosity data of the benzene + *n*-tetradecane system. Results of the representation showed that this model is able to represent the data of this system on the whole temperature, pressure, and composition range under study with an average absolute deviation of 2.0%.

List of symbols

a	attractive parameter in the PR EoS
b	co-volume parameter in the PR EoS
f	objective function, defined in Eq. (29)
g_{ij}	binary interaction parameter in Eq. (28)
G	Gibbs energy
K	viscosity function, defined in Eq. (2)
M	molecular weight
N	number of components
N_p	number of data points
p	pressure (MPa)
R	ideal gas constant
R_η	roughness factor
t	time (s)
T	temperature (K)
V	molar volume ($\text{m}^3 \text{mol}^{-1}$)
V_0	characteristic volume ($\text{m}^3 \text{mol}^{-1}$)
w_i	weight fraction of component i

x_i	mole fraction of component i
Z	compressibility factor

Greek letters

α	alpha function in the PR EoS
φ_i	fugacity coefficient of component i
η	viscosity (mPa s)
ρ	density (g cm^{-3})
ω	acentric factor in the PR EoS

Subscripts

c	critical property
i, j	components (i, j)
mix	mixture property
0	reference state

Superscripts

calc	calculated property
EoS	equation of state
EX	excess property
expl	experimental property
id	ideal solution
0	pure substance
*	reduced property
\neq	activation state

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