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Dynamic Viscosity of the Binary System 1-Propanol + Toluene as a Function of Temperature and Pressure[†]

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The viscosity of the binary system 1-propanol + toluene has been measured with a falling-body viscometer for seven compositions as well as for the pure alcohol in the temperature range (293.15 to 353.15) K and up to 100 MPa with an experimental uncertainty of ± 2 %. At 0.1 MPa, the viscosity has been measured with a classical capillary viscometer (Ubbelohde) with an uncertainty of ± 1 %. A total of 216 experimental data points are reported. The viscosity behavior of this binary system is interpreted as the results of changes in the free volume and the breaking or weakening of hydrogen bonds. These data have been used to study the performance of two compositional models and a free-volume model.

1. Introduction

To study and understand the behavior of alcohol + (hydrocarbon or petroleum) systems under various operating conditions, their thermophysical properties are needed. Since these fluids may be multicomponent mixtures involving paraffinic, naphthenic, and aromatic compounds as well as alcohols, it is impossible to experimentally determine all their properties at all temperature, pressure, and composition (T,p,x) conditions. As a consequence, different property models are required to describe the behavior of these fluids. However, experimental property studies of simplified mixtures can provide valuable information about their behavior under various T,p,x conditions from both a fundamental and an applied point of view.

In this work, the focus is on mixtures involving 1-propanol and toluene. Although the viscosity is an important fluid property, which is required in a wide range of engineering disciplines, only a few experimental studies have previously been performed for alcohol + hydrocarbon systems under pressure.[1,2] Due to the lack of high-pressure viscosity measurements, an extensive experimental study has been initiated on binary systems composed of alcohol and C_7 hydrocarbons to provide experimental data and to study the influence on the viscosity behavior related to different chemical families. Recently, the viscosity has been measured for ethanol + toluene[3] and for ethanol + heptane.[4] In this work, the viscosity is measured for 1-propanol + toluene over the entire composition range, up to 100 MPa, and in the temperature range (293.15 to 353.15) K using a falling-body viscometer. These data are used in a study of the performance of two viscosity models to predict the viscosity of mixtures based on pure compound properties: two mixing laws[5,6] and a recently developed model based on the concept of the free volume.[7,8]

2. Experimental Techniques

The dynamic viscosity η was measured under pressure using a falling-body viscometer of the type designed by Daugé et al.[9] to measure the liquid and dense phase viscosity of fluids with a low viscosity. The pressure within the viscometer was measured by a HBM-P3M pressure transducer (HBM brand) with an uncertainty of 0.2 MPa. The temperature was measured inside the viscometer by a Pt100 probe connected to a classical AOIP thermometer with an uncertainty of 0.5 K. The temperature of the sample in the viscometer was controlled by a circulating fluid. Further, the viscometer was placed in an automated air-pulsed thermal regulator box to ensure a homogeneous temperature surrounding the viscometer. For fluids, which are in the liquid state at atmospheric pressure, the filling procedure of the viscometer is described in Zéberg-Mikkelsen et al.[3]

The basic principle of the falling-body viscometer is that a sinker falls through a fluid of unknown viscosity under a given T,P condition. It has been underlined by Daugé et al.[9] that for this type of viscometer and for fluids with a low viscosity a working equation of the functional form $\eta(T,P) = f[(\rho_S - \rho_L)\Delta\tau]$ should be used. This working equation relates the dynamic viscosity to the difference between the densities of the sinker ρ_S and of the fluid ρ_L and the falling time between two detection sensors $\Delta\tau$, when the velocity of the sinker is constant. For fluids with a very low viscosity (lower than 0.3 mPa·s) such as methane, Daugé et al.[9] used a second-order polynomial in $(\rho_S - \rho_L)\Delta\tau$, which implies the requirement of three reference fluids to perform the calibration of the viscometer. Since the viscosity in this work is higher than 0.3 mPa·s, it was found suitable to use a linear relation for the working equation as follows

$$\eta(T,P) = K_a(T,P) + K_b(T,P)(\rho_S - \rho_L)\Delta\tau \qquad (1)$$

which relates the dynamic viscosity to two apparatus constants K_a and K_b. A similar working equation has recently been used.[3,10] The calibration of the viscometer was performed with toluene[11] and phenyldodecane[12] at each T,p condition of interest. It can be mentioned here the toluene has been proposed as reference liquid after water,[13,14] and one of the first experimental viscosity data for toluene, at high pressure, was performed by Assael et al.[15] using the precise vibrating wire technique developed by Wakeham and co-workers.[16,17] For our experimental technique, a detailed description of the calibration procedure and the used reference viscosities and densities of

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the calibrating fluids is given in Zéberg-Mikkelsen et al.[3] Since the density of the used stainless steel sinker ($\rho_S = 8700\ \mathrm{kg \cdot m^{-3}}$) is about 10 times higher than the density of the fluids considered in this work, an error in the fluid density of 0.1 % results in an error of around 1/8000 in the dynamic viscosity. Further, in this work, $\Delta\tau$ corresponds to the average value of six measurements of the falling time at thermal and mechanical equilibrium with a reproducibility of 0.5 %. The overall uncertainty for the reported dynamic viscosities is of the order of ± 2 %, found at the highest pressure, when taking into account the uncertainty due to the calibration, the temperature, the pressure, and the density. The accuracy of the device has been checked several times. For instance, recently,[3] the same instrument has been used to measure the dynamic viscosity of methanol between (293.15 and 353.15) K up to 100 MPa. These data have been further used in a study about a new reference correlation[19] for the viscosity of methanol, taking into account many methanol literature data. It is mentioned in this last paper that our data agree with the correlation with an average absolute deviation of 1.0 %, which is very satisfactory.

In this work, the densities of 1-propanol, toluene, and their binary mixtures were taken from Xiang et al.,[18] where they have been measured up to 65 MPa and in the temperature range (293.15 to 353.15) K for the same compositions considered in this work. The uncertainty reported for these density measurements is $0.5\ \mathrm{kg \cdot m^{-3}}$. For pressures above 65 MPa, the required densities were obtained by an extrapolation of the experimental densities using the Tait type relation described in Assael et al.[11]

At atmospheric pressure (0.1 MPa), the dynamic viscosity was obtained by measuring the kinematic viscosity with a classical capillary viscometer (Ubbelohde). For this purpose, several tubes connected to an automatic AVS350 Schott Geräte Analyzer were used. The temperature of the fluid was controlled within 0.1 K using a thermostatic bath. When multiplying the kinematic viscosity with the density, the dynamic viscosity was obtained with an uncertainty of less than ± 1 %. The tubes are provided with a well-known constant which is regularly checked using certified Cannon oils.

The compounds used in this study are commercially available chemicals with the following purities: 1-propanol (CAS 71-23-8) from Sigma-Aldrich with a chemical purity > 99.9 % (Gas Chromatography) and a molar mass $M_w = 60.1\ \mathrm{g \cdot mol^{-1}}$; toluene (CAS 108-88-3) from Sigma-Aldrich with a chemical purity > 9.9 % and $M_w = 92.14\ \mathrm{g \cdot mol^{-1}}$. The pure compounds were used as received and stored in hermetically sealed bottles. The binary 1-propanol (1) + toluene (2) mixtures were prepared immediately before use by weighing at atmospheric pressure and ambient temperature using a high-precision Sartorius balance with an uncertainty of 0.001 g. For each mixture, a sample of 250 g was prepared, which, taking into account the uncertainty of the balance, resulted in an uncertainty in the mole fraction of less than $2 \cdot 10^{-5}$.

3. Results

The measured dynamic viscosities of 1-propanol and the seven binary mixtures in the temperature range (293.15 to 353.15) K at each 20 K and for pressures up to 100 MPa in steps of 20 MPa are given in Table 1 as a function of temperature T, pressure p, and mole fraction of 1-propanol x_1 ($x_1 = 0.125, 0.25, 0.5, 0.625, 0.75, 0.875$).

The measured 1-propanol viscosities have been compared with literature values,[20-24] which are available up to 100 MPa in the temperature range (293.15 to 353.15) K. Some interpolation procedures have been performed to obtain values corresponding to the pressures considered either in this experimental work or in the literature. Figure 1 shows the deviations of the 1-propanol viscosities measured in this work from the literature values. Within the experimental uncertainty, this figure shows a very good agreement between the 1-propanol viscosities of this work and those reported in the literature.

For all the mixtures, the viscosity increases with increasing pressure and decreasing temperature. Within the considered T,p range, 1-propanol is more viscous than toluene. In Figures 2 and 3, the variation of the viscosity versus concentration is shown for various isobars at (293.15 and 333.15) K, respectively. Table 1 seems to show the presence of a minimum compositional dependency of the viscosity located at high pressure and low content of 1-propanol. This can be explained as the result of the occurrence of a volume expansion, when the two pure compounds are mixed, due to disruption of the ordered molecular structure within the liquid and a weakening or breaking of the formed hydrogen bonds between 1-propanol molecules. In Watson et al.,[19] based on the behavior of the experimental density data and the discussion with respect to the excess molar volume, isothermal compressibility, and isobaric thermal expansivity, it has been found that a volume expansion occurs for this binary system. This minimum compositional dependency of the viscosity can also be seen on Figures 4, 5, and 6. These figures display the variation of the viscosity as a function of composition of the binary system for the four temperatures for 0.1 MPa in Figure 4, 40 MPa in Figure 5, and 100 MPa in Figure 6.

4. Models

To study of the performance of different viscosity models to predict the viscosity of the binary system 1-propanol + toluene, the following definitions are used

$$\begin{aligned} \Delta_i &= 1 - \eta_{\mathrm{calc},i}/\eta_{\mathrm{exp},i} \\ \mathrm{AAD} &= \frac{1}{\mathrm{NP}} \sum_{i=1}^{\mathrm{NP}} |\Delta_i| \\ \mathrm{Bias} &= \frac{1}{\mathrm{NP}} \sum_{i=1}^{\mathrm{NP}} \Delta_i \\ \Delta_{\max} &= \mathrm{Maximum}|\Delta_i| \end{aligned} \tag{2}$$

where NP is the number of data points; $\eta_{\exp}$ is the experimental viscosity; and η_{calc} is the calculated viscosity. The AAD (average absolute deviation) indicates how close the calculated values are to the experimental values, while the quantity Bias is an indication of how well the calculated values are distributed around the experimental values. The quantity $\Delta_{\max}$ refers to the maximum absolute deviation.

Further, since the dilute gas viscosity part in the free volume model considered requires pure component properties, such as the molar mass or critical properties, these properties have been taken from Zhang et al.[25]

4.1. Compositional Models. Several compositional models have been developed to calculate the viscosity of liquid mixtures. The objective of these compositional models is to predict the viscosity of liquid mixtures using only the viscosity and molar volume of the pure compounds along with the composition. Two of the most well-known compositional models for binary systems are

$$\ln(\eta_{\mathrm{mix}}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) \tag{3}$$

which is generally referred as the "ideal" Grunberg and Nissan[5] compositional model, and the one of Katti and Chaudhri[6]

$$\ln(\eta_{\text{mix}} v_{\text{mix}}) = x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2) \tag{4}$$

where v_i is the molar volume of system i.

These two compositional viscosity models are totally predictive in the sense that only pure component properties are required. They are primarily applicable to solutions having weak intermolecular interactions.[5,6] In this work, subscript 1 refers to 1-propanol, whereas subscript 2 refers to toluene.

To calculate the viscosity of the different binary mixtures with eqs 3 and 4, the reported viscosities for the pure compounds in this work (Table 1) and in Assael et al.[11] were used. Further,

Table 1. Density ρ (from Watson et al.[19] up to 60 MPa, Data in Italic Are Extrapolated Values) and Dynamic Viscosities η for 1-Propanol (1) + Toluene (2) Mixtures versus Temperature T, Pressure p, and Mole Fraction x_1[a]

	293.15 K		313.15 K		333.15 K		353.15 K	
p/MPa	ρ/kg·m^{-3}	η/mPa·s	ρ/kg·m^{-3}	η/mPa·s	ρ/kg·m^{-3}	η/mPa·s	ρ/kg·m^{-3}	η/mPa·s
				$x_1 = 0$				
0.1	867.1	0.590	847.8	0.469	828.8	0.380	809.7	0.318
20	881.1	0.687	863.5	0.546	846.6	0.446	829.9	0.372
40	893.3	0.791	877.0	0.628	861.4	0.513	846.1	0.428
60	904.2	0.903	889.0	0.715	874.5	0.584	860.1	0.487
80	*914.2*	1.024	*899.6*	0.807	*886.0*	0.657	*872.3*	0.548
100	*923.3*	1.156	*909.2*	0.906	*896.3*	0.735	*883.3*	0.612
				$x_1 = 0.125$				
0.1	860.6	0.611	841.3	0.479	822	0.388	802.7	0.322
20	874.5	0.698	857.3	0.548	839.8	0.443	822.9	0.367
40	886.9	0.799	870.8	0.625	854.8	0.512	839.4	0.421
60	897.9	0.905	882.7	0.704	867.8	0.581	853.6	0.477
80	*907.7*	1.018	*893.3*	0.788	*879.3*	0.650	*872.3*	0.535
100	*916.8*	1.137	*902.9*	0.877	*889.7*	0.719	*883.3*	0.597
				$x_1 = 0.25$				
0.1	854.5	0.636	835.1	0.495	815.6	0.396	795.9	0.325
20	868.5	0.742	851.1	0.580	833.6	0.457	816.3	0.371
40	880.9	0.849	864.7	0.664	848.6	0.530	833	0.430
60	891.8	0.964	876.6	0.750	861.4	0.601	847.2	0.489
80	*901.7*	1.091	*887.4*	0.840	*872.8*	0.671	*859.5*	0.550
100	*910.7*	1.231	*897.2*	0.933	*883.0*	0.739	*870.5*	0.612
				$x_1 = 0.375$				
0.1	848.1	0.747	829	0.554	809.5	0.431	789.9	0.346
20	861.9	0.834	844.9	0.627	827.4	0.490	810.2	0.391
40	874.2	0.959	858.4	0.720	842.4	0.568	826.8	0.451
60	885.2	1.100	870.4	0.820	855.3	0.647	840.9	0.513
80	*895.1*	1.264	*880.9*	0.924	*866.7*	0.727	*853.3*	0.576
100	*904.2*	1.456	*890.5*	1.034	*877.0*	0.807	*864.3*	0.640
				$x_1 = 0.5$				
0.1	841.2	0.875	822.4	0.625	803.2	0.472	783.8	0.369
20	855.1	1.010	838.4	0.707	821.1	0.537	804.2	0.415
40	867.4	1.159	851.9	0.827	836	0.620	820.8	0.479
60	878.3	1.312	863.7	0.950	848.9	0.704	835	0.547
80	*888.1*	1.483	*874.3*	1.072	*860.2*	0.789	*847.3*	0.621
100	*897.1*	1.677	*883.8*	1.191	*870.4*	0.876	*858.3*	0.702
				$x_1 = 0.625$				
0.1	833.5	1.055	815.2	0.728	796.3	0.532	777	0.404
20	847.4	1.217	831.2	0.838	814.2	0.606	797.3	0.455
40	859.7	1.391	844.6	0.973	829.1	0.706	813.7	0.529
60	870.6	1.575	856.3	1.107	841.8	0.804	827.7	0.606
80	*880.5*	1.787	*866.8*	1.234	*853.2*	0.901	*839.8*	0.689
100	*889.6*	2.036	*876.2*	1.349	*863.3*	0.997	*850.6*	0.779
				$x_1 = 0.75$				
0.1	825.1	1.312	807.3	0.876	788.7	0.617	769	0.454
20	839.2	1.524	823	1.023	806.6	0.717	789.1	0.520
40	851.3	1.708	836.4	1.185	821.2	0.837	805.4	0.603
60	862.1	1.908	848.2	1.347	834	0.955	818.9	0.689
80	*871.8*	2.152	*858.6*	1.496	*845.1*	1.070	*831.1*	0.779
100	*880.6*	2.452	*868.1*	1.626	*855.1*	1.183	*841.7*	0.877
				$x_1 = 0.875$				
0.1	815.3	1.685	797.9	1.087	779.8	0.740	760.6	0.526
20	829.4	1.922	813.6	1.242	797.5	0.859	780.7	0.607
40	841.7	2.169	826.9	1.452	812	0.999	796.6	0.701
60	852.3	2.445	838.7	1.664	824.8	1.137	810.3	0.798
80	*862.0*	2.790	*849.2*	1.860	*836.0*	1.274	*822.0*	0.906
100	*870.8*	3.229	*858.6*	2.029	*846.1*	1.407	*832.5*	1.027
				$x_1 = 1$				
0.1	803.5	2.204	787.6	1.383	770.5	0.913	752.2	0.630
20	817.7	2.545	803.3	1.603	788.4	1.086	772.1	0.734
40	829.9	2.855	816.6	1.871	802.6	1.263	787.7	0.845
60	840.7	3.191	828.3	2.146	815.2	1.439	801.7	0.962
80	*850.3*	3.613	*838.9*	2.401	*836.0*	1.614	*813.5*	1.092
100	*859.1*	4.149	*848.4*	2.618	*846.1*	1.786	*824.1*	1.242

[a] Values from toluene are taken from Assael et al.[11] and Watson et al.[19]

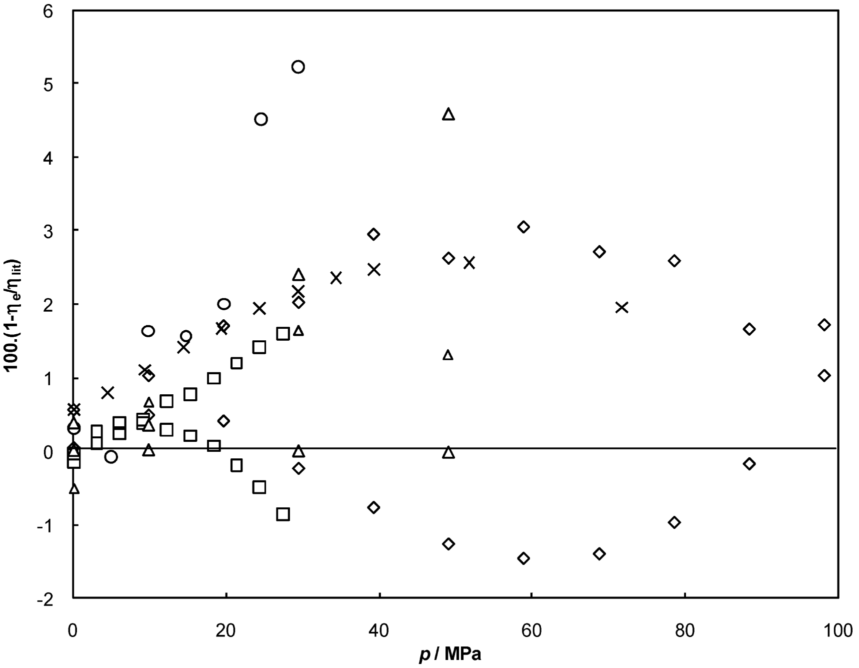

Figure 1. Comparison of dynamic viscosities for 1-propanol versus the temperature up to 100 MPa, shown as the deviation, $(1 - \eta_e/\eta_{lit})$, between the experimental values, η_e, and literature values, η_{lit}: ◇, ref 20; Δ, ref 21; □, ref 22; ×, ref 23; ○, ref 24.

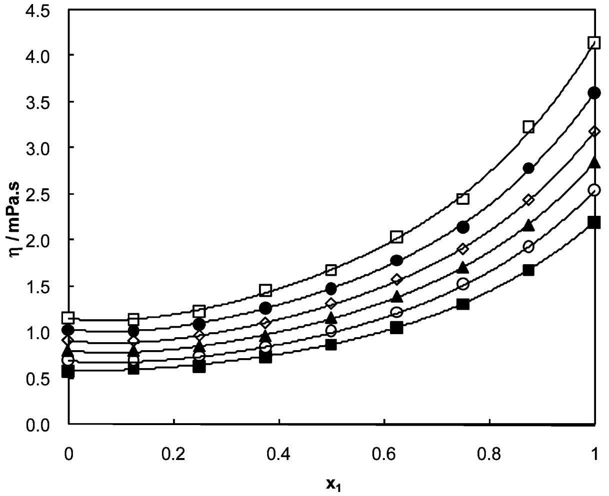

Figure 2. Dynamic viscosity η for 1-propanol (1) + toluene (2) versus the mole fraction x_1 at $T = 293.15$ K for: ■, $p = 0.1$ MPa; ○, $p = 20$ MPa; ▲, 40 $p =$ MPa; ◇, 60 $p =$ MPa; ●, 80 $p =$ MPa; and □, $p = 100$ MPa.

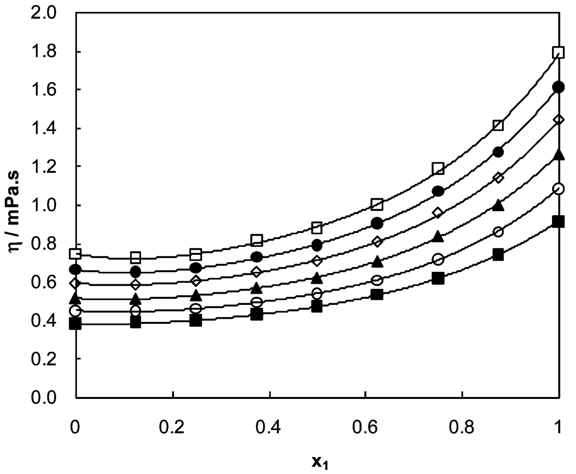

Figure 3. Dynamic viscosity η for 1-propanol (1) + toluene (2) versus the mole fraction x_1 at $T = 333.15$ K for: ■, 0.1 $p =$ MPa; ○, $p = 20$ MPa; ▲, $p = 40$ MPa; ◇, $p = 60$ MPa; ●, $p = 80$ MPa; and □, $p = 100$ MPa.

the required molar volumes of the pure compounds and the binary mixtures were estimated from the experimental and extrapolated densities.[19] The resulting deviations between the predicted viscosities and the experimental values give, for the Grunberg−Nissan model, an AAD = 21.66 %, a Bias = −21.66 %, and a Δ_{max} = 34.67 % found at 293.15 K, 20 MPa, and 37.5 mol % 1-propanol and, for the Katti−Chaudhri model, an AAD = 21.90 %, a Bias = −21.90 %, and a Δ_{max} = 35.07 % found at 293.15 K, 20 MPa, and 37.5 mol % 1-propanol. Overall, the prediction of the viscosity of the two binary systems can be considered not so satisfactory even for such an apparently simple system. Including the molar volume of the mixtures in the Katti−Chaudhri compositional model, additional information about the mixtures is incorporated, but for the two binary systems, the performance of the Katti−Chaudri compositional model is not improved at all. In the Grunberg−Nissan compositional model, the variation of the viscosity versus composition is monotonous since no interactions between the components are taken into account. These interactions do appear for the studied mixture, as the variation of the viscosity versus composition for this system is not monotonous. This fact can be an explanation of the poor representation of the viscosity data of the mixtures for both models.

To account for the intermolecular interactions within binary systems, Grunberg and Nissan[5] introduced the following modification of their compositional model

$$\ln(\eta_{mix}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + x_1 x_2 d_{1,2} \tag{5}$$

whereas Katti and Chaudhri[6] derived the following compositional model

$$\ln(\eta_{mix} v_{mix}) = x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2) + \frac{x_1 x_2 W_{1,2}}{RT} \tag{6}$$

In these equations, the binary parameters $d_{1,2}$ and $W_{1,2}$ are adjustable quantities supposed to be characteristic of the

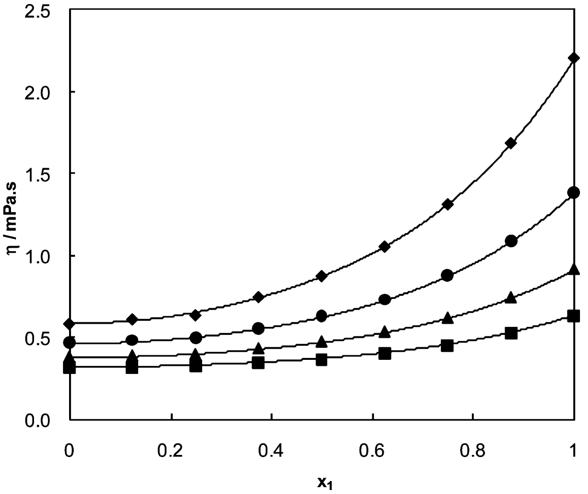

Figure 4. Dynamic viscosity η for 1-propanol (1) + toluene (2) versus the mole fraction x_1 at $p = 0.1$ MPa K for: ■, $T = 293.15$ K; ▲, $T = 313.15$ K; ●, $T = 333.15$ K; ◆, $T = 353.15$ K.

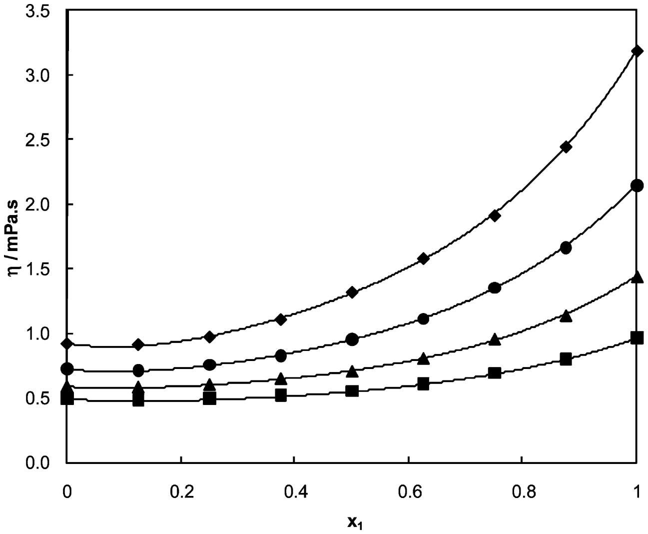

Figure 5. Dynamic viscosity η for 1-propanol (1) + toluene (2) versus the mole fraction x_1 at $p = 60$ MPa K for: ■, $T = 293.15$ K; ▲, $T = 313.15$ K; ●, $T = 333.15$ K; ◆, $T = 353.15$ K.

intermolecular interactions between the two components. The modeling of the viscosity gives $d_{1,2} = -1.039378$, resulting in an AAD = 1.93 %, a Bias = 0.01 %, and a $\Delta_{\max} = 6.85$ % found at 353.15 K, 0.1 MPa, and 37.5 mol % 1-propanol, and $W_{1,2} = -5539.618$ J·mol^{-1}, resulting in an AAD = 1.54 %, a Bias = −0.24 %, and a $\Delta_{\max} = 5.41$ % found at 293.15 K, 100 MPa, and 12.5 mol % 1-propanol. These results show that the Grunberg−Nissan and the Katti−Chaudhri compositional models can model the viscosity of this asymmetrical binary systems within or close to the experimental uncertainty of ± 2 %, when only one adjustable parameter is introduced. Further, it can be seen that the two binary interaction parameters are negative, corresponding to a departure from the "ideal" compositional models with lower viscosity data. But in such a case, these two models are not predictive any longer because they need one adjustable parameter.

4.2. Free-Volume Model. On the basis of the free-volume concept, an approach has been proposed to model the viscosity of Newtonian fluids in the gaseous and dense states.[7,8] In this approach, the total viscosity η can be separated into a dilute gas viscosity term η_0 and an additional term $\Delta\eta$, in the following way

$$\eta = \eta_0 + \Delta\eta \tag{7}$$

The term $\Delta\eta$ characterizes the passage in the dense state and is connected to the molecular structure via a representation of the free-volume fraction in the following way

$$\Delta\eta = \frac{\rho N_a \zeta L^2}{M_w} \tag{8}$$

where N_a is Avogadro's constant; ζ is the friction coefficient of a molecule; and L^2 is an average characteristic molecular quadratic length. The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process. Moreover, the free volume fraction $f_v = (v_f/v)$ (with $v_f = v - v_0$, v the specific molecular volume, and v_0 the molecular volume of reference or hard core volume) is defined for a given temperature T as

$$f_v = \left(\frac{RT}{E}\right)^{3/2} \tag{9}$$

by assuming that the molecule is in a state in which the molecular potential energy of interaction with its neighbors is E/N_a. Further, it has been assumed[7,8] that $E = E_0 + pM_w/\rho$, where the term $pM_w/\rho = pv$ is related to the energy necessary to form the vacant vacuums available for the diffusion of the molecules, and where $E_0 = \alpha\rho$ is the energy barrier, which the molecule has to exceed to diffuse.

On the basis of the empirical free-volume relation by Doolittle,[27] the following expression for the friction coefficient has been proposed[7,8]

$$\zeta = \zeta_0 \exp\left[\frac{B}{f_v}\right] \tag{10}$$

where B is characteristic of the free volume overlap. The quantity ζ_0 has been defined[7,8] as

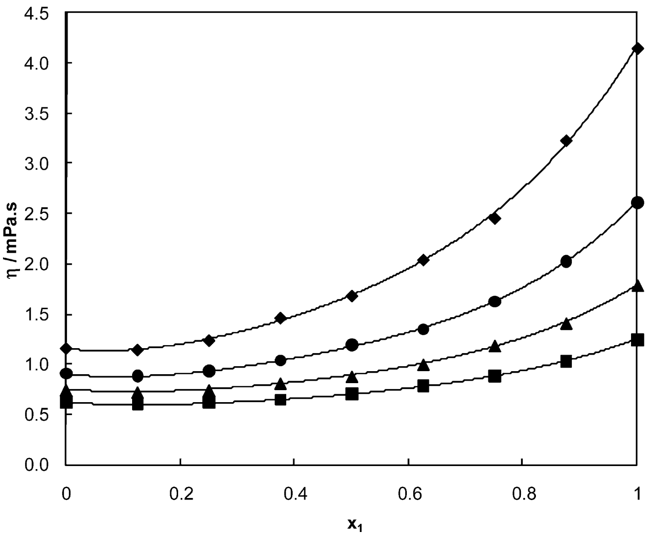

Figure 6. Dynamic viscosity η for 1-propanol (1) + toluene (2) versus the mole fraction x_1 at $P = 100$ MPa K for: ■, $T = 293.15$ K; ▲, $T = 313.15$ K; ●, $T = 333.15$ K; ◆, $T = 353.15$ K.

Table 2. Characteristic Parameters for Pure Compounds Used in the Free-Volume Model

	α/J·m^3·mol^{-1}·kg^{-1}	B	l/nm
1-propanol	189.1536	0.00638131	0.0151666
toluene[28]	75.6836	0.00925373	0.0727323

$$\zeta_0 = \frac{E}{N_a b_f}\sqrt{\frac{M_w}{3RT}} \tag{11}$$

where b_f is the dissipation length of the energy E.

The general expression for the free-volume viscosity model is obtained by combining eqs 7 through 11 and is given as

$$\eta = \eta_0 + l\left(\frac{\alpha\rho^2 + pM_w}{\sqrt{3RTM_w}}\right)\exp\left[B\left(\frac{\alpha\rho^2 + pM_w}{RT\rho}\right)^{3/2}\right] \tag{12}$$

or

$$\eta = \eta_0 + \rho l\sqrt{\frac{RT}{3M_w}}f_v^{-2/3}\exp\left[\frac{B}{f_v}\right] \tag{13}$$

where $l = L^2/b_f$ is homogeneous with a characteristic molecular length. This equation involves three physical parameters, either l, α, and B or l, f_v, and B, which are characteristic of the molecule. This model has been shown to accurately represent the viscosity behavior of various hydrocarbons over wide ranges of temperature and pressure in the gaseous, liquid, and dense states.

The dilute gas viscosity η_0 can be obtained from any appropriate model. In this work, the model by Chung et al.[26] was used since it is capable of predicting the dilute gas viscosity of several polar and nonpolar fluids within an uncertainty of 1.5 %.

By using the experimental viscosity (Table 1) and the density values reported in Watson et al.[19] and the extrapolated values, the three characteristic parameters in eq 12 were determined for 1-propanol, whereas they have already been determined for toluene.[28] The fitted parameters as well as those for toluene[28] are given in Table 2. The adjustment of the three parameters against 1-propanol data (24 points) gives an AAD of 3.17 %, a Δ_{max} of 7.37 %, and a Bias of 0.28 %. Recall here that for toluene[4,28] AAD = 0.67 %, Δ_{max} = 1.70 %, and Bias = 0.05 %.

To apply the free-volume model to mixtures, eq 13 was used with the following simple compositional models

$$B_{mix} = \sum_{i=1}^{n} x_i B_i; \quad l_{mix} = \sum_{i=1}^{n} x_i l_i \tag{14}$$

and where the free-volume fraction of the mixture $f_{v,mix}$ was determined by the following expression

$$f_{v,mix} = \sum_{i=1}^{n} x_i f_{v,i} \tag{15}$$

where the free-volume fractions of the pure compounds $f_{v,i}$ was estimated by eq 9 using $E = \alpha\rho + pM_w/\rho$. These mixing rules have been successfully used in Zéberg-Mikkelsen et al.[4] The dilute gas viscosity of the mixtures was estimated by the compositional model proposed by Wilke.[29] This compositional model is a function of the composition, the molar mass, and the dilute gas viscosity of the pure compounds. Note that this model is fully predictive for the mixtures.

The comparison of the predicted viscosities with the experimental values (168 points for the mixture) resulted in an AAD of 5.77 %, a Δ_{max} of 22.06 %, and a Bias (found at 293.15 K, 0.1 MPa, and 75 mol % 1-propanol) of 2.72 % which are satisfactory, considering the simple structure of the model, since only three adjustable parameters are needed for each pure compound along with the experimental density of the fluid. This model is much more predictive for the mixture than the compositional models discussed above.

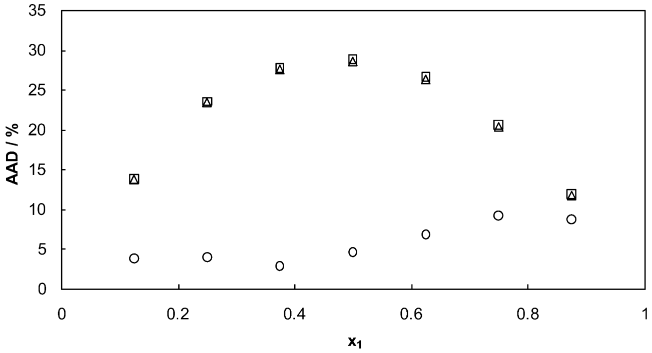

Figure 7. AAD comparison versus the mole fraction x_1 for: Δ, Grunberg and Nissan model; □, Katti and Chaudhri model; ○, the free-volume model.

Figure 7 shows a comparison of the AAD of the models of Grunberg−Nissan and Katti−Chaudhri with no adjustable parameter and the free-volume model with respect to the molar fraction x_1. It shows that the first two models show the same type of results with a maximum AAD around $x_1 = 0.5$, whereas for the free volume model, the maximum AAD can be seen around $x_1 = 0.75$.

5. Conclusion

A total of 216 experimental dynamic viscosity measurements are reported for the binary system 1-propanol + toluene covering the entire composition range for temperatures between (293.15 and 353.15) K and up to 100 MPa. At 0.1 MPa, the dynamic viscosity was measured by a classical capillary viscometer (Ubbelohde) with an experimental uncertainty of ± 1 %, whereas the viscosity under pressure was measured with a falling-body viscometer with an experimental uncertainty of ± 2 %.

The experimental data for this binary system (168 data) were used to evaluate the performance of two compositional models and the free-volume viscosity model. This evaluation showed that the free-volume model can predict the viscosity of this binary system within an acceptable and satisfactory uncertainty for industrial applications, although the system is very asymmetrical. The compositional models cannot satisfactorily predict the viscosity of the binary mixtures; they can represent the viscosity of this binary system but only when using one adjustable parameter (i.e., in a nonpredictive way).

The classical compositional models can only be applied to liquid or dense fluids, whereas the free-volume model is applicable to gases, liquids, and dense fluids. Because of this, this model is more suitable for industrial processes involving different phases or phase changes. Moreover, from a fundamental point of view, the free-volume model provides some insight on the microstructure of these complex fluid systems although the knowledge of the variation of the density versus pressure and temperature is required. The model could be fully predictive for a mixture as far as a predictive equation of state is used.

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