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Viscosity of Toluene + Cyclopentane Mixtures: Measurements and Prediction

M. J. Assael,[1, 3] **N. K. Dalaouti,**[1] **and J. H. Dymond**[2]

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New measurements of the viscosity of binary mixtures of toluene + cyclopentane are presented. The measurements, performed in a vibrating-wire viscometer, cover the temperature range from 210 to 310 K at pressures up to 25 MPa. The concentrations studied are 60 and 30%, by weight, toluene. The uncertainty of the measurements, confirmed at room temperature and higher temperatures with the measurement of the viscosity of water, is estimated to be ±0.5%, increasing to ±1% at temperatures below 240 K. The present measurements are employed to examine the predictive power of two recent theoretically based schemes proposed for the calculation of the viscosity of mixtures.

KEY WORDS: cyclopentane; high pressures; mixtures; toluene; vibrating wire; viscosity.

1. INTRODUCTION

There are very few theoretical approaches for the prediction of the viscosity of liquid mixtures. Indeed, most of the schemes employed [1] are purely empirical and can strictly be applied only to the systems used for their derivations. The reason for this situation is based on a distinctive lack of accurate experimental data covering a wide range of conditions. Only lately have such measurements started to appear in the literature.

Three theoretical approaches have so far been proposed. The corresponding-states approach has been widely used for hydrocarbon [2] and refrigerant [3] mixtures. Its accuracy, however, is directly dependent upon the availability of good experimental data in order to improve the correlation.

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[1] Faculty of Chemical Engineering, Aristotle University, 54006 Thessaloniki, Greece.
[2] Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom.
[3] To whom correspondence should be addressed.

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Dymond and Assael employed an approach based on considerations of the hard-sphere theory, to predict the transport properties of liquids up to high pressures. The scheme has successfully been employed for the correlation of pure components such as hydrocarbons [4, 5], alcohols [6], and refrigerants [7], but so far its application has been restricted to mixtures of homologous series [8] only. With respect to mixtures, this approach is based only on mixing rules using parameters of the pure components and, as such, it is a purely predictive scheme.

Vesovic and Wakeham [9, 10] recently extended a theoretically based scheme [11, 12] for the prediction of the transport properties of fluid mixtures starting from those of the pure components, to high-pressure gaseous mixtures. In a recent paper Assael et al. [13] modified this scheme by making use of the hard-sphere theory and applied it to the prediction of two liquid mixtures.

The measurements of toluene + cyclopentane presented in this paper, as they extend to a wide range of conditions, allow the examination of the predictive power of the above latter two schemes. The choice of the liquids employed was dictated by the fact that toluene has already been proposed as a viscosity-standard liquid by the Subcommittee of Transport Properties of the International Union of Pure and Applied Chemistry, while cyclopentane is also under consideration.

2. EXPERIMENTAL

The measurements of the viscosity of the toluene + cyclopentane mixtures were performed in a vibrating-wire viscometer, and the whole assembly is the one used for previous measurements of the viscosity of pure toluene [14] and cyclopentane [15]. Thus, the viscometer and the whole assembly were described in detail elsewhere [14, 16, 17]. The accuracy of the measurements is estimated to be ±0.5%, increasing to 1% at temperatures below 240 K. This estimate is confirmed by the measurements of the viscosity of water at temperatures above its freezing temperature. The samples of toluene and cyclopentane were supplied by BDH Chemicals Ltd. and Fluka, with nominal purities of better than 99.9 and 99.5%, respectively. Both samples were dried over molecular sieves.

For the density of toluene the measurements of Magee and Bruno [18] were used, which were correlated to a Tait-type equation with an accuracy of ±0.09% [14]. The density of cyclopentane was calculated by an equation of state reported by Baonza et al. [19], with an accuracy of ±0.06%. The density of the mixture was calculated from the densities of the pure components assuming no change of volume upon mixing. The mixtures studied, 60 and 30%, by weight, toluene, were prepared gravimetrically and the uncertainty in their composition was less than 0.005%.

3. RESULTS

The viscosity measurements of the binary mixtures of toluene and cyclopentane at 0.101 MPa are presented as a function of temperature in Table I. In the same table, our previously reported measurements of the pure components [14, 15] are also shown for comparison purposes. It is interesting to note that, although at room temperature the viscosity of toluene is higher than that of cyclopentane by about 30%, this difference increases to about 80% at 223 K. Hence, the present measurements are expected to be a good test for the predictive power of the two schemes considered here.

The mixture measurements, as well as those of the pure components, were fitted to the following equation:

$$\ln\left(\frac{\eta}{\eta(293.15\ \mathrm{K})}\right)=\sum_{k=0}^{4} d_k T_{\mathrm{r}}^{k} \qquad (1)$$

Table I. Measurements of the Viscosity of Toluene + Cyclopentane Mixture at 0.101 MPa

T (K)	ρ ($\mathrm{kg \cdot m^{-3}}$)	η ($\mu\mathrm{Pa \cdot s}$)
	100%, by weight, toluene	
363.088	799.6	291.6
353.096	809.4	317.6
342.527	819.7	349.1
332.613	829.2	382.4
322.789	838.5	421.9
312.935	847.9	466.9
303.765	856.5	517.1
293.330	866.2	585.8
283.572	875.3	662.6
273.280	884.9	765.0
262.952	894.4	896.7
252.856	903.8	1067
243.049	912.8	1290
233.299	921.9	1593
223.644	930.8	2030
213.722	940.1	2720

Table I. *(Continued)*

T (K)	ρ ($kg \cdot m^{-3}$)	η ($\mu Pa \cdot s$)
60%, by weight, toluene		
308.412	798.7	433.5
302.800	804.2	458.0
293.233	813.6	503.9
283.517	822.9	560.8
273.178	832.8	632.4
262.723	842.6	724.0
253.011	851.7	822.6
243.064	860.9	959.9
232.987	870.1	1140
223.511	878.8	1355
215.713	885.8	1593
30%, by weight, toluene		
308.453	762.8	384.2
303.420	767.9	406.3
293.324	777.9	450.8
283.103	787.9	504.7
272.865	797.8	568.8
262.837	807.3	645.5
253.339	816.2	732.9
243.231	825.5	851.4
233.329	834.5	997.6
223.813	843.0	1192
217.782	848.4	1332
0%, by weight, toluene		
308.675	729.8	371.6
303.535	735.1	393.7
293.445	745.2	437.2
283.166	755.4	493.8
273.212	765.1	558.3
263.029	774.8	636.4
253.305	783.8	734.6
243.341	793.0	840.8
233.206	802.0	988.0
223.153	810.9	1166
218.739	814.7	1259

Table II. Coefficients of Eqs.(1), (2), and (5), Critical Constants, and Scaling Factors

	100%	60%	30%	0%
d_0	34.054	21.134	14.622	19.829
d_1	−219.46	−65.385	−36.452	−119.762
d_2	556.183	81.583	32.785	306.252
d_3	−653.601	−48.467	−11.531	−378.604
d_4	292.762	11.135	0.576	180.615
T_c (K)	591.75	—	—	511.7
η (293.15 K) (μPa · s)	586.9	504.9	451.7	439.1
h_0	8.657415	25.325022	173.010428	8.651127
h_1	0.013137	0.082070	0.189708	0.029798
h_2	0.373310	0.796114	−0.709766	0.098027
h_3	0	0.132140	−0.490496	1.596349
h_4	0.282222	0.840349	0.828432	0
h_5	0	0	0	0.560572
h_6	0.055111	0.021457	0.031879	−0.348191
ρ_c (kg · m^{-3})	290.2	—	—	269.75
ρ_o (kg · m^{-3})	—	813.6	778.1	—
σ_{ij} (nm)	0.5852	0.5617	0.5617	0.5404
ε_{ij}/k_B (K)	485.6	426.5	426.5	396.6
R_η (−)	1.06	—	—	1.23
v_1 (10^{-6} m^3 · mol^{-1})	152.536	—	—	254.835
v_2 (10^{-6} m^3 · mol^{-1})	−525.768	—	—	−1502.70
v_3 (10^{-6} m^3 · mol^{-1})	1341.767	—	—	4422.421
v_4 (10^{-6} m^3 · mol^{-1})	−1585.622	—	—	−5805.67
v_5 (10^{-6} m^3 · mol^{-1})	704.246	—	—	2839.825

The coefficients d_k and the value of the viscosity at 293.15 K are given in Table II. For the pure liquids, $T_r = T/T_c$, where T_c is the critical temperature shown in Table II, while for the mixtures, $T_r = T/293.15$ K. The maximum deviation of the experimental viscosity values of the pure fluids and the mixtures from the values calculated by Eq. (1) is less than 0.5%.

The measurements of the viscosity of the two binary mixtures at higher pressures are shown in Tables III and IV. For interpolation purposes, these data and the viscosities of the pure components were fitted to an equation of the form

$$\eta(\rho_r, T_r) = h_0 \exp\left(\frac{h_1}{T_r^4} + \frac{h_2}{T_r} + h_3 T_r^2\right) \frac{\rho_r}{1 - \rho_r(h_4 + h_5 T_r^{0.5} + h_6 T_r^2)} \tag{2}$$

The coefficients h_k for the pure fluids and the mixtures are shown in Table II. For the pure liquids, $\rho_r = \rho/\rho_c$, where ρ_c is the critical density, while for the

Table III. Measurements of the Viscosity of Toluene + Cyclopentane as a Function of Pressure (60 %, by Weight, Toluene)

T (K)	P (MPa)	ρ (kg · m^{-3})	η (μPa · s)
216.088	0.101	885.5	1585
216.033	1.16	886.1	1600
215.958	6.26	888.8	1672
215.843	8.17	889.9	1704
215.756	10.26	891.1	1739
215.681	12.21	892.1	1770
215.635	14.18	893.2	1804
215.663	15.81	893.9	1826
215.720	17.98	895.0	1861
233.270	0.101	869.9	1132
233.270	2.20	871.1	1146
233.264	4.26	872.3	1166
233.252	5.99	873.3	1186
233.244	8.12	874.5	1206
233.234	10.48	875.9	1224
233.213	12.35	876.9	1248
233.202	14.13	877.9	1265
233.202	16.07	879.0	1280
233.189	18.21	880.1	1305
233.195	20.38	881.3	1325
253.231	0.101	851.5	819.0
253.231	2.10	852.8	832.5
253.231	4.17	854.2	844.6
253.224	6.13	855.4	857.5
253.224	8.16	856.7	872.6
253.224	10.12	858.0	885.0
253.211	12.45	859.3	898.3
253.211	14.48	860.7	917.1
253.185	16.28	861.8	926.8
253.181	18.98	863.4	945.1
272.828	0.101	833.1	633.3
272.837	2.04	834.5	643.5
272.828	3.94	836.0	652.5
272.821	6.00	837.4	662.3
272.821	8.14	839.0	672.1
272.821	10.08	840.3	683.3
272.821	12.28	841.9	693.9
272.821	14.20	843.2	703.6
272.814	16.09	844.4	713.9
272.814	18.02	845.7	722.8
272.821	19.48	846.7	731.3
293.034	0.101	813.7	504.4
293.034	2.06	815.4	511.5
293.034	4.19	817.2	519.8
293.034	6.47	819.0	528.9
293.034	7.90	820.2	535.5
293.034	10.00	821.9	544.0

Table III. *(Continued)*

T (K)	P (MPa)	ρ (kg · m^{-3})	η (μPa · s)
293.038	12.09	823.5	551.2
293.038	14.12	825.0	560.9
293.038	16.10	826.5	567.5
293.038	18.13	828.0	576.3
293.038	20.00	829.4	584.4
293.052	22.02	830.8	592.3
293.066	23.68	832.0	598.4
308.360	0.101	798.8	431.6
308.360	1.89	800.5	438.7
308.360	4.11	802.5	445.2
308.367	6.04	804.3	452.3
308.367	8.10	806.1	459.4
308.373	10.11	807.8	467.3
308.385	12.04	809.5	473.3
308.392	14.10	811.1	481.3
308.392	16.10	812.8	487.8
308.401	18.05	814.3	494.5
308.412	20.10	815.9	501.9
308.417	22.01	817.4	508.7

Table IV. Measurements of the Viscosity of Toluene + Cyclopentane as a Function of Pressure (30 %, by Weight, Toluene)

T (K)	P (MPa)	ρ (kg · m^{-3})	η (μPa · s)
217.782	0.101	848.4	1332
217.859	2.09	849.4	1351
218.018	4.06	850.3	1364
218.292	5.93	851.0	1375
218.393	8.20	852.1	1407
218.437	10.16	853.1	1429
218.437	12.08	854.1	1446
218.370	14.34	855.3	1481
218.343	16.10	856.2	1505
233.329	0.101	834.5	997.6
233.334	2.15	835.7	1011
233.346	4.17	836.9	1027
233.353	6.23	838.1	1046
233.353	8.18	839.2	1064
233.346	10.16	840.3	1082
233.329	12.23	841.5	1098
233.329	14.19	842.6	1115
233.329	16.07	843.6	1129
233.329	17.98	844.6	1146
233.346	19.86	845.6	1162

Table IV. *(Continued)*

T (K)	P (MPa)	ρ $(\mathrm{kg \cdot m^{-3}})$	η $(\mu\mathrm{Pa \cdot s})$
253.407	0.101	816.1	732.0
253.407	2.11	817.5	743.7
253.407	4.23	818.9	757.1
253.407	6.20	820.2	769.0
253.407	8.25	821.6	780.3
253.407	10.21	822.8	791.3
253.382	12.18	824.1	806.8
253.382	14.24	825.4	819.7
253.382	16.08	826.5	832.1
253.369	17.98	827.7	844.3
253.369	19.94	828.8	855.3
253.369	22.26	830.2	871.2
273.032	0.101	797.6	567.2
273.036	2.15	799.2	577.8
273.036	4.20	800.8	587.1
273.036	6.23	802.3	598.1
273.036	7.83	803.5	606.1
273.032	8.68	804.1	609.0
273.036	12.16	806.6	624.0
273.036	14.20	808.0	634.4
273.036	16.11	809.4	645.6
273.050	18.03	810.6	654.5
273.050	20.10	812.0	664.5
273.050	21.94	813.2	673.0
273.078	23.35	814.1	681.6
292.958	0.101	778.3	450.8
292.958	2.11	780.1	459.2
292.958	4.09	781.8	466.3
292.958	6.10	783.5	474.8
292.958	8.17	785.3	482.5
292.958	10.16	786.9	490.4
292.958	12.22	788.5	499.8
292.958	14.19	790.1	506.6
292.960	16.24	791.7	515.3
292.979	18.18	793.2	522.7
292.993	20.36	794.8	530.8
293.002	21.91	795.9	537.0
293.036	23.20	796.8	541.4
308.254	0.101	763.0	382.0
308.254	1.92	764.8	388.6
308.254	4.05	766.9	395.8
308.238	6.10	768.9	402.6
308.245	7.97	770.6	409.2
308.227	10.14	772.6	417.8
308.227	12.11	774.4	423.2
308.238	14.16	776.1	431.9
308.245	16.13	777.8	437.2
308.254	18.17	779.5	444.7
308.284	20.56	781.4	453.1

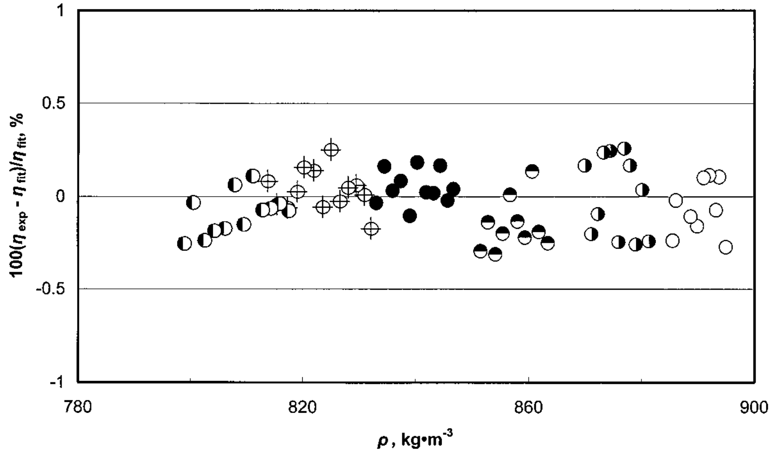

Fig. 1. Deviations of the viscosity measurements of toluene + cyclopentane (60 %, by weight, toluene), from the values calculated from Eq. (2): (○) 218 K; (◑) 233 K; (◒) 253 K; (●) 273 K; (⊕) 293 K; (◐) 308 K.

mixtures, $\rho_r = \rho/\rho_o$ and ρ_o corresponds to the density at 293.15 K and at atmospheric pressure. Values for ρ_c and ρ_o are given in Table II.

The deviations of the viscosity measurements of the two mixtures from the above equation are shown in Figs. 1 and 2. It can be seen that the maximum deviation is less than 0.5 %. The maximum deviation of the

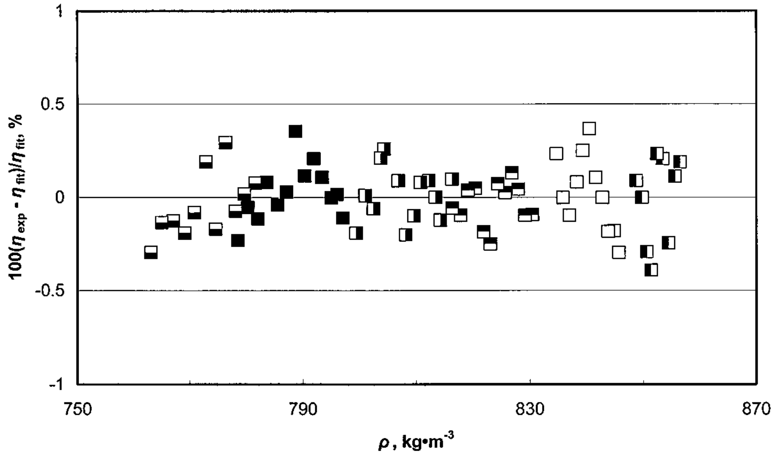

Fig. 2. Deviations of the viscosity measurements of toluene + cyclopentane (30 %, by weight, toluene), from the values calculated from Eq. (2): (◧) 218 K; (□) 233 K; (⬒) 253 K; (◨) 273 K; (■) 293 K; (⬓) 308 K.

measurements of the viscosity of toluene was also 0.5% [14], while the measurements of the viscosity of cyclopentane deviated from the above correlation by less then 0.7% [15].

To our knowledge no one else has measured the viscosity of these mixtures.

4. THEORETICAL ANALYSIS

In view of the marked differences between the viscosities of toluene and cyclopentane at room temperature and the temperature dependence of their viscosities, the present measurements on their mixtures are expected to provide a good test of the predictive power of theoretically based methods. In this section, results are presented using the Dymond–Assael and the Wakeham–Vesovic schemes.

It is also worth pointing out that the simple mole-fraction or mass-fraction average that engineers tend to use to calculate viscosities of mixtures from values for the pure components, in this case, overestimates the mixture viscosity up to 25%.

4.1. The Dymond–Assael Scheme

The Dymond–Assael scheme [20] for the prediction of dense-fluid experimental viscosity and thermal conductivity data over wide temperature and pressure ranges was developed on the basis of hard-sphere theory. In the specific case of viscosity, this scheme introduces a reduced viscosity, η^*, defined by the equation

$$\eta^* = 6.035 \times 10^8 \left(\frac{1}{MRT}\right)^{1/2} \frac{\eta V^{2/3}}{R_\eta} \tag{3}$$

where V is the molar volume ($\mathrm{m^3 \cdot mol^{-1}}$), M is the molar mass, R is the universal gas constant, and R_η is a roughness factor introduced to account for nonspherical-shape effects.

It turns out [20] that this reduced viscosity is a function only of the volume ratio, V/V_o, where V_o is a characteristic volume, which corresponds in a hard-sphere system to the volume of close-packing. The universal curve is expressed by the equation

$$\log \eta^* = \sum_{k=0}^{7} a_{\eta k} (V_o/V)^k \tag{4}$$

The values of the coefficients $\alpha_{\eta k}$ are given in Table V.

Table V. Coefficients $a_{\eta k}$, b_k, and c_k

k	$a_{\eta k}$	b_k	c_k
0	1.0945	0.46649	0.1281
1	−9.26324	−0.57015	−0.1108
2	71.0385	0.19164	0.0962
3	−301.9012	−0.3708	−0.0271
4	797.69	0.00241	0.0024
5	−1221.9770	—	—
6	987.5574	—	—
7	−319.4636	—	—

In the case of the pure components the above two equations were optimized with experimental data, and the characteristic volume V_o was found from

$$V_o = \sum_{k=1}^{5} v_k (T/T_c)^{k-1} \tag{5}$$

with the coefficients v_k and the optimum values for R_η given in Table II. Hence, Eqs. (3)–(5) form a consistent scheme by which the viscosity, η, of the pure components can be calculated. It should further be pointed out that, since the characteristic volume V_o is just a weak function of the temperature, it can be calculated from atmospheric-pressure measurements and then employed to predict high-pressure viscosity values.

In the case of alkane mixtures [8], to predict the viscosity of mixtures from the pure components it was assumed that the mixture behaves as a single-component liquid with molecular parameters given by the mole-fraction average of the individual components i, i.e.,

$$V_{o,\,\text{mix}} = \sum_i x_i V_{o,\,i} \qquad \text{and} \qquad R_{\eta,\,\text{mix}} = \sum_i x_i R_{\eta,\,i} \tag{6}$$

where x_i is the mole fraction of component i. This assumption gave excellent results in the case of alkane mixtures. In this case, however, the prediction was rather disappointing and calculated values that differed from the experimental ones by as much as 20% are shown in Fig. 3.

We, therefore, considered the mass-fraction average instead of the mole-fraction average in Eqs. (6). This idea was tried in the case of normal alkane mixtures but found to be less satisfactory. However, for these toluene + cyclopentane mixtures, the mass-fraction average values of the roughness parameters and the characteristic volumes produced viscosity

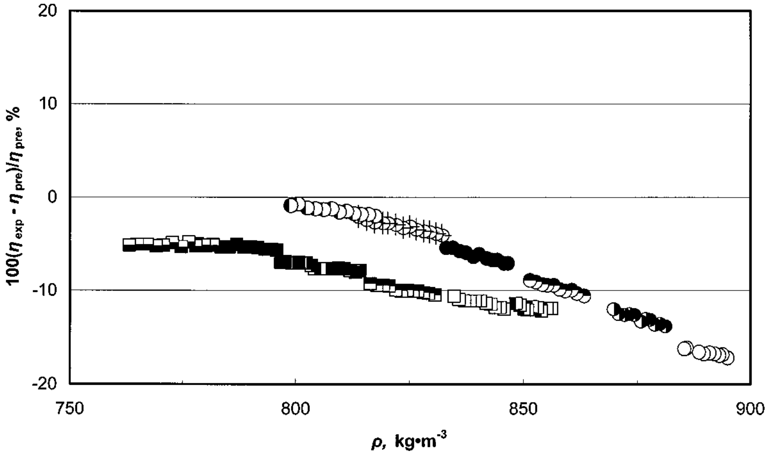

Fig. 3. Deviations of the viscosity measurements of toluene + cyclopentane from the values predicted from the Dymond–Assael scheme, employing mole-fraction averages for V_o and R_η: 60%, by weight, toluene—(○) 218 K, (◑) 233 K, (◓) 253 K, (●) 273 K, (⊕) 293 K, and (◐) 308 K; 30%, by weight, toluene—(◧) 218 K, (□) 233 K, (⬒) 253 K, (◨) 273 K, (■) 293 K, and (⬓) 308 K.

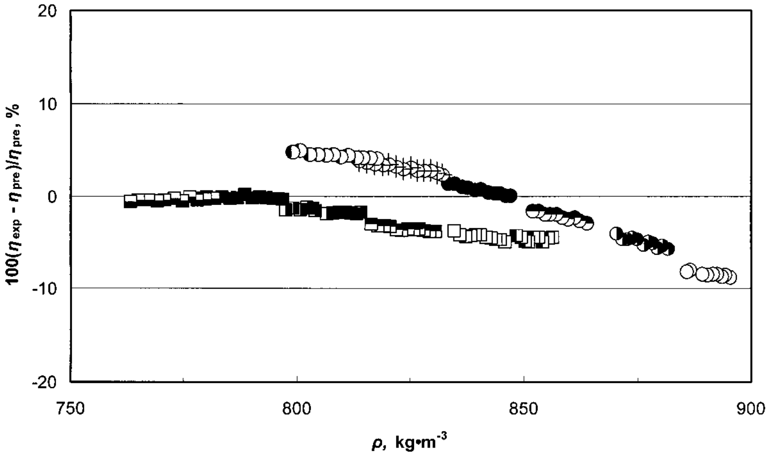

Fig. 4. Deviations of the viscosity measurements of toluene + cyclopentane from the values predicted from the Dymond–Assael scheme, employing mass-fraction averages for V_o and R_η: 60%, by weight, toluene—(○) 218 K, (◑) 233 K, (◓) 253 K, (●) 273 K, (⊕) 293 K, and (◐) 308 K; 30%, by weight, toluene—(◧) 218 K, (□) 233 K, (⬒) 253 K, (◨) 273 K, (■) 293 K, and (⬓) 308 K.

values that differ from the experimental results by 4% on average (with a maximum of 8%), which is considered very satisfactory. The deviations are shown in Fig. 4.

4.2. The Wakeham–Vesovic Scheme

According to the Wakeham–Vesovic scheme [9, 10], the viscosity η of a dense-gas mixture containing N components can be expressed by the equation [11]

$$\eta(\rho_{\mathrm{m}}, T) = -\begin{vmatrix} H_{11} & \cdots & H_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix} + \kappa_{\mathrm{mix}} \tag{7}$$

where ρ_m is its molar density, and

$$Y_i = x_i \left[1 + \sum_{j=1}^{N} \frac{m_j}{(m_i + m_j)} x_j a_{ij} \bar{\chi}_{ij} \rho_{\mathrm{m}} \right] \tag{8}$$

$$H_{ii} = \frac{x_i^2 \bar{\chi}_{ii}}{\eta_i^{\circ}} + \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{x_i x_j \bar{\chi}_{ii}}{2\eta_{ij}^{\circ} A_{ij}^{*}} \frac{m_i m_j}{(m_i + m_j)^2} \left(\frac{20}{3} + \frac{4m_j}{m_i} A_{ij}^{*} \right) \tag{9}$$

$$H_{ij(j \neq i)} = -\frac{x_i x_j \bar{\chi}_{ij}}{2\eta_{ij}^{\circ} A_{ij}^{*}} \frac{m_i m_j}{(m_i + m_j)^2} \left(\frac{20}{3} - 4A_{ij}^{*} \right) \tag{10}$$

$$\kappa_{\mathrm{mix}} = \left(\frac{16}{5\pi} \right) \frac{15}{16} \rho_{\mathrm{m}}^2 \sum_{j=1}^{N} \sum_{i=1}^{N} x_i x_j \bar{\chi}_{ij} a_{ij}^2 \eta_{ij}^{\circ} \tag{11}$$

In the above equations m_i and m_j are molecular masses of species i and j. The viscosity η_t° of the pure component i in the dilute-gas limit area, as well as the dilute-gas limit interaction viscosity for species i and j, η_{ij}°, can be calculated from [21]

$$\eta_{ij}^{\circ} = \frac{5}{16} \left[\frac{2m_i m_j}{(m_i + m_j)} \frac{k_{\mathrm{B}} T}{\pi} \right]^{1/2} \frac{1}{\sigma_{ij}^2 \Omega_{ij}^{*}(T^{*})} \tag{12}$$

where

$$\ln \Omega_{ij}^{*}(T^{*}) = \sum_{k=0}^{4} b_k [\ln(T/(\varepsilon_{ij}/k_{\mathrm{B}}))]^k \tag{13}$$

In these equations, k_B is the Boltzmann constant, σ_{ij} and ε_{ij}/k_B are the length and energy scaling parameters calculated from the critical constants [13] and shown in Table II, while coefficients b_k are given in Table V.

A_{ij}^* is a weak functional of the intermolecular potential for the *i–j* interaction, and it is obtained from [21]

$$\ln A_{ij}^*(T^*) = \sum_{k=0}^{4} c_k [\ln(T/(\varepsilon_{ij}/k_B))]^k \tag{14}$$

The coefficients c_k are given in Table V.

In Eqs. (8)–(11), $\bar{\chi}_{ij}$ is the pseudo-radial distribution function for the molecules *i* and *j*, in the presence of all the other species in the mixture, obtained according to Vesovic and Wakeham [10] as

$$\bar{\chi}_{ij}(\rho, T) = 1 + \frac{2}{5} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1) + \frac{[\frac{6}{5}(\bar{\chi}_i - 1)^{1/3}(\bar{\chi}_j - 1)^{1/3} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1)^{2/3}}{(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}} \tag{15}$$

The pseudo-radial distribution function for the pure fluid was expressed in terms of the experimental viscosity η_i, at the same molar density and temperature as

$$\bar{\chi}_i(\rho, T) = \frac{\beta}{2} \frac{(\eta_i - \rho_m a_{ii} \eta_i^{\circ})}{\rho_m^2 a_{ii}^2 \eta_i^{\circ}} + \beta \left[\left(\frac{(\eta_i - \rho_m a_{ii} \eta_i^{\circ})}{2\rho_m^2 a_{ii}^2 \eta_i^{\circ}} \right)^2 - \frac{1}{\beta \rho_m^2 a_{ii}^2} \right]^{1/2} \tag{16}$$

where $\beta = 0.830$. We note that in its general form Eq. (16) has two solutions, as its two terms can be combined with a positive or a negative sign [10]. In the case of liquids, only the positive sign produces physically realistic solutions [10].

Finally, for the parameter α_{ii} that accounts for the mean-free-path shortening in an *i–i* collision in a dense gas, originally defined [11] as

$$a_{ii} = \tfrac{8}{15} N_A \pi \sigma_{ii}^3 \tag{17}$$

we have adopted our previous approach [13] relating it to the characteristic close-packed volume $V_{o,i}$—defined in Eq. (5)—as

$$a_{ii} = 0.8 \times 2.961 V_{o,i} \tag{18}$$

In Eq. (17), N_A is Avogadro's number. The interaction parameter α_{ij} was calculated by using the mixing rule proposed by Di Pippo et al. [11],

$$a_{ij} = \tfrac{1}{8}(a_{ii}^{1/3} + a_{jj}^{1/3})^3 \tag{19}$$

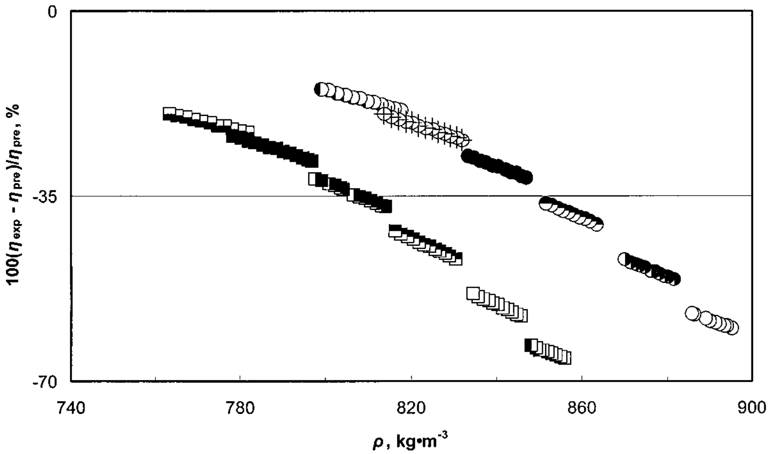

Fig. 5. Deviations of the viscosity measurements of toluene + cyclopentane from the values predicted from the Wakeham–Vesovic scheme: 60 %, by weight, toluene—(○) 218 K, (◑) 233 K, (◓) 253 K, (●) 273 K, (⊕) 293 K, and (◐) 308 K; 30 %, by weight, toluene—(◧) 218 K, (□) 233 K, (⬒) 253 K, (◨) 273 K, (■) 293 K, and (⬓) 308 K.

Equations (7)–(19) were employed to calculate the viscosity of the two mixtures of this study. It should be pointed out that the scheme requires the viscosity of the two pure components at the same temperature and molar density as those of the mixture. To calculate these at the same molar density, extrapolation of Eqs. (3)–(5) was employed. In the case of the viscosity of toluene, this resulted in values at very high pressures, while in the case of the viscosity of cyclopentane, this resulted in values at very low densities. The ratio of the viscosity of the pure components obtained was between 3 and 25.

The results are in agreement with our preliminary calculations in mixtures of *n*-hexane + toluene and *n*-hexane + cyclohexane [13]. For those mixtures it was found that when the ratio of the viscosity of the pure components was less than 4, the predicted values differed from the measurements by up to 15 %, while at higher ratios this difference increased [13]. In the case of toluene + cyclopentane mixtures the predicted values are much higher than the experimental measurements as shown in Fig. 5. The difference is between 14 and 23 % when the pure component viscosity ratio is less than 4 but increases markedly for higher ratios.

5. CONCLUSIONS

New measurements of toluene + cyclopentane mixtures were presented. The measurements, performed in a vibrating-wire viscometer, cover the temperature range from 210 to 310 K at pressures up to 25 MPa. The concentrations studied are 60 and 30%, by weight, toluene. The uncertainty of the measurements, confirmed at room temperature and higher temperatures with the measurement of the viscosity of water, is estimated to be ±0.5%, increasing to ±1% at temperatures below 240 K. The measurements were employed to examine the predictive power of two theoretically based schemes.

In the case of the Dymond–Assael scheme, a mass-fraction average of the characteristic volumes and of the roughness parameters of the pure components gave very satisfactory results. This is contrary to previous experience that indicated that a mole-fraction average and not a mass-fraction average should be employed. This clearly needs to be investigated further with experimental measurements carried out on other key liquid mixtures over a wide range of thermodynamic states.

In the case of the Wakeham–Vesovic scheme, the present results are in agreement with previous preliminary observations that the uncertainty of the scheme is related to the ratio of the viscosity of the pure components at the same molar density. At ratios higher than 4, the uncertainty rises rapidly. This needs to be investigated further, as this is the only scheme that can be applied to very different types of molecules.

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