International Journal of Thermophysics, Vol. 24, No. 4, July 2003 (© 2003)

High-Pressure Viscosity and Density Measurements for the Asymmetric Binary System cis-Decalin + 2,2,4,4,6,8,8-Heptamethylnonane

M. Barrouhou,[1] C. K. Zebérg-Mikkelsen,[1] A. Baylaucq,[1] and C. Boned[1,2]

Received December 18, 2002

Measurements of the viscosity and density of seven binary mixtures composed of cis-decahydronaphthalene (cis-decalin) + 2,2,4,4,6,8,8-heptamethylnonane along with the pure compounds have been performed in the temperature range 293.15 to 353.15 K and at pressures up to 100 MPa. The viscosity was measured with a falling-body viscometer, except at 0.1 MPa where a classical capillary viscometer (Ubbelohde) was used. The experimental uncertainty for the measured viscosities is less than 2% at high pressures. The density was measured up to 60 MPa with a resonance densimeter and extrapolated with a Tait-type relationship up to 100 MPa. The uncertainty for the reported densities is less than $1\ \mathrm{kg \cdot m^{-3}}$. The measured data have been used in an evaluation of the simple mixing laws of Grunberg and Nissan and of Katti and Chaudhri, which require only the density and viscosity of the pure compounds. This evaluation showed that these mixing laws can accurately represent the viscosity of this asymmetric binary system within an average absolute deviation of 1%.

KEY WORDS: 2,2,4,4,6,8,8-heptamethylnonane; cis-decalin; density; high pressure; hydrocarbon mixtures; viscosity.

1. INTRODUCTION

Within the oil industry, as well as other industries, the viscosity is an important property required in many engineering disciplines ranging from the design of transport equipment to the simulation of petroleum reservoirs. For these applications it is more convenient to use models in order to obtain the viscosity of the involved fluids, since it is impossible to measure

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[1] Laboratoire des Fluides Complexes, UMR CNRS, Faculté des Sciences et Techniques, Université de Pau, Avenue de l'Université, BP 1155, 64013 Pau Cedex, France.

[2] To whom correspondence should be addressed. E-mail: christian.boned@univ-pau.fr

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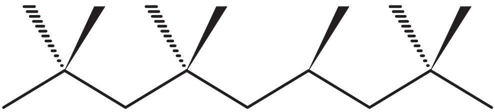
the viscosity at all temperatures, pressures, and compositions. However, experimental viscosity measurements are required in order to develop and evaluate the performance of models incorporating the effects of temperature, pressure, and composition. Due to the importance of hydrocarbons in the oil industry and the high pressure conditions encountered in oil reservoirs, most experimental studies of the viscosity versus pressure and temperature have been performed on hydrocarbon fluids. Most of these studies have been performed on light or intermediate hydrocarbons, primarily paraffins, and their mixtures, whereas studies of polycyclic naphthenic and aromatic compounds are less frequent, although these compounds are also constituents of oils and petroleum fluids. In addition, during the exploration process, oil accumulations exposed to biodegradation or alteration have been discovered. These fluids have a higher content of naphthenic and heavy hydrocarbons, because biodegradation and alteration lead to the vanishing, on decomposition, of the intermediate ‘‘normal“ alkanes between C_6 and C_{16}, resulting in fluids with a more dissimilar or asymmetrical molecular distribution.

Since there are only a few studies of mixtures composed of polycyclic naphthenic compounds with highly branched heavy alkanes in the literature and in order to provide and study such asymmetrical hydrocarbon mixtures, an experimental study of the dynamic viscosity and the density of the binary system composed of the polycyclic naphthene cis-decahydronaphthalene (cis-decalin) and the highly branched alkane 2,2,4,4,6,8,8-heptamethylnonane has been performed up to 100 MPa from 293.15 to 353.15 K.

cis-decalin



2,2,4,4,6,8,8-heptamethylnonane

Fig. 1. Molecular structure of cis-decalin and 2,2,4,-4,6,8,8-heptamethylnonane.

The molecular structures of these two compounds are shown in Fig. 1. Furthermore, this work follows a recent experimental study of the viscosity of two binary systems composed of methylcyclohexane + 2,2,4,4,6,8,8-heptamethylnonane [1] and methylcyclohexane + cis-decalin [2] undertaken in the laboratory in order to study and provide data for naphthenic fluids with highly branched compounds for the evaluation of performance of different representative models incorporating the effects of temperature, pressure, and composition.

2. EXPERIMENTAL TECHNIQUES

The dynamic viscosity η was measured up to 100 MPa using a falling-body viscometer of the type designed by Ducoulombier et al. [3]. In this apparatus, a stainless steel cylinder falls through the fluid of unknown viscosity under selected conditions. The viscosity is a function of the falling time, the difference between the density of the cylinder and the studied fluid, and an apparatus constant, which is determined by calibration for each considered temperature and pressure condition. The technical details for this viscometer are described in Ref. 4. The calibration was performed using toluene [5], and *n*-decane [6, 7] was used to verify the calibration. At 0.1 MPa the dynamic viscosity was obtained by measuring the kinematic viscosity, $\nu = \eta/\rho$ where ρ is the density, by a classical capillary viscometer (Ubbelohde). For this purpose several tubes were used. The density was measured for pressures between 0.1 and 60 MPa with an Anton-Paar DMA60 resonance densimeter combined with an additional 512P high pressure cell. The calibration of the densimeter was performed using water and vacuum as described in Ref. 8. The density measurements were extrapolated up to 100 MPa using the following Tait-type equation, as suggested in Ref. 4, for the variation of the density with pressure,

$$\frac{1}{\rho} = \frac{1}{\rho_0} + A \ln\left(1 + \frac{P - P_0}{B}\right) \tag{1}$$

where A and B are two adjustable constants and ρ_0 is the density at P_0, which in this work was chosen to be 0.1 MPa. This method has been discussed in Ref. 4 and evaluated using values taken from Dymond et al. [9] for pure alkanes and binary mixtures up to 500 MPa. Furthermore, it should be stressed that an error of $1\ \mathrm{kg \cdot m^{-3}}$ in the density corresponds to an error of 1/8000 in the viscosity, as mentioned in Ref. 4.

For the high pressure viscosity and density measurements, the uncertainty in the temperature was estimated to be ±0.5 and ±0.05 K, respectively. The uncertainty in the pressure was estimated to be ±0.1 MPa for the viscosity measurements and ±0.05 MPa for the density measurements (except at 0.1 MPa). The overall uncertainty in the reported density values is less than 1 $\text{kg}\cdot\text{m}^{-3}$, while the relative uncertainty in the viscosity values is of the order of 2% at high pressure. As previously mentioned [1, 4, 10–12], this uncertainty is comparable to the uncertainties obtained by other authors for similar experimental devices. For the measurements of the kinematic viscosity performed with the classical capillary viscometer at atmospheric pressure, the uncertainty in the temperature was ±0.05 K. After multiplying the kinematic viscosity by the density, the dynamic viscosity is obtained with an uncertainty of less than 1%.

The two compounds used in this study are commercially available chemicals with the following purity levels: cis-decalin (Fluka), $C_{10}H_{18}$, molecular weight $M_w = 138.26\ \text{g}\cdot\text{mol}^{-1}$, chemical purity > 98% (GC: Gas Chromatography), but 99.1% on the certificate on the website of Fluka www.sigmaaldrich.com, and 2,2,4,4,6,8,8-heptamethylnonane (Aldrich), $C_{16}H_{34}$, molecular weight $M_w = 226.45\ \text{g}\cdot\text{mol}^{-1}$, chemical purity > 98% (GLC: gas liquid chromatography), but 99.2% on the certificate on the website of Aldrich www.sigmaaldrich.com. The impurities are not mentioned. No further purification of the pure compounds was performed. The binary mixtures composed of cis-decalin (1) and 2,2,4,4,6,8,8-heptamethylnonane (2) were prepared by weighing at atmospheric pressure and ambient temperature using a Mettler balance with an uncertainty of 0.001 g in order to obtain the following mole fractions of cis-decalin, $x_1 = 0.125$, 0.250, 0.375, 0.500, 0.625, 0.750, and 0.875. Immediately after their preparation, the samples were poured into a capillary glass funnel for the transfer of the samples by gravity to the measuring cells. The pure fluids, not degassed, were stored in hermetically sealed bottles. Finally, the studied samples are in the liquid state within the experimental temperature and pressure ranges of this work.

3. RESULTS

For the pure compounds and the seven binary mixtures, measurements of the dynamic viscosity, η, and the density, ρ, were performed from 293.15 to 353.15 K in steps of 10 K. The viscosity was measured at the following six pressures (0.1, 20, 40, 60, 80, and 100 MPa). A total of 378 experimental viscosity data were obtained, 84 data for the two pure compounds and 294 data for the seven binary mixtures. The density measurements were carried out for pressures from 0.1 to 60 MPa in steps of 5 MPa, resulting in 91 measured values per sample. The isothermal density measurements were extrapolated with the aid of the Tait-type relationship, Eq. (1), in order to evaluate the densities at 80 and 100 MPa corresponding to 28 values per sample.

Table I presents the measured dynamic viscosity and the corresponding density values of the studied samples composed of cis-decalin and

Table I. Dynamic Viscosity η and Density ρ Versus Temperature T, Pressure P, and Mole Fraction x for Binary Mixtures Composed of cis-Decalin (1) and 2,2,4,4,6,8,8-Heptamethylnonane (2)

		$x_1 = 0.000$		$x_1 = 0.125$		$x_1 = 0.250$	
T (K)	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)
293.15	0.1	784.8	3.782	792.8	3.680	802.2	3.640
293.15	20	797.6	5.477	805.3	5.318	814.6	5.197
293.15	40	808.5	7.791	816.2	7.501	825.4	7.318
293.15	60	818.1	11.13	825.8	10.594	834.8	10.209
293.15	80	826.7[a]	15.92	834.3[a]	14.932	843.3[a]	14.105
293.15	100	834.4[a]	22.77	842.1[a]	20.977	851.0[a]	19.323
303.15	0.1	778.0	2.984	785.9	2.919	795.2	2.871
303.15	20	791.6	4.237	799.2	4.153	808.4	4.039
303.15	40	803.0	5.960	810.5	5.791	819.6	5.537
303.15	60	812.9	8.308	820.4	7.999	829.4	7.562
303.15	80	821.6[a]	11.48	829.0[a]	10.966	838.1[a]	10.288
303.15	100	829.5[a]	15.73	836.8[a]	14.936	845.9[a]	13.942
313.15	0.1	771.3	2.411	779.1	2.364	788.4	2.334
313.15	20	785.5	3.411	793.1	3.279	802.1	3.250
313.15	40	797.4	4.700	804.9	4.514	813.8	4.435
313.15	60	807.7	6.426	815.1	6.155	824.0	5.943
313.15	80	816.7[a]	8.710	824.1[a]	8.309	833.0[a]	7.834
313.15	100	824.8[a]	11.71	832.3[a]	11.114	841.1[a]	10.187
323.15	0.1	764.6	2.018	772.4	1.961	781.6	1.934
323.15	20	779.5	2.841	787.0	2.770	796.0	2.695
323.15	40	791.9	3.904	799.3	3.771	808.1	3.603
323.15	60	802.6	5.271	809.9	5.035	818.7	4.750
323.15	80	811.9[a]	7.007	819.2[a]	6.611	828.0[a]	6.178
323.15	100	820.3[a]	9.194	827.5[a]	8.557	836.4[a]	7.938
333.15	0.1	757.8	1.682	765.5	1.646	774.7	1.633
333.15	20	773.5	2.315	781.0	2.312	789.9	2.247
333.15	40	786.4	3.139	793.7	3.113	802.6	2.970
333.15	60	797.4	4.197	804.6	4.123	813.4	3.880
333.15	80	806.9[a]	5.537	814.1[a]	5.381	822.8[a]	5.058
333.15	100	815.4[a]	7.222	822.6[a]	6.886	831.3[a]	6.416
343.15	0.1	751.0	1.446	758.7	1.405	767.7	1.392
343.15	20	767.6	1.975	775.1	1.964	783.8	1.900
343.15	40	780.9	2.627	788.3	2.606	797.0	2.493
343.15	60	792.4	3.448	799.6	3.402	808.3	3.215
343.15	80	802.2[a]	4.475	809.4[a]	4.372	818.1[a]	4.112
343.15	100	810.9[a]	5.750	818.1[a]	5.497	826.9[a]	5.155
353.15	0.1	744.2	1.245	751.9	1.214	760.8	1.205
353.15	20	761.6	1.703	769.1	1.689	777.7	1.647
353.15	40	775.6	2.274	782.8	2.217	791.4	2.159
353.15	60	787.4	2.985	794.6	2.868	803.1	2.785
353.15	80	797.4[a]	3.860	804.7[a]	3.662	813.2[a]	3.543
353.15	100	806.4[a]	4.923	813.7[a]	4.624	822.1[a]	4.455

Table I. *(Continued)*

		$x_1 = 0.375$		$x_1 = 0.500$		$x_1 = 0.625$	
T (K)	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)
293.15	0.1	812.7	3.559	824.7	3.505	838.6	3.456
293.15	20	825.0	5.075	836.8	4.872	850.5	4.709
293.15	40	835.6	6.978	847.3	6.625	860.8	6.279
293.15	60	845.1	9.537	856.7	8.930	870.1	8.339
293.15	80	853.5[a]	12.939	865.1[a]	11.927	878.5[a]	11.030
293.15	100	861.2[a]	17.428	872.7[a]	15.793	886.1[a]	14.533
303.15	0.1	805.7	2.830	817.6	2.797	831.4	2.765
303.15	20	818.7	3.967	830.3	3.800	843.9	3.728
303.15	40	829.8	5.359	841.3	5.081	854.7	4.912
303.15	60	839.5	7.194	851.0	6.762	864.3	6.428
303.15	80	848.1[a]	9.600	859.6[a]	8.955	873.0[a]	8.358
303.15	100	856.0[a]	12.743	867.5[a]	11.802	880.9[a]	10.805
313.15	0.1	798.7	2.303	810.5	2.279	824.2	2.259
313.15	20	812.3	3.187	823.9	3.068	837.3	3.033
313.15	40	823.8	4.296	835.4	4.087	848.7	3.956
313.15	60	834.0	5.695	845.4	5.373	858.6	5.116
313.15	80	842.8[a]	7.439	854.2[a]	6.975	867.3[a]	6.555
313.15	100	850.9[a]	9.590	862.2[a]	8.952	875.3[a]	8.328
323.15	0.1	791.8	1.911	803.6	1.897	817.1	1.884
323.15	20	806.0	2.650	817.5	2.584	830.9	2.550
323.15	40	818.1	3.539	829.4	3.390	842.7	3.316
323.15	60	828.5	4.632	839.8	4.381	852.9	4.235
323.15	80	837.9[a]	5.895	849.0[a]	5.540	862.1[a]	5.321
323.15	100	846.3[a]	7.538	857.3[a]	6.948	870.4[a]	6.591
333.15	0.1	784.9	1.614	796.6	1.604	810.0	1.597
333.15	20	799.9	2.200	811.3	2.157	824.4	2.147
333.15	40	812.4	2.895	823.7	2.807	836.7	2.775
333.15	60	823.2	3.771	834.4	3.569	847.3	3.526
333.15	80	832.6[a]	4.861	843.7[a]	4.563	856.7[a]	4.412
333.15	100	841.1[a]	6.162	852.2[a]	5.740	865.2[a]	5.445
343.15	0.1	777.9	1.380	789.5	1.370	802.8	1.363
343.15	20	793.7	1.871	805.0	1.863	818.1	1.833
343.15	40	806.7	2.442	817.9	2.408	830.7	2.342
343.15	60	818.0	3.135	829.1	3.079	841.8	2.953
343.15	80	827.8[a]	3.994	838.8[a]	3.837	851.6[a]	3.672
343.15	100	836.5[a]	4.989	847.6[a]	4.656	860.3[a]	4.511
353.15	0.1	770.8	1.193	782.4	1.188	795.6	1.183
353.15	20	787.5	1.636	798.8	1.571	811.6	1.569
353.15	40	801.1	2.118	812.2	2.027	824.9	2.000
353.15	60	812.7	2.700	823.8	2.577	836.3	2.513
353.15	80	822.7[a]	3.394	833.7[a]	3.233	846.3[a]	3.113
353.15	100	831.6[a]	4.217	842.7[a]	4.011	855.3[a]	3.807

Table I. *(Continued)*

		$x_1 = 0.750$		$x_1 = 0.875$		$x_1 = 1.000$	
T (K)	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)
293.15	0.1	854.7	3.402	873.7	3.377	896.8	3.355
293.15	20	866.3	4.576	885.1	4.475	907.9	4.389
293.15	40	876.6	5.968	895.2	5.766	917.9	5.589
293.15	60	885.8	7.797	904.3	7.428	926.8	7.096
293.15	80	894.1[a]	10.188	912.6[a]	9.554	935.0[a]	8.974
293.15	100	901.7[a]	13.298	920.3[a]	12.263	942.5[a]	11.302
303.15	0.1	847.5	2.736	866.2	2.713	889.1	2.704
303.15	20	859.7	3.619	878.2	3.551	901.0	3.455
303.15	40	870.4	4.672	888.7	4.546	911.3	4.391
303.15	60	879.9	6.029	898.2	5.783	920.6	5.533
303.15	80	888.5[a]	7.767	906.6[a]	7.314	928.9[a]	6.909
303.15	100	896.3[a]	9.982	914.3[a]	9.200	936.6[a]	8.555
313.15	0.1	840.2	2.254	858.8	2.228	881.5	2.214
313.15	20	853.0	2.977	871.4	2.904	893.9	2.873
313.15	40	864.1	3.850	882.4	3.705	904.7	3.623
313.15	60	874.0	4.911	892.1	4.676	914.4	4.517
313.15	80	882.8[a]	6.186	900.9[a]	5.835	923.1[a]	5.567
313.15	100	890.9[a]	7.704	908.9[a]	7.210	931.1[a]	6.785
323.15	0.1	832.9	1.876	851.4	1.870	873.9	1.861
323.15	20	846.4	2.512	864.5	2.434	886.9	2.425
323.15	40	858.0	3.230	876.0	3.102	898.1	3.046
323.15	60	868.2	4.090	886.1	3.883	908.2	3.775
323.15	80	877.4[a]	5.077	895.2[a]	4.783	917.4[a]	4.617
323.15	100	885.6[a]	6.220	903.5[a]	5.806	925.7[a]	5.577
333.15	0.1	825.6	1.590	844.0	1.581	866.4	1.571
333.15	20	839.8	2.096	857.8	2.052	880.0	2.043
333.15	40	851.9	2.689	869.7	2.583	891.6	2.549
333.15	60	862.4	3.375	880.1	3.188	902.2	3.139
333.15	80	871.7[a]	4.184	889.5[a]	3.928	911.3[a]	3.817
333.15	100	880.1[a]	5.129	897.9[a]	4.788	919.7[a]	4.586
343.15	0.1	818.3	1.363	836.5	1.356	858.8	1.346
343.15	20	833.3	1.813	851.1	1.774	872.9	1.762
343.15	40	845.8	2.281	863.4	2.201	885.3	2.174
343.15	60	856.8	2.867	874.3	2.709	896.0	2.655
343.15	80	866.4[a]	3.524	883.9[a]	3.303	905.6[a]	3.209
343.15	100	875.1[a]	4.308	892.6[a]	3.988	914.3[a]	3.842
353.15	0.1	811.0	1.183	829.0	1.177	851.1	1.173
353.15	20	826.7	1.551	844.3	1.535	866.1	1.540
353.15	40	839.8	1.971	857.3	1.907	878.8	1.882
353.15	60	851.2	2.470	868.5	2.368	890.0	2.282
353.15	80	861.0[a]	2.992	878.4[a]	2.868	899.8[a]	2.740
353.15	100	869.8[a]	3.651	887.3[a]	3.392	908.6[a]	3.257

[a] Density values obtained by extrapolation using the Tait-type equation, Eq. (1).

2,2,4,4,6,8,8-heptamethylnonane as a function of temperature T, pressure P, and mole fraction of cis-decalin (x_1). A comparative analysis of the deviations for the reported viscosities for 2,2,4,4,6,8,8-heptamethylnonane with values reported in the literature is given in Ref. 1, showing that the obtained deviations are within the experimental uncertainty claimed for the viscosity measurements by the different authors.

For the equimolar mixture, the viscosity versus pressure is shown in Fig. 2 for various isotherms, whereas Fig. 3 shows the viscosity versus temperature for different pressures of this equimolar mixture. Figures 4 and 5 show for the same mixture the density versus pressure for various isotherms and the density versus temperature for various isobars, respectively.

Figures 2 through 5 along with Table I reveal a general behavior consistent with previous observations made by other authors and by ourselves on different liquid hydrocarbon systems. The pressure dependence of the viscosity at constant temperature $(\partial\eta/\partial P)_T$ is greater than zero, and the shape of the curves for changes in the viscosity with pressure is increasing. For case of 2,2,4,4,6,8,8-heptamethylnonane, this increase is very pronounced due to an important reduction of the fluid mobility. This may be related to the interlinking effects due to the highly branched molecular structure. Also for cis-decalin, a more important increase in the viscosity is observed compared with normal alkanes, when brought under pressure.

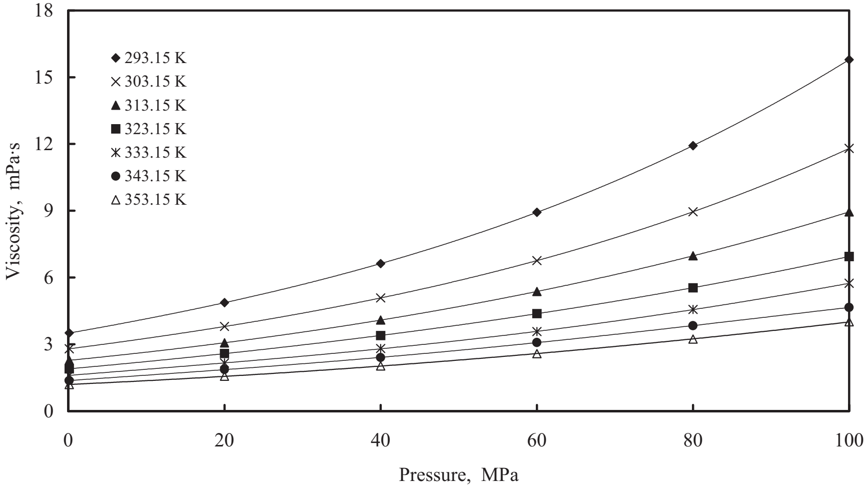


Fig. 2. Dynamic viscosity versus pressure for the equimolar binary mixture at various temperatures.

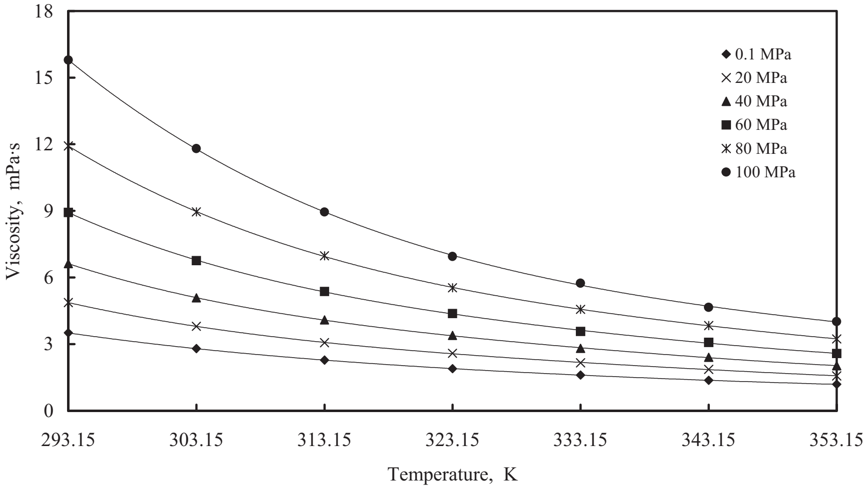


Fig. 3. Dynamic viscosity versus temperature for the equimolar binary mixture at various pressures.

Consequently, the same pressure effect on the viscosity is found for the studied mixtures. On the contrary, the temperature dependence of the viscosity at constant pressure $(\partial\eta/\partial T)_P$ is always less than zero. For the density at constant temperature, the curves are concave, which is associated with a negative second derivative. The shape of the isothermal curves of the

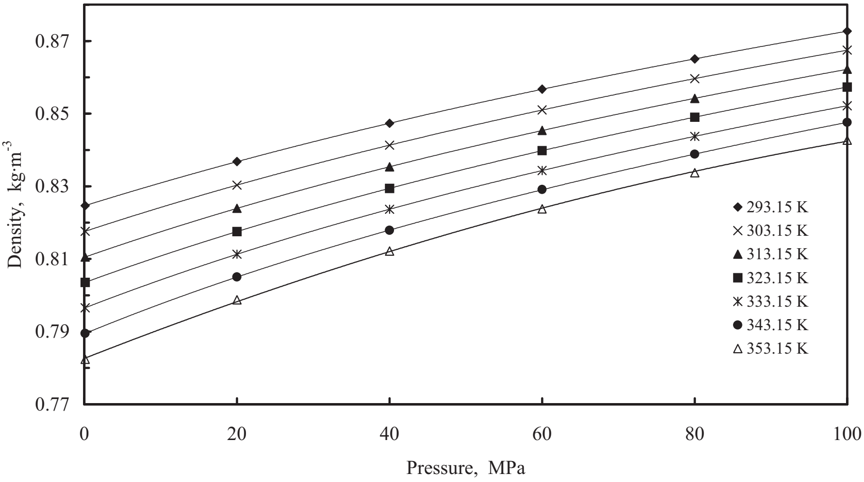


Fig. 4. Density versus pressure for the equimolar binary mixture at various temperatures.

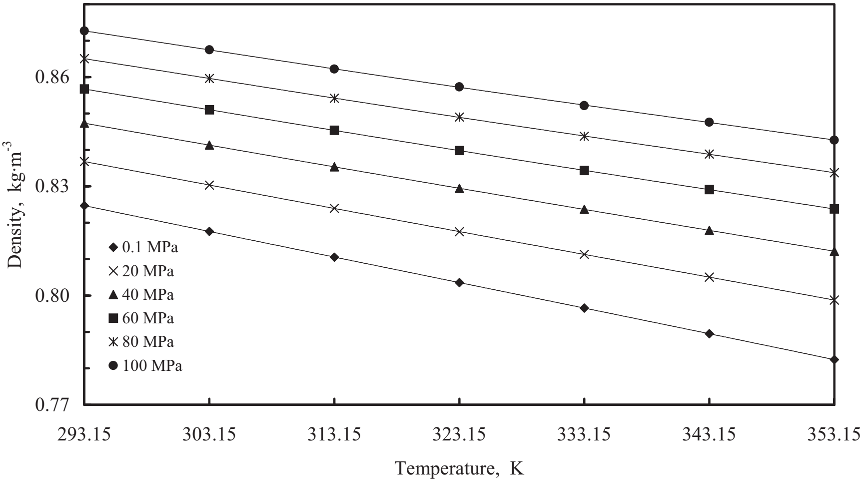


Fig. 5. Density versus temperature for the equimolar binary mixture at various pressures.

density versus pressure is compatible with the logarithmic relationship used in the Tait-type density equation used to model the influence of pressure on density. This relationship has been used in this work to extrapolate the densities to 100 MPa. Furthermore, it should be noted that the variations of the density with temperature are practically linear due to the small temperature interval (293.15 to 353.15 K) considered in this investigation.

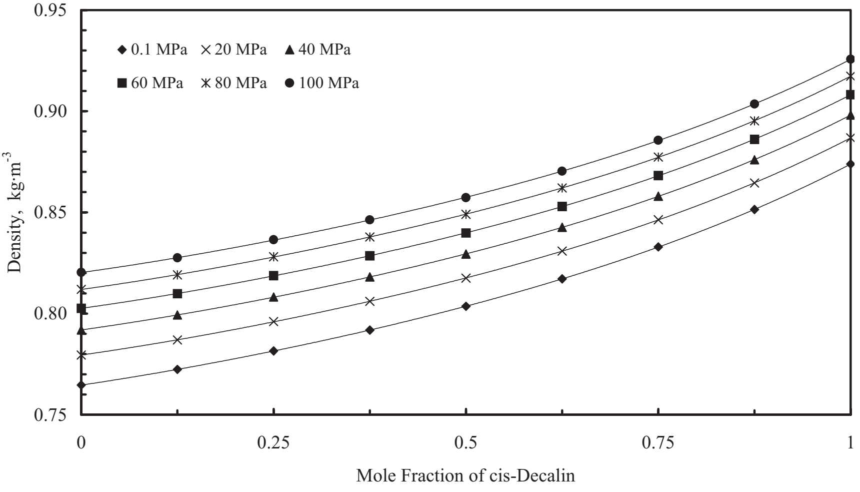


Fig. 6. Density versus the mole fraction of cis-decalin for various isobars at 323.15K.

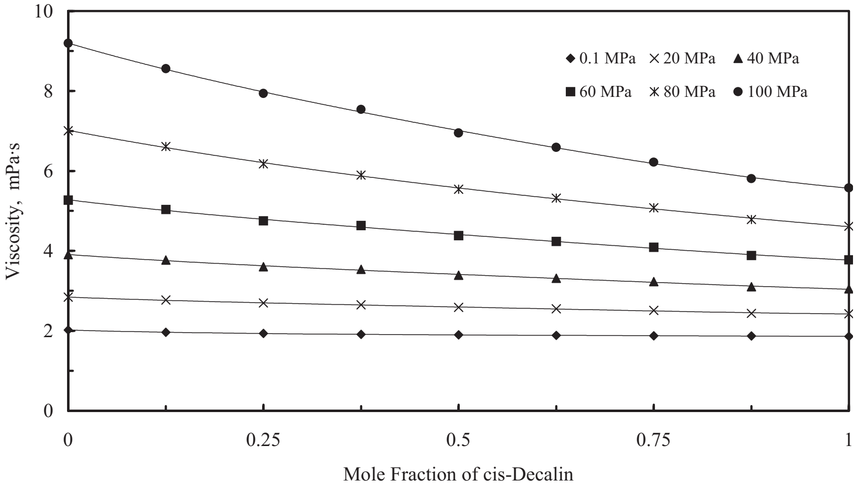


Fig. 7. Dynamic viscosity versus the mole fraction of cis-decalin for various isobars at 323.15 K.

Furthermore, Fig. 6 presents the density at 323.15 K as a function of the composition for different pressures. In Fig. 7 the viscosity is shown as a function of the composition at 323.15 K for several isobars, whereas Figs. 8 and 9 present the density and the viscosity at 80 MPa versus the composition for several isotherms. These figures show a monotonic decrease in the

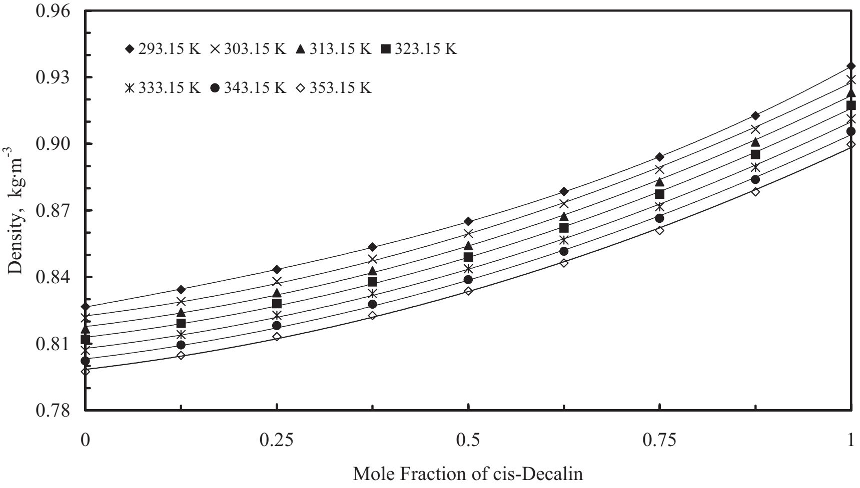


Fig. 8. Density versus the mole fraction of cis-decalin for various isotherms at 80 MPa.

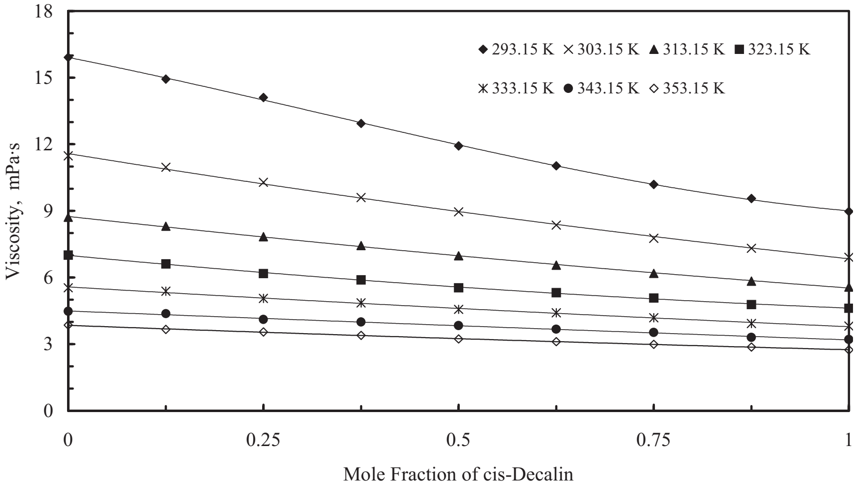


Fig. 9. Dynamic viscosity versus the mole fraction of cis-decalin for various isotherms at 80 MPa.

viscosity with increasing composition of cis-decalin at constant temperature and pressure. Similar plots can be obtained for other temperatures and pressures.

4. DISCUSSION

The viscosity and density data obtained for the binary system cis-decalin (1) + 2,2,4,4,6,8,8-heptamethylnonane (2) have been used to carry out a preliminary study focusing on simple mixing laws, which have been derived in order to predict the viscosity of liquid mixtures based on the viscosity and density of the pure compounds along with the composition. One of these mixing laws is the well-known Grunberg and Nissan mixing law [13], which for a binary mixture can be written as

$$\ln(\eta_{mx}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) \tag{2}$$

where η is the viscosity and x is the composition. Subscript mx refers to the mixture, whereas subscripts 1 and 2 refer to cis-decalin and 2,2,4,4,6,8,8-heptamethylnonane, respectively. By comparing the calculated viscosities from Eq. (2) with the experimental values for the binary mixtures (294 data points), an overall absolute average deviation (AAD) of 0.98% is obtained with a maximum absolute deviation (MD) of 3.10% at 303.15 K and 100 MPa for the binary containing 25 mol% cis-decalin and 75 mol%

2,2,4,4,6,8,8-heptamethylnonane. Although the binary system is composed of two very different compounds, the performance of the Grunberg–Nissan mixing law is very satisfactory, especially taking into account the simplicity of the mixing law, which only requires the viscosity and composition of the pure compounds. Although the performance of the Grunberg–Nissan mixing law for this binary system is very good, it should be stressed that with this relationship, the variation of the viscosity with composition is usually monotonic and any interactions between molecules influencing the global viscosity is not explicitly taken into account. But by introducing an adjustable parameter believed to be in some way representative of the interactions within the binary system, Grunberg and Nissan [13] proposed the following expression for viscosity modeling of real binary systems:

$$\ln(\eta_{mx}) = x_1 \ln(\eta_1) + x_2 \ln(\eta_2) + x_1 x_2 d_{1,2} \tag{3}$$

The $d_{1,2}$ parameter is a quantity characteristic of the intermolecular interactions between component 1 and component 2. By modeling the viscosity data given in Table I for the binary system studied in this work, the adjustable parameter ($d_{1,2} = -0.0255712$) has been obtained, resulting in an AAD of 0.89% and a MD of 3.59% again at 303.15 K and 100 MPa for the binary mixture composed of 25 mol% cis-decalin and 75 mol% 2,2,4,4,6,8,8-heptamethylnonane. The introduction of an adjustable parameter in the Grunberg–Nissan mixing law for this binary system improves the overall performance slightly, whereas an increase in the MD is obtained. Further, it should be stressed that the model is no longer predictive when an adjustable binary parameter is introduced. Finally, the small value of the $d_{1,2}$ parameter and the slightly improved viscosity modeling results might be related more to the uncertainty of the experimental results than a "realistic" description of the system compared with the totally predictive performance of the "ideal" Grunberg–Nissan mixing law in which the $d_{1,2}$ parameter is equal to zero.

Another property, which can be obtained from the measured viscosity and density values, is the excess activation energy for viscous flow ΔG^{E}, which appears in the following expression for a binary mixture,

$$\ln(\eta_{mx} v_{mx}) = x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2) + \frac{\Delta G^{\mathrm{E}}}{RT} \tag{4}$$

where R is the gas constant, T is the temperature, $v = M_{\mathrm{w}}/\rho$ is the molar volume, M_{w} is the molecular weight, and ρ is the density. For a binary mixture the molar mass is defined as $M_{\mathrm{w}} = x_1 M_{\mathrm{w},1} + x_2 M_{\mathrm{w},2}$. Equation (4) is a modified form of the mixing law proposed by Katti and Chaudhri [14] and is theoretically justified by Eyring's representation of the dynamic viscosity of a pure fluid [15]. Also, the quantity ηv is obtained from the time-correlation expression for shear viscosity [16]. It should be stressed that the quantities ηv and ΔG^{E} have a theoretical background, while the corrective term in Eq. (3) does not. By using the experimental viscosity and density data given in Table I, the excess activation energy for viscous flow ΔG^{E} has been estimated, showing that ΔG^{E} is positive for this binary system. For some authors [17, 18] a negative value for the excess activation energy of viscous flow means that the predominant effect in the mixture is the breaking up of the ordered structure present in the pure liquids. Other authors [19, 20] interpret the negative values of the excess activation energy of viscous flow by the fact that the repulsive forces of interaction are the forces which predominate, corresponding to the breaking of bonds within the ordered structure. According to this, a positive excess activation energy for viscous flow should correspond to the interlinking of molecules or the association of bonds within the ordered molecular structure. In our case, the excess activation energy for viscous flow is positive, which may be the effect of molecular interlinking interactions due to the molecular structure of the involved compounds, see Fig. 1. The maximum value of ΔG^{E} for the binary system cis-decalin + 2,2,4,4,6,8,8-heptamethylnonane is approximately 180 $\mathrm{J \cdot mol^{-1}}$ obtained at 343.15 K and 60 MPa for the equimolar binary mixture. This should correspond to weak interlinking molecular interactions and consequently to a weakly interacting system. In comparison, for the asymmetrical binary system methylcyclohexane + 2,2,4,4,6,8,8-heptamethylnoane, the maximum value is 700 $\mathrm{J \cdot mol^{-1}}$ [1], whereas for a very associative system, such as water + alcohol [12], ΔG^{E} can reach 5000 $\mathrm{J \cdot mol^{-1}}$.

For an ideal mixture $\Delta G^{\mathrm{E}} = 0$ and Eq. (4) reduces to the ideal Katti–Chaudhri mixing law as follows:

$$\ln(\eta_{mx} v_{mx}) = x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2) \tag{5}$$

In this case using the reported densities in order to obtain v_{mx}, an AAD of 3.07% is obtained, when the calculated viscosities from Eq. (5) are compared with the experimental values. The resultant MD is 6.18% obtained at 343.15 K and 60 MPa for the equimolar binary mixture. Although the Katti–Chaudhri mixing law also incorporates the density in the viscosity calculations, the more simple Grunberg–Nissan mixing law (no density data are required in Eq. (2)) gives better predictions for this binary system.

However, Eq. (4) can also be used to model the viscosity of real mixtures by introducing an expression for ΔG^{E} in order to take into account the non ideal behavior of real mixtures. A similar expression as the one introduced in the Grunberg–Nissan mixing law (Eq. (3)) can be written for ΔG^{E},

$$\Delta G^{\mathrm{E}} = x_1 x_2 W_{1,2} \tag{6}$$

where $W_{1,2}$ is a quantity characteristic of intermolecular interactions between component 1 and 2 responsible for the excess activation energy for viscous flow. By modeling the viscosity data given in Table I, the adjustable parameter ($W_{1,2} = 431.985\ \mathrm{J \cdot mol^{-1}}$) has been obtained, resulting in an AAD of 0.86% and a MD of 3.06% found at 303.15 K and 100 MPa for the binary mixture composed of 25 mol% cis-decalin and 75 mol% 2,2,4,4,6,8,8-heptamethylnonane. The estimated $W_{1,2}$ parameter is positive, indicating that interlinking molecular forces dominate between cis-decalin and 2,2,4,4,6,8,8-heptamethylnonane. The obtained AAD is within the experimental uncertainty (2%) and similar to the results obtained by the simple Grunberg–Nissan mixing law in Eq. (2).

5. CONCLUSION

The viscosity and density of the asymmetrical binary system cis-decalin + 2,2,4,4,6,8,8-heptamethylnonane have been measured for the two pure compounds and seven binary mixtures in the temperature range 293.15 to 353.15 K and up to 100 MPa. For this binary system the excess activation energy of viscous flow is positive (maximum value of $180\ \mathrm{J \cdot mol^{-1}}$), which corresponds to a very weakly interacting system due to the possible interlinking between the molecules. The obtained viscosity and density data will be used in future more extensive evaluations of the performance of different viscosity models incorporating the effects of temperature, pressure, and composition. But a preliminary study of simple mixing rules (Grunberg–Nissan and Katti–Chaudhri) showed that these mixing laws can accurately represent the viscosity of this asymmetric binary system within the experimental uncertainty. This study is also a part of a more general study of the physical properties concerning systems with very dissimilar and asymmetrical compounds undertaken in this laboratory.

ACKNOWLEDGMENTS

Financial funding of C. K. Zéberg-Mikkelsen is provided by the EC Marie Curie Individual Fellowship Contract No. ENK6-CT-2001-50040. Total is thanked for its financial support.

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