International Journal of Thermophysics, Vol. 24, No. 2, March 2003 (© 2003)

Viscosity and Density Measurements of Binary Mixtures Composed of Methylcyclohexane + cis-Decalin Versus Temperature and Pressure

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Received October 3, 2002

Viscosity and density measurements have been carried out for binary mixtures composed of methylcyclohexane + cis-decalin 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 atmospheric pressure where an Ubbelohde viscometer was used. The experimental uncertainty for the measured viscosities is 2%. The density was measured up to 60 MPa and extrapolated by a Tait-type relationship to 100 MPa. For the reported densities the uncertainty is less than $1\ \mathrm{kg \cdot m^{-3}}$. 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, showed that they can represent the viscosity of the binary mixtures with an average absolute deviation of 2%, corresponding to the experimental uncertainty.

KEY WORDS: cis-decalin; density; high pressure; hydrocarbon mixtures; methylcyclohexane; 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 fluids of interest, since it is impossible to measure the viscosity at all temperatures, pressures, and compositions. However, experimental viscosity measurements are required in order to

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0195-928X/03/0300-0361/0

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. However, 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 oils are multicomponent mixtures composed of these types of chemical species. Furthermore, oil accumulations exposed to biodegradation or alteration have been discovered. These fluids have a higher content of naphthenic and heavy hydrocarbons, because the intermediate alkanes (paraffins) between C_6 and C_{16} are the first compounds to vanish.

Since naphthenic compounds are important constituents in some oils and because, to the knowledge of the authors, no studies of the viscosity and density of mixtures only composed of naphthenic compounds versus temperature, pressure, and composition have been reported, an experimental study of the viscosity and density has been performed in this work in the temperature range 293.15 to 353.15 K and at pressures up to 100 MPa for the binary system composed of methylcyclohexane and cis-decahydronaphthalene (cis-decalin) in order to provide data for the evaluation of predictive models for naphthenic fluids.

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. [1]. 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. 2. The calibration was performed using toluene [3], and n-decane [4, 5] 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 512 P high pressure cell. The calibration of the densimeter was performed using water and vacuum as described in Ref. 6. The density measurements were extrapolated up to 100 MPa using the following Tait-type equation, as suggested in Ref. 2, for the variation of the density versus 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. 2 and evaluated using values taken from Dymond et al. [7] 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 discussed in Ref. 2.

For the high-pressure viscosity and density measurements, the uncertainty in the temperature was estimated to be ±0.5 K 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 $1\ \mathrm{kg \cdot m^{-3}}$, while the relative uncertainty in the viscosity values is of the order of 2% at high pressure. As discussed previously in Refs. 2 and 8 to 10, 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 work are commercially available chemicals with the following purity levels: methylcyclohexane from Aldrich with a purity >99% and a molar mass $M_w = 98.19\ \mathrm{g \cdot mol^{-1}}$, and cis-decalin from Fluka with a purity >98% and a molar mass $M_w = 138.26\ \mathrm{g \cdot mol^{-1}}$. The binary mixtures composed of methylcyclohexane (1) and cis-decalin (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 methylcyclohexane, $x_1 = 0.125$, 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. The studied samples are in the liquid state within the experimental temperature and pressure ranges of this study.

3. RESULTS

For the pure compounds and the seven binary mixtures, measurements of the dynamic viscosity and the density were performed from 293.15 to

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

		$x_1 = 0.000$		$x_1 = 0.125$		$x_1 = 0.250$	
T (K)	P (MPa)	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})
293.15	0.1	3.355	896.8	2.749	884.5	2.287	870.7
293.15	20	4.389	907.9	3.625	895.9	2.899	882.7
293.15	40	5.589	917.9	4.568	906.2	3.619	893.4
293.15	60	7.096	926.8	5.739	915.5	4.505	902.6
293.15	80	8.974	935.0[a]	7.183	924.0[a]	5.588	911.0[a]
293.15	100	11.302	942.5[a]	8.953	931.9[a]	6.904	918.7[a]
303.15	0.1	2.704	889.1	2.241	876.3	1.912	862.5
303.15	20	3.455	901.0	2.887	888.8	2.394	875.4
303.15	40	4.391	911.3	3.634	899.4	2.994	886.4
303.15	60	5.533	920.6	4.543	908.9	3.712	896.4
303.15	80	6.909	928.9[a]	5.633	917.2[a]	4.559	905.1[a]
303.15	100	8.555	936.6[a]	6.930	924.7[a]	5.551	913.0[a]
313.15	0.1	2.214	881.5	1.858	868.7	1.600	854.8
313.15	20	2.873	893.9	2.464	881.5	1.999	868.2
313.15	40	3.623	904.7	3.061	892.7	2.497	879.4
313.15	60	4.517	914.4	3.778	902.6	3.080	889.9
313.15	80	5.567	923.1[a]	4.623	911.5[a]	3.752	899.1[a]
313.15	100	6.785	931.1[a]	5.611	919.5[a]	4.517	907.5[a]
323.15	0.1	1.861	873.9	1.578	861.0	1.367	847.1
323.15	20	2.425	886.9	2.106	874.5	1.765	860.9
323.15	40	3.046	898.1	2.623	886.2	2.182	872.9
323.15	60	3.775	908.2	3.221	896.5	2.659	883.4
323.15	80	4.617	917.4[a]	3.903	905.5[a]	3.197	893.1[a]
323.15	100	5.577	925.7[a]	4.669	913.8[a]	3.794	901.7[a]
333.15	0.1	1.571	866.4	1.345	853.1	1.180	839.2
333.15	20	2.043	880.0	1.793	867.1	1.520	853.9
333.15	40	2.549	891.6	2.217	879.3	1.875	866.4
333.15	60	3.139	902.2	2.707	889.9	2.279	877.3
333.15	80	3.817	911.3[a]	3.263	899.4[a]	2.729	886.9[a]
333.15	100	4.586	919.7[a]	3.886	908.0[a]	3.225	895.7[a]
343.15	0.1	1.346	858.8	1.168	845.3	1.022	831.1
343.15	20	1.762	872.9	1.529	860.2	1.313	846.5
343.15	40	2.174	885.3	1.869	872.8	1.620	859.5
343.15	60	2.655	896.0	2.264	883.7	1.965	870.8
343.15	80	3.209	905.6[a]	2.717	893.4[a]	2.350	880.7[a]
343.15	100	3.842	914.3[a]	3.233	902.1[a]	2.776	889.6[a]
353.15	0.1	1.173	851.1	1.021	837.5	0.906	823.2
353.15	20	1.540	866.1	1.318	853.1	1.140	839.6
353.15	40	1.882	878.8	1.618	866.2	1.398	853.1
353.15	60	2.282	890.0	1.961	877.7	1.687	864.6
353.15	80	2.740	899.8[a]	2.347	887.7[a]	2.005	874.8[a]
353.15	100	3.257	908.6[a]	2.775	896.8[a]	2.350	883.8[a]

Table I. *(Continued)*

		$x_1 = 0.375$		$x_1 = 0.500$		$x_1 = 0.625$	
T (K)	P (MPa)	η (mPa · s)	ρ (kg·m^{-3})	η (mPa · s)	ρ (kg·m^{-3})	η (mPa · s)	ρ (kg·m^{-3})
293.15	0.1	1.867	856.0	1.541	840.9	1.300	824.7
293.15	20	2.342	868.5	1.944	853.7	1.648	838.3
293.15	40	2.921	879.2	2.450	864.9	2.015	850.1
293.15	60	3.634	889.0	3.026	874.8	2.459	860.2
293.15	80	4.504	897.8[a]	3.651	883.7[a]	2.991	869.6[a]
293.15	100	5.560	905.7[a]	4.313	891.7[a]	3.623	878.1[a]
303.15	0.1	1.567	847.9	1.312	832.6	1.096	816.4
303.15	20	1.968	861.1	1.704	846.6	1.416	830.8
303.15	40	2.433	872.5	2.115	858.2	1.738	843.0
303.15	60	2.994	882.9	2.568	868.7	2.103	853.9
303.15	80	3.660	891.5[a]	3.062	877.8[a]	2.510	862.8[a]
303.15	100	4.443	899.6[a]	3.593	886.2[a]	2.958	871.2[a]
313.15	0.1	1.326	839.9	1.123	824.6	0.944	808.2
313.15	20	1.724	853.7	1.469	839.1	1.201	823.3
313.15	40	2.130	865.6	1.812	851.5	1.489	836.2
313.15	60	2.594	876.0	2.181	862.0	1.815	847.1
313.15	80	3.115	885.4[a]	2.573	871.7[a]	2.163	856.8[a]
313.15	100	3.691	893.9[a]	2.981	880.3[a]	2.522	865.6[a]
323.15	0.1	1.168	832.3	0.986	816.6	0.837	800.0
323.15	20	1.486	846.7	1.262	831.8	1.053	815.7
323.15	40	1.839	859.2	1.550	844.4	1.288	829.4
323.15	60	2.231	870.2	1.874	855.6	1.560	840.8
323.15	80	2.644	880.0[a]	2.230	865.4[a]	1.869	850.8[a]
323.15	100	3.067	888.9[a]	2.616	874.1[a]	2.217	859.9[a]
333.15	0.1	0.990	824.3	0.860	808.5	0.726	791.3
333.15	20	1.271	839.7	1.094	824.2	0.922	808.2
333.15	40	1.573	852.7	1.360	837.7	1.133	822.3
333.15	60	1.905	864.1	1.652	849.4	1.367	834.2
333.15	80	2.256	874.0[a]	1.957	859.6[a]	1.620	844.7[a]
333.15	100	2.617	883.1[a]	2.271	868.8[a]	1.890	854.0[a]
343.15	0.1	0.869	816.2	0.765	800.2	0.632	783.1
343.15	20	1.132	832.4	0.945	817.5	0.808	801.1
343.15	40	1.389	845.9	1.156	831.2	0.998	815.4
343.15	60	1.666	857.4	1.394	843.4	1.205	827.9
343.15	80	1.961	867.6[a]	1.658	853.6[a]	1.427	838.4[a]
343.15	100	2.271	876.8[a]	1.944	862.9[a]	1.664	847.9[a]
353.15	0.1	0.773	808.2	0.682	792.0	0.568	774.7
353.15	20	1.001	825.0	0.819	809.8	0.703	793.6
353.15	40	1.236	839.4	1.002	824.3	0.873	808.7
353.15	60	1.487	851.4	1.215	837.1	1.063	821.6
353.15	80	1.747	862.3[a]	1.448	847.7[a]	1.263	832.8[a]
353.15	100	2.008	872.0[a]	1.693	857.2[a]	1.469	842.7[a]

Table I. *(Continued)*

		$x_1 = 0.750$		$x_1 = 0.875$		$x_1 = 1.000$	
T (K)	P (MPa)	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})	η (mPa·s)	ρ (kg·m^{-3})
293.15	0.1	1.076	805.2	0.894	789.1	0.736	769.2
293.15	20	1.344	819.5	1.118	803.8	0.937	784.6
293.15	40	1.642	832.2	1.360	816.6	1.138	797.6
293.15	60	1.992	843.2	1.633	827.3	1.366	808.9
293.15	80	2.399	853.1[a]	1.938	836.8[a]	1.622	818.9[a]
293.15	100	2.869	862.1[a]	2.277	845.4[a]	1.910	827.9[a]
303.15	0.1	0.935	795.4	0.776	780.4	0.640	760.5
303.15	20	1.147	812.1	0.958	796.1	0.811	776.8
303.15	40	1.402	825.2	1.170	809.2	0.999	790.4
303.15	60	1.693	836.5	1.408	820.8	1.203	802.2
303.15	80	2.021	845.9[a]	1.672	830.8[a]	1.422	812.5[a]
303.15	100	2.385	854.4[a]	1.962	839.9[a]	1.652	821.8[a]
313.15	0.1	0.824	788.7	0.674	771.9	0.568	751.7
313.15	20	1.003	805.2	0.839	788.5	0.721	769.0
313.15	40	1.231	818.9	1.030	801.9	0.885	783.4
313.15	60	1.487	830.5	1.243	814.0	1.067	795.6
313.15	80	1.768	840.8[a]	1.476	824.2[a]	1.266	806.2[a]
313.15	100	2.075	850.0[a]	1.727	833.4[a]	1.479	815.7[a]
323.15	0.1	0.701	779.6	0.604	763.1	0.505	742.9
323.15	20	0.882	797.5	0.746	780.7	0.650	761.3
323.15	40	1.084	811.8	0.916	795.2	0.802	776.3
323.15	60	1.308	824.1	1.104	807.7	0.969	789.1
323.15	80	1.554	834.4[a]	1.306	818.7[a]	1.147	800.3[a]
323.15	100	1.820	843.7[a]	1.521	828.4[a]	1.335	810.2[a]
333.15	0.1	0.629	770.9	0.534	754.5	0.453	734.0
333.15	20	0.775	789.9	0.662	773.2	0.577	753.6
333.15	40	0.954	804.9	0.817	788.4	0.709	769.3
333.15	60	1.153	817.5	0.988	801.2	0.857	782.6
333.15	80	1.371	828.4[a]	1.169	811.9[a]	1.018	794.0[a]
333.15	100	1.605	838.0[a]	1.355	821.7[a]	1.192	804.1[a]
343.15	0.1	0.570	762.6	0.484	745.7	0.409	724.9
343.15	20	0.679	782.2	0.590	765.7	0.510	746.0
343.15	40	0.833	797.9	0.722	781.5	0.632	762.4
343.15	60	1.007	811.2	0.869	795.0	0.767	776.3
343.15	80	1.199	822.4[a]	1.030	806.4[a]	0.912	788.0[a]
343.15	100	1.409	832.5[a]	1.205	816.6[a]	1.063	798.4[a]
353.15	0.1	0.483	755.7	0.413	736.9	0.371	715.9
353.15	20	0.595	774.8	0.515	757.8	0.461	738.2
353.15	40	0.741	791.4	0.641	774.7	0.567	755.6
353.15	60	0.899	805.0	0.778	788.5	0.687	770.0
353.15	80	1.068	817.2[a]	0.925	800.5[a]	0.820	782.1[a]
353.15	100	1.244	828.2[a]	1.081	811.1[a]	0.964	792.8[a]

[a] Densities determined by extrapolation using the Tait-type equation, Eq. (1).

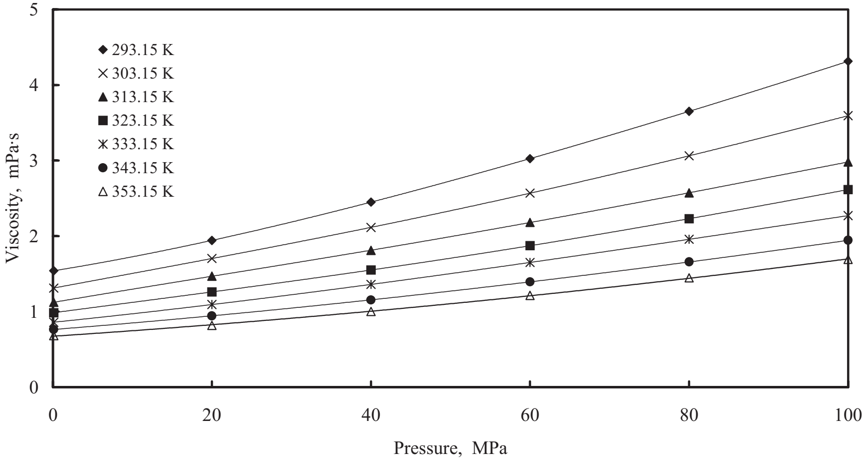

Fig. 1. Viscosity versus pressure for the binary mixture composed of 50 mol% methylcyclohexane and 50 mol% cis-decalin at various temperatures.

353.15 K in steps of 10 K, corresponding to 7 temperatures. The viscosity was measured at the following 6 pressures (0.1, 20, 40, 60, 80, and 100 MPa). A total of 378 experimental viscosity data were obtained, corresponding to 84 data for the two pure compounds and 294 data for the seven binary mixtures. The density measurements were carried out for pressures ranging from 0.1 to 60 MPa in steps of 5 MPa, resulting in 91

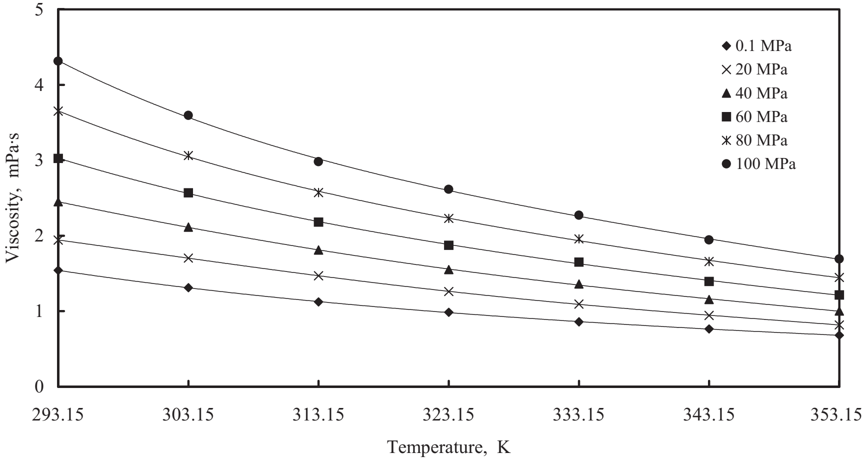

Fig. 2. Viscosity versus temperature for the binary mixture composed of 50 mol% methylcyclohexane and 50 mol% cis-decalin at various pressures.

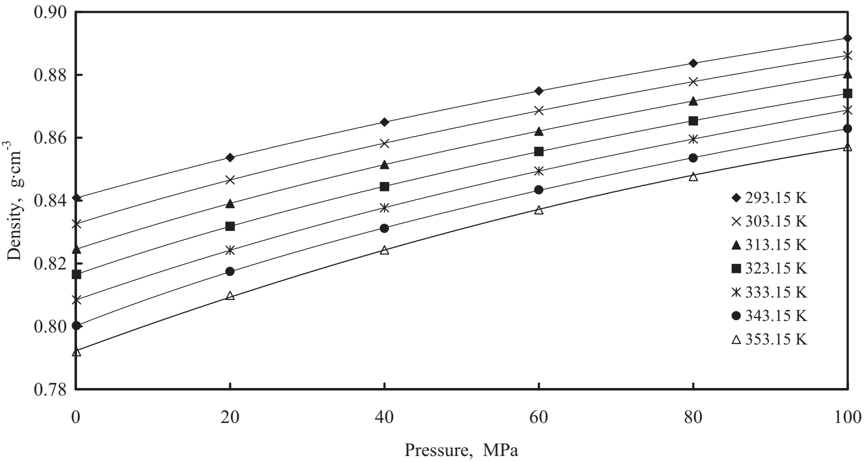

Fig. 3. Density versus pressure for the binary mixture composed of 50 mol% methylcyclohexane and 50 mol% cis-decalin at various temperatures.

measured values for each sample. In order to obtain the densities at 80 and 100 MPa, the isothermal density measurements were extrapolated up to 100 MPa with the aid of the Tait-type relationship given in Eq. (1), corresponding to 28 values for each sample.

The measured dynamic viscosity and density values of the studied samples are reported in Table I as a function of temperature T, pressure P,

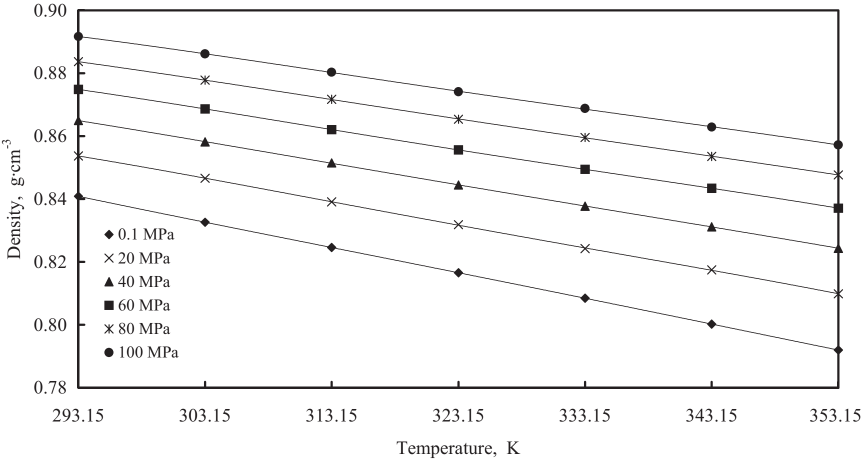

Fig. 4. Density versus temperature for the binary mixture composed of 50 mol% methylcyclohexane and 50 mol% cis-decalin at various pressures.

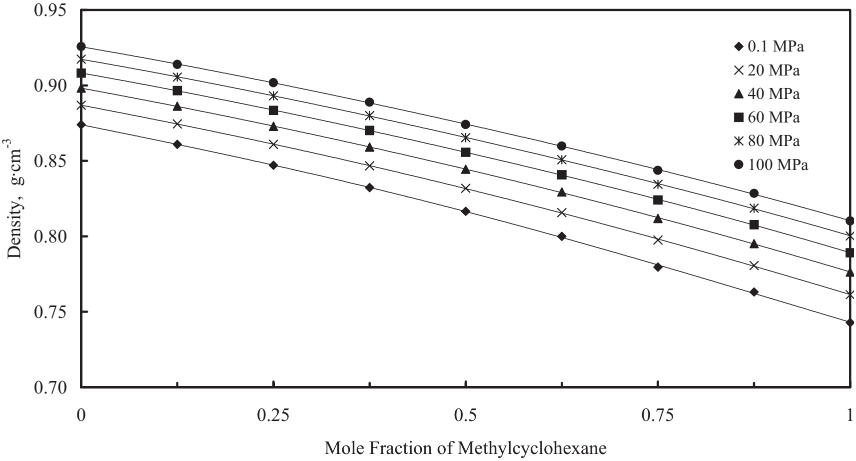

Fig. 5. Density versus the mole fraction of methylcyclohexane at 323.15 K for various isobars.

and mole fraction of methylcyclohexane (x_1). The viscosity of the equimolar mixture is shown in Fig. 1 versus pressure for various isotherms and in Fig. 2 versus temperature for various isobars. Figures 3 and 4 show the density behavior of the equimolar mixture versus pressure for various isotherms and versus temperature for various isobars, respectively. Figures 1 to 4 along with Table I reveal a general behavior consistent with

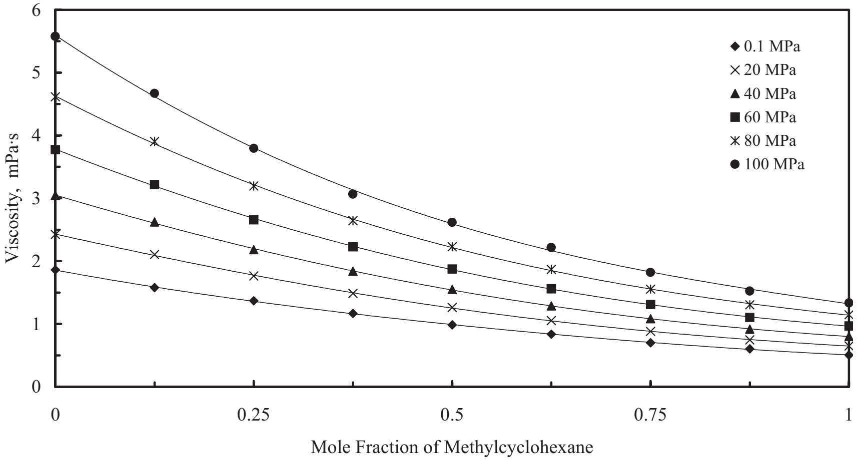

Fig. 6. Viscosity versus the mole fraction of methylcyclohexane at 323.15 K for various isobars.

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 viscosity with pressure is sharply increasing. 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 density versus pressure is compatible with the logarithmic relationship used in the Tait-type density relation 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. Furthermore, Fig. 5 presents the density at 323.15 K as a function of the composition for different pressures. In Fig. 6 the viscosity as a function of the composition at 323.15 K is shown for several isobars, whereas Fig. 7 presents the viscosity at 60 MPa versus the composition for several isotherms. These figures show a monotonic decrease in the viscosity with increasing composition of methylcyclohexane at constant temperature and pressure. Similar plots can be obtained for other temperatures and pressures.

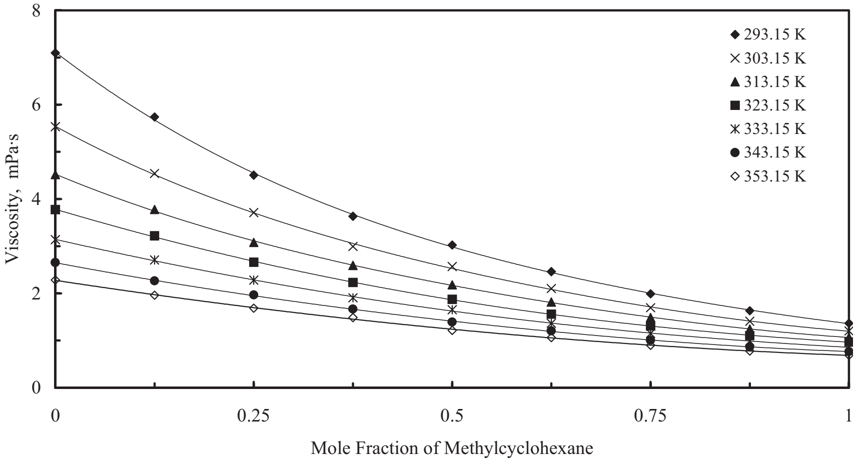

Fig. 7. Viscosity versus the mole fraction of methylcyclohexane at 60 MPa for various isotherms.

4. DISCUSSION

The viscosity and density data obtained for the binary system methylcyclohexane (1) + cis-decalin (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. Two of the more well-known mixing laws derived for binary mixtures are the Grunberg–Nissan [11] and Katti–Chaudhri [12] laws.

For the case of the Grunberg–Nissan mixing law, 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, an overall absolute average deviation (AAD) of 2.18% is obtained by comparing the calculated values with the experimental values for the binary system methylcyclohexane + cis-decalin. The maximum absolute deviation (MxD) is 7.71% obtained at 293.15 K and 100 MPa for the equimolar mixture. The results are comparable to the experimental uncertainty of 2% and can be considered satisfactory, since the Grunberg–Nissan mixing law is totally predictive in the sense that no adjustable parameter is required, only the viscosity and composition of the pure compounds. However, with this relationship, the variation of the viscosity with composition becomes monotonic, and any interactions between the pure compounds influencing the total viscosity is not taken into account. The Grunberg–Nissan mixing law can be modified by introducing an adjustable parameter believed to be representative in some way of the interactions within the binary system. The following expression given in Eq. (3) is the original expression proposed by Grunberg and Nissan [11] 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 quantitative characteristic of the intermolecular interactions between component 1 and component 2. By modeling the viscosity data given in Table I, the adjustable parameter ($d_{1,2} = -0.0860129$) has been obtained, resulting in an AAD of 1.79% and a MxD of 5.42%, again at 293.15 K and 100 MPa for the equimolar mixture. The obtained results are satisfactory in the sense that the AAD is within the experimental uncertainty of 2%. The introduction of an adjustable parameter in the Grunberg–Nissan mixing law improves only slightly the viscosity correlation compared to the results obtained by Eq. (2) for the binary system methylcyclohexane + cis-decalin. Furthermore, it should be stressed that the model is no longer totally predictive, when an adjustable binary parameter is introduced.

The Katti–Chaudhri mixing law for a binary mixture can be expressed as

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

where $v = M_w/\rho$ is the molar volume, M_w is the molar mass, and ρ is the density. For a binary mixture the molar mass is defined as $M_w = x_1 M_{w,1} + x_2 M_{w,2}$. By applying this mixing law to the binary system methylcyclohexane + cis-decalin using the experimental pure component viscosities and densities along with the mixture densities, an AAD of 2.02% is obtained when comparing the calculated viscosities with the experimental values. The resultant MxD is 7.17%, which is obtained at 293.15 K and 100 MPa for the equimolar mixture. Although the Katti–Chaudhri mixing law also incorporates the density in the viscosity calculations, similar results are obtained for the binary system compared with those obtained with the more simple mixing law of Grunberg and Nissan given in Eq. (2). The Katti–Chaudhri mixing law can be modified by introducing an adjustable parameter $w_{1,2}$ representative of the interactions within the binary system,

$$\ln(\eta_{mx} v_{mx}) = x_1 \ln(\eta_1 v_1) + x_2 \ln(\eta_2 v_2) + x_1 x_2 w_{1,2} \tag{5}$$

The adjustable parameter ($w_{1,2} = -0.07078856$) has been estimated by a least-squares minimization procedure using the data given in Table I. The resulting AAD is 1.74% with a MxD of 5.29%, again at 293.15 K and 100 MPa for the equimolar mixture. These results are similar to those obtained with the Grunberg–Nissan mixing law, when an adjustable parameter is introduced (Eq. (3)).

Finally, according to the literature [13–17], the negative values of $w_{1,2}$ (the excess activation energy for viscous flow is defined by $x_1 x_2 \mathrm{RT} w_{1,2}$) means that the predominant effect in the mixture is the breaking up of the ordered structures present in the pure liquid, and the low values of the excess activation energy for viscous flow indicate that this effect is small in this case. In other words, the repulsive forces of interaction are the forces which predominate, corresponding to the breaking of the bonds within the ordered structure.

5. CONCLUSION

The viscosity and density of methylcyclohexane, cis-decalin, and seven binary mixtures have been measured in the liquid state in the temperature range 293.15 to 353.15 K and at pressures up to 100 MPa. The experimental uncertainty for the viscosity measurements is less than 2%, and these measurements have been performed with a falling-body viscometer, except at 0.1 MPa where a classical capillary viscometer has been used. For the density values the uncertainty is less than $1\ \mathrm{kg \cdot m^{-3}}$. The viscosity and density data obtained in this study will be used in a future evaluation of the performance of different representative viscosity models incorporating the effects of temperature, pressure and composition. Such models may range from simple empirical correlations to models with a physical and theoretical background. However, a preliminary study has been carried out in this work focusing on the simple mixing laws by Grunberg–Nisaan [11] and Katti–Chaudhri [12], showing that these mixing laws can represent the viscosity of the binary system methylcyclohexane + cis-decalin within the experimental uncertainty. Similar results are obtained with both mixing laws, despite the fact that the molar volume is incorporated in the Katti–Chaudhri mixing law. Finally, this study is part of a more general study concerning hydrocarbon and petroleum systems undertaken in the laboratory.

ACKNOWLEDGEMENTS

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

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