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High-Pressure Viscosity and Density Measurements of the Ternary System Methylcyclohexane + *cis*-Decalin + 2,2,4,4,6,8,8-Heptamethylnonane

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Measurements of the dynamic viscosity and density of a ternary system composed of methylcyclohexane + *cis*-decahydronaphthalene (*cis*-decalin) + 2,2,4,4,6,8,8-heptamethylnonane have been performed for 13 different compositions at 7 isotherms in the range 293.15 K to 353.15 K and 6 isobars 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 <2%. 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 <1 $kg \cdot m^{-3}$. The measured data (546 data points for the viscosity) have been used in an evaluation of the simple mixing laws of Grunberg and Nissan and of Katti and Chaudhri. This evaluation showed that these mixing laws, despite their simplicity, can represent the viscosity of this asymmetrical ternary system with a satisfactory accuracy.

1. Introduction

An extensive experimental study of the dynamic viscosity η along with the density ρ of the ternary system composed of the highly branched alkane 2,2,4,4,6,8,8-heptamethylnonane and the two naphthenic compounds methylcyclohexane and *cis*-decahydronaphthalene (*cis*-decalin) has been performed up to 100 MPa from 293.15 K to 353.15 K. This system was chosen in order to provide data for asymmetrical systems containing naphthenes and heavy, highly branched paraffins, since these components are also important constituents of oils and petroleum fluids, such as oil accumulations exposed to biodegradation or alteration. In these accumulations the fluids have a higher content of naphthenic and heavy hydrocarbons, because biodegradation and alteration result in decomposition loss of the intermediate “normal“ alkanes between C_6 and C_{16}, resulting in fluids with a more dissimilar or asymmetrical molecular distribution.

The three pure compounds and the three additional binary systems have already been studied under the abovementioned temperature and pressure conditions,[1−3] resulting in 126 data points for the three pure compounds and 882 data points for the three binary systems with an uncertainty for the density of <1 $kg \cdot m^{-3}$ and for the viscosity of <2% at high pressure. To complete this extensive study of the ternary system methylcyclohexane + *cis*-decalin + 2,2,4,4,6,8,8-heptamethylnonane and to provide a representative coverage of the ternary diagram, the viscosity and density of 13 ternary mixtures (see Figure 1) have been measured under the same temperature and pressure conditions as those for the pure compounds and the binary systems.

It should be stressed here that experimental data are of great importance in the development and evaluation of property models of fundamental and industrial interest.

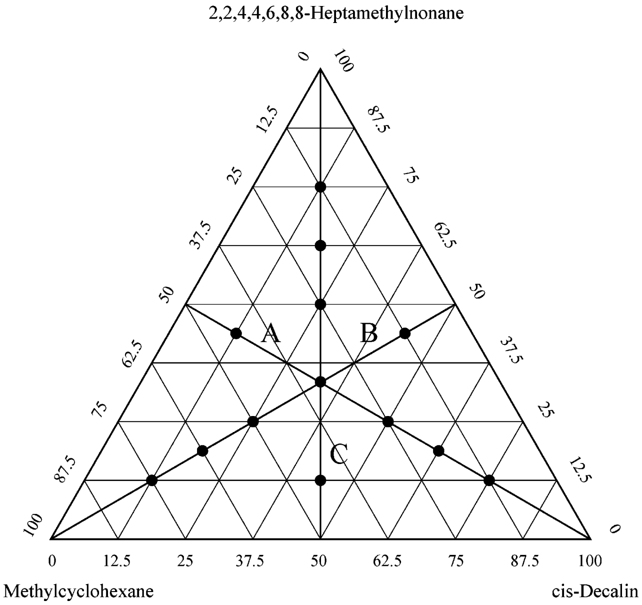

Figure 1. Ternary diagram representing the composition in mole percent of the studied ternary mixtures shown as points on lines A, B, and C, respectively.

The viscosity is one of these properties and is required in many engineering disciplines ranging from the design of transport equipment to simulations of petroleum reservoirs. As already mentioned in previous papers,[4−6] despite this importance, most experimental studies reported in the literature on mixtures have primarily been performed versus temperature and composition at atmospheric pressure, whereas studies under pressure are less frequent, especially for multicomponent fluids. The experimental studies performed under pressure have generally been conducted on binary systems versus temperature and composition, whereas there are only a few systematic and extensive studies of ternary mixtures.[4−7] Because of this,

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Table 1. Density ρ and Viscosity η versus Temperature T and Pressure P for Ternary Mixtures Composed of Methylcyclohexane (1) + *cis*-Decalin (2) + 2,2,4,4,6,8,8-Heptamethylnonane (3)

		$x_1 = x_2 = 0.1250$; $x_3 = 0.7500$		$x_1 = x_2 = 0.1875$; $x_3 = 0.6250$		$x_1 = x_2 = 0.2500$; $x_3 = 0.5000$		$x_1 = x_3 = 0.4375$; $x_2 = 0.1250$		$x_1 = 0.1250$; $x_2 = x_3 = 0.4375$		$x_1 = x_2 = x_3 =$ 0.3333	
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	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	792.7	3.12_2	797.7	2.83_5	803.4	2.54_3	791.3	1.96_7	820.7	2.95_7	812.5	2.18_3
293.15	20	805.7	4.46_1	810.7	4.01_7	816.4	3.46_6	804.9	2.67_3	833.0	4.08_7	825.5	2.93_4
293.15	40	816.8	6.20_6	821.7	5.47_2	827.4	4.62_8	816.2	3.51_1	843.8	5.44_7	836.6	3.81_0
293.15	60	826.2	8.58_7	831.4	7.41_2	837.2	6.14_5	826.2	4.57_6	853.2	7.23_7	846.3	4.93_2
293.15	80	834.7^a	11.8_0	840.0^a	9.96_7	845.7^a	8.10_0	834.8^a	5.91_5	861.6^a	9.56_5	854.9^a	6.34_7
293.15	100	842.4^a	16.1_0	847.7^a	13.3_1	853.4^a	10.6_0	842.6^a	7.58_3	869.2^a	12.5_7	862.6^a	8.11_6
303.15	0.1	785.9	2.50_8	790.8	2.28_9	796.5	2.07_8	784.2	1.63_3	813.7	2.38_9	805.2	1.80_0
303.15	20	799.3	3.52_9	804.5	3.17_0	810.0	2.79_6	798.4	2.19_4	826.6	3.23_5	818.7	2.38_9
303.15	40	810.8	4.81_3	816.1	4.27_7	821.5	3.67_0	810.2	2.86_3	837.8	4.28_5	830.5	3.08_0
303.15	60	820.7	6.53_3	825.9	5.71_6	831.5	4.80_2	820.5	3.69_1	847.5	5.62_3	840.7	3.94_3
303.15	80	829.5^a	8.82_4	834.6^a	7.57_5	840.4^a	6.25_5	829.7^a	4.71_0	856.3^a	7.31_8	849.9^a	5.01_4
303.15	100	837.5^a	11.8_6	842.3^a	9.96_9	848.4^a	8.11_5	837.9^a	5.95_6	864.2^a	9.45_4	858.2^a	6.33_5
313.15	0.1	779.1	2.05_9	783.8	1.89_5	789.5	1.73_4	777.0	1.38_1	806.7	1.97_1	798.0	1.51_0
313.15	20	793.2	2.90_3	797.8	2.59_9	803.8	2.33_0	791.7	1.86_4	820.3	2.67_2	812.4	2.02_2
313.15	40	805.2	3.94_9	809.7	3.45_4	815.6	3.03_3	804.0	2.41_6	831.9	3.53_0	824.2	2.59_6
313.15	60	815.8	5.27_2	820.2	4.55_6	826.2	3.92_7	814.9	3.07_7	842.2	4.57_9	834.9	3.28_4
313.15	80	824.9^a	6.92_2	829.5^a	5.95_7	835.6^a	5.04_8	824.5^a	3.85_6	851.3^a	5.84_4	844.3^a	4.09_5
313.15	100	833.1^a	8.96_3	837.9^a	7.72_2	844.0^a	6.44_1	833.1^a	4.76_5	859.7^a	7.35_3	852.7^a	5.04_1
323.15	0.1	772.5	1.71_8	776.9	1.60_7	782.5	1.46_2	769.6	1.18_0	799.7	1.65_1	790.7	1.28_9
323.15	20	787.0	2.39_7	791.6	2.18_7	797.3	1.98_7	785.4	1.60_7	814.0	2.25_7	805.8	1.71_5
323.15	40	799.5	3.21_6	804.3	2.90_2	809.7	2.60_0	798.2	2.07_0	826.0	2.94_3	817.8	2.20_2
323.15	60	810.7	4.23_6	815.0	3.78_6	820.9	3.34_8	809.5	2.61_3	836.8	3.77_8	829.3	2.77_4
323.15	80	820.3^a	5.49_0	824.6^a	4.86_4	830.2^a	4.24_8	818.9^a	3.24_1	846.1^a	4.78_0	838.7^a	3.43_5
323.15	100	829.0^a	7.01_7	833.1^a	6.16_5	838.8^a	5.31_7	827.5^a	3.99_7	854.6^a	5.96_9	847.4^a	4.19_0
333.15	0.1	765.9	1.45_5	770.0	1.36_4	775.2	1.25_6	762.3	1.02_4	792.7	1.40_9	783.3	1.11_1
333.15	20	781.8	2.02_5	786.0	1.87_2	791.1	1.70_8	778.9	1.38_2	807.8	1.90_8	799.2	1.47_4
333.15	40	794.9	2.69_5	799.2	2.45_6	804.5	2.21_7	792.5	1.76_5	820.7	2.46_8	812.5	1.88_6
333.15	60	806.0	3.51_9	810.3	3.17_4	815.5	2.83_3	804.0	2.22_3	831.4	3.14_7	823.7	2.37_3
333.15	80	815.7^a	4.51_6	820.0^a	4.04_2	825.2^a	3.56_6	814.0^a	2.76_3	841.1^a	3.96_0	833.6^a	2.94_2
333.15	100	824.4^a	5.67_3	828.6^a	5.04_8	833.9^a	4.40_1	822.9^a	3.39_6	849.8^a	4.88_8	842.5^a	3.57_2
343.15	0.1	759.1	1.25_9	763.1	1.17_6	768.2	1.08_8	755.0	0.90_2	785.5	1.21_4	775.9	0.97_2
343.15	20	775.9	1.75_5	780.1	1.59_3	785.2	1.48_4	772.6	1.21_2	801.8	1.61_8	792.6	1.30_2
343.15	40	789.4	2.31_1	793.9	2.05_9	798.8	1.91_0	786.7	1.53_7	815.0	2.06_1	806.5	1.64_4
343.15	60	800.6	2.97_3	804.8	2.61_7	810.4	2.40_7	798.6	1.91_9	826.3	2.60_1	817.9	2.03_8
343.15	80	810.6^a	3.77_7	814.5^a	3.30_3	820.4^a	2.99_9	808.9^a	2.37_9	835.7^a	3.27_2	828.3^a	2.50_3
343.15	100	819.2^a	4.68_9	823.1^a	4.08_6	829.4^a	3.65_4	818.1^a	2.93_9	844.2^a	4.04_9	837.4^a	3.00_9
353.15	0.1	752.1	1.09_2	756.1	1.03_4	761.1	0.95_6	747.6	0.78_9	778.3	1.06_1	768.5	0.85_8
353.15	20	769.7	1.50_0	773.9	1.38_4	778.6	1.26_4	766.2	1.06_7	795.2	1.41_8	786.0	1.12_9
353.15	40	783.8	1.95_9	787.8	1.78_8	793.0	1.62_3	780.8	1.35_1	808.9	1.79_6	800.2	1.42_9
353.15	60	795.6	2.50_7	799.7	2.26_3	805.1	2.04_8	793.1	1.69_2	820.7	2.24_4	812.3	1.77_4
353.15	80	805.7^a	3.15_6	809.8^a	2.81_9	815.6^a	2.54_7	803.8^a	2.09_4	830.8^a	2.76_8	822.8^a	2.16_9
353.15	100	814.6^a	3.91_7	818.8^a	3.46_2	824.9^a	3.12_6	813.1^a	2.56_4	839.9^a	3.37_5	832.2^a	2.61_5

		$x_1 = 0.5000$; $x_2 = x_3 = 0.2500$		$x_1 = x_3 = 0.2500$; $x_2 = 0.5000$		$x_1 = 0.6250$; $x_2 = x_3 = 0.1875$		$x_1 = x_3 = 0.1875$; $x_2 = 0.6250$		$x_1 = 0.7500$; $x_2 = x_3 = 0.1250$		$x_1 = x_2 = 0.4375$; $x_3 = 0.1250$		$x_1 = x_3 = 0.1250$; $x_2 = 0.7500$	
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	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
293.15	0.1	804.5	1.70_3	830.9	2.41_6	798.0	1.39_3	845.8	2.57_3	789.5	1.13_3	828.1	1.76_9	861.1	2.76_9
293.15	20	817.8	2.25_2	843.6	3.19_6	811.9	1.81_9	858.1	3.45_3	803.8	1.48_3	841.1	2.31_3	873.2	3.64_4
293.15	40	829.2	2.87_1	854.4	4.14_2	823.8	2.28_6	868.6	4.44_1	816.0	1.83_6	852.3	2.91_1	883.6	4.70_8
293.15	60	839.2	3.63_5	863.9	5.34_3	834.0	2.85_6	878.2	5.69_8	826.7	2.25_1	862.2	3.64_5	892.7	6.03_5
293.15	80	848.1^a	4.56_5	872.2^a	6.84_7	843.1^a	3.53_8	886.7^a	7.27_4	836.1^a	2.73_1	870.9^a	4.53_0	901.1^a	7.66_9
293.15	100	856.2^a	5.68_5	879.8^a	8.71_5	851.3^a	4.34_9	894.5^a	9.23_5	844.7^a	3.28_0	878.9^a	5.58_7	908.7^a	9.66_1
303.15	0.1	797.0	1.43_2	823.7	1.98_6	790.4	1.18_0	838.4	2.11_9	781.6	0.97_0	820.6	1.48_1	853.5	2.26_4
303.15	20	811.3	1.85_4	836.8	2.62_0	805.1	1.53_0	851.1	2.79_3	796.6	1.25_3	834.0	1.92_0	866.3	2.96_7
303.15	40	823.6	2.34_0	848.1	3.36_4	817.3	1.91_3	862.3	3.59_9	809.4	1.54_7	845.9	2.40_6	876.6	3.77_8
303.15	60	833.6	2.93_9	857.9	4.28_2	827.9	2.36_8	872.3	4.57_9	820.4	1.89_3	856.0	2.98_7	886.8	4.77_7
303.15	80	843.0^a	3.67_2	866.7^a	5.41_1	837.3^a	2.90_6	881.0^a	5.76_3	829.9^a	2.29_8	865.3^a	3.67_8	895.2^a	6.00_1
303.15	100	851.4^a	4.56_3	874.7^a	6.78_8	845.8^a	3.53_7	889.1^a	7.18_7	838.5^a	2.76_8	873.7^a	4.49_4	903.1^a	7.49_2
313.15	0.1	789.7	1.21_3	816.4	1.65_8	782.7	1.01_4	831.2	1.76_2	773.7	0.84_4	813.0	1.26_0	845.9	1.87_5
313.15	20	804.3	1.57_4	830.1	2.16_3	797.9	1.31_4	844.4	2.30_5	789.4	1.09_3	827.2	1.61_8	859.2	2.50_1
313.15	40	816.8	1.99_9	841.8	2.75_9	810.7	1.64_4	856.0	2.94_8	802.6	1.35_1	839.3	2.03_1	870.2	3.18_8
313.15	60	827.7	2.49_6	852.2	3.48_7	821.8	2.02_8	866.3	3.72_0	814.1	1.64_2	850.5	2.51_3	880.3	4.00_3
313.15	80	837.2^a	3.06_9	861.4^a	4.36_2	831.7^a	2.46_8	875.5^a	4.63_0	824.2^a	1.96_3	859.8^a	3.06_7	889.1^a	4.95_2
313.15	100	845.9^a	3.72_1	869.7^a	5.40_5	840.7^a	2.96_5	883.9^a	5.69_5	833.2^a	2.31_4	868.5^a	3.69_7	897.2^a	6.04_7
323.15	0.1	782.2	1.05_0	809.1	1.40_8	775.0	0.88_4	823.8	1.48_7	765.7	0.73_8	805.3	1.08_4	838.4	1.58_5
323.15	20	797.8	1.36_9	823.7	1.83_2	791.0	1.15_0	838.0	1.96_5	782.5	0.95_7	820.2	1.42_9	852.2	2.11_4
323.15	40	810.7	1.72_9	835.8	2.35_5	804.3	1.44_2	849.7	2.50_1	796.6	1.18_6	833.0	1.78_6	864.0	2.69_1
323.15	60	822.2	2.14_8	846.8	2.96_6	816.2	1.76_9	860.5	3.13_2	808.4	1.44_3	844.1	2.19_5	874.4	3.36_3
323.15	80	831.6^a	2.62_9	856.1^a	3.66_8	826.2^a	2.12_9	869.9^a	3.86_1	818.7^a	1.72_7	854.1^a	2.65_3	883.8^a	4.13_5
323.15	100	840.4^a	3.17_3	864.7^a	4.46_6	835.4^a	2.51_9	878.5^a	4.69_4	828.0^a	2.03_6	863.0^a	3.16_2	892.3^a	5.00_9
333.15	0.1	774.7	0.91_6	801.8	1.20_7	767.2	0.77_4	816.5	1.28_0	757.7	0.65_4	797.7	0.94_5	831.0	1.35_8
333.15	20	791.1	1.19_8	817.0	1.58_4	784.5	1.00_1	831.4	1.68_2	775.6	0.85_5	813.6	1.23_5	845.6	1.77_3
333.15	40	804.9	1.50_3	830.0	2.00_0	798.8	1.25_3	844.1	2.11_9	790.1	1.06_6	826.9	1.53_2	858.0	2.23_3
333.15	60	816.5	1.86_1	840.9	2.50_4	810.5	1.54_0	855.1	2.64_0	802.8	1.30_0	838.4	1.88_6	868.7	2.78_4
333.15	80	826.8^a	2.27_7	850.7^a	3.10_4	820.7^a	1.86_2	864.8^a	3.25_1	813.5^a	1.55_6	848.4^a	2.30_1	878.2^a	3.43_0

Table 1 (Continued)

		$x_1 = 0.5000$; $x_2 = x_3 = 0.2500$		$x_1 = x_3 = 0.2500$; $x_2 = 0.5000$		$x_1 = 0.6250$; $x_2 = x_3 = 0.1875$		$x_1 = x_3 = 0.1875$; $x_2 = 0.6250$		$x_1 = 0.7500$; $x_2 = x_3 = 0.1250$		$x_1 = x_2 = 0.4375$; $x_3 = 0.1250$		$x_1 = x_3 = 0.1250$; $x_2 = 0.7500$	
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	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
333.15	100	836.0[a]	2.73_3	859.6[a]	3.78_3	829.7[a]	2.20_4	873.6[a]	3.93_1	823.1[a]	1.81_9	857.3[a]	2.76_2	886.9[a]	4.15_3
343.15	0.1	767.2	0.80_8	794.4	1.04_7	759.5	0.68_8	809.0	1.10_9	749.7	0.58_7	789.9	0.82_8	823.6	1.17_6
343.15	20	784.6	1.04_7	810.6	1.38_6	777.8	0.88_0	824.7	1.45_1	768.7	0.76_4	806.6	1.09_2	838.9	1.53_6
343.15	40	798.8	1.31_2	823.9	1.73_9	792.7	1.09_8	837.8	1.80_5	783.9	0.95_2	820.5	1.34_9	851.6	1.91_4
343.15	60	810.8	1.61_8	835.4	2.15_3	804.9	1.34_1	849.3	2.21_8	797.1	1.15_4	832.3	1.64_6	862.7	2.36_4
343.15	80	821.1[a]	1.98_2	845.4[a]	2.65_0	815.4[a]	1.62_1	859.0[a]	2.71_0	807.7[a]	1.37_9	842.5[a]	1.99_6	872.4[a]	2.87_7
343.15	100	830.4[a]	2.37_4	854.4[a]	3.18_3	824.8[a]	1.91_6	867.9[a]	3.25_1	817.5[a]	1.60_7	851.7[a]	2.37_7	881.1[a]	3.46_7
353.15	0.1	759.5	0.71_6	786.9	0.92_2	751.5	0.61_9	801.5	0.98_0	741.6	0.52_6	782.0	0.73_6	816.0	1.03_1
353.15	20	778.0	0.91_4	804.0	1.22_3	770.9	0.77_8	817.7	1.29_4	761.8	0.67_7	799.8	0.95_8	832.0	1.33_4
353.15	40	793.0	1.14_7	817.9	1.52_3	786.0	0.97_0	831.5	1.60_5	777.7	0.84_3	814.1	1.18_1	845.2	1.68_6
353.15	60	805.2	1.41_3	829.8	1.87_8	798.7	1.18_9	843.3	1.96_2	790.9	1.03_0	826.8	1.43_2	856.6	2.08_1
353.15	80	815.9[a]	1.71_3	839.7[a]	2.29_2	809.6[a]	1.43_2	853.6[a]	2.36_4	802.2[a]	1.23_7	837.2[a]	1.71_1	866.7[a]	2.50_6
353.15	100	825.4[a]	2.04_8	848.7[a]	2.77^0	819.1[a]	1.70_0	862.7[a]	2.81_5	812.2[a]	1.45_5	846.8[a]	2.01_7	875.7[a]	2.95_2

[a] Extrapolated values using eq 1.

models incorporating the effects of temperature, pressure, and composition have primarily been developed on the basis of pure compounds and binary mixtures, although multicomponent mixtures are common in the oil industry, often under severe conditions and with compositional changes.

This study is a part of a more general study concerning various systems (associative and nonassociative mixtures, various binary mixtures with compounds of different chemical families, ternary systems, and even systems with more than three components) undertaken during several years by the laboratory.

2. Experimental Techniques

The dynamic viscosity was measured up to 100 MPa using a falling-body viscometer of the type designed by Ducoulombier et al.[8] In this apparatus, a stainless steel cylinder falls through the fluid of unknown viscosity under given conditions. The viscosity is a function of the falling time, the difference between the density of the cylinder and the 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 by Et-Tahir et al.[9] The calibration was performed using toluene,[10] and decane[11,12] was used to verify the calibration. At 0.1 MPa the dynamic viscosity was obtained by measuring the kinematic viscosity, $\nu = \eta/\rho$, with 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 by Lagourette et al.[13] The density measurements were extrapolated up to 100 MPa using the following Tait-type equation[9] for the isothermal variation of the density with pressure

$$\frac{1}{\rho(P,T)} = \frac{1}{\rho(0.1\ \mathrm{MPa},T)} + A \ln\left(1 + \frac{P/\mathrm{MPa} - 0.1}{B}\right) \quad (1)$$

where A and B are two adjustable constants. This method has been discussed[9] and evaluated using values taken from Dymond et al.[14] for pure alkanes and binary mixtures up to 500 MPa. Further, an error of 1 kg·m^{-3} in the density leads to an error of 1/8000 in the viscosity.[9]

For the high-pressure viscosity measurements and the 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 uncertainties in the reported density values are <1 kg·m^{-3}, while the relative uncertainty in the viscosity values is of the order of 2% at high pressure. As discussed previously,[9,15−17] this uncertainty is comparable with 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 <1%.

The three compounds used in this study are commercially available chemicals with the following purity levels: methylcyclohexane from Aldrich with a chemical purity > 99% (gas−liquid chromatography) and molecular weight $M_w = 98.19$ g·mol^{-1}, *cis*-decalin from Fluka with a chemical purity > 98% (gas chromatography) and $M_w = 138.36$ g·mol^{-1}, and 2,2,4,4,6,8,8-heptamethylnonane from Aldrich with a chemical purity > 98% (gas chromatography) and $M_w = 226.45$ g·mol^{-1}. No further purification or degassing of the pure compounds was performed. The ternary mixtures composed of methylcyclohexane (1), *cis*-decalin (2), and 2,2,4,4,6,8,8-heptamethylnonane (3) 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 13 compositions shown in Figure 1. An error of 0.001 g on weighing of any of the three compounds leads to an error of <0.002 mol % on the composition of the mixture. The samples were prepared immediately before their use, and the pure fluids were stored in hermetically sealed bottles. The samples studied in this work are in the liquid state within the experimental temperature and pressure ranges.

3. Results and Discussion

For the 13 ternary mixtures, measurements of the dynamic viscosity and the density were performed from 293.15 K to 353.15 K in steps of 10 K. The viscosity was measured at the following pressures, (0.1, 20, 40, 60, 80, and 100) MPa. A total of 546 experimental viscosity data were obtained, corresponding to 42 measurements per mixture. 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 mixture. The isothermal density measurements were extrapolated with the aid of the Tait-type relationship, eq 1, to obtain the densities at (80 and 100) MPa, corresponding to 28 values per mixture.

Table 1 presents the measured values of the dynamic viscosity and the corresponding density values of the

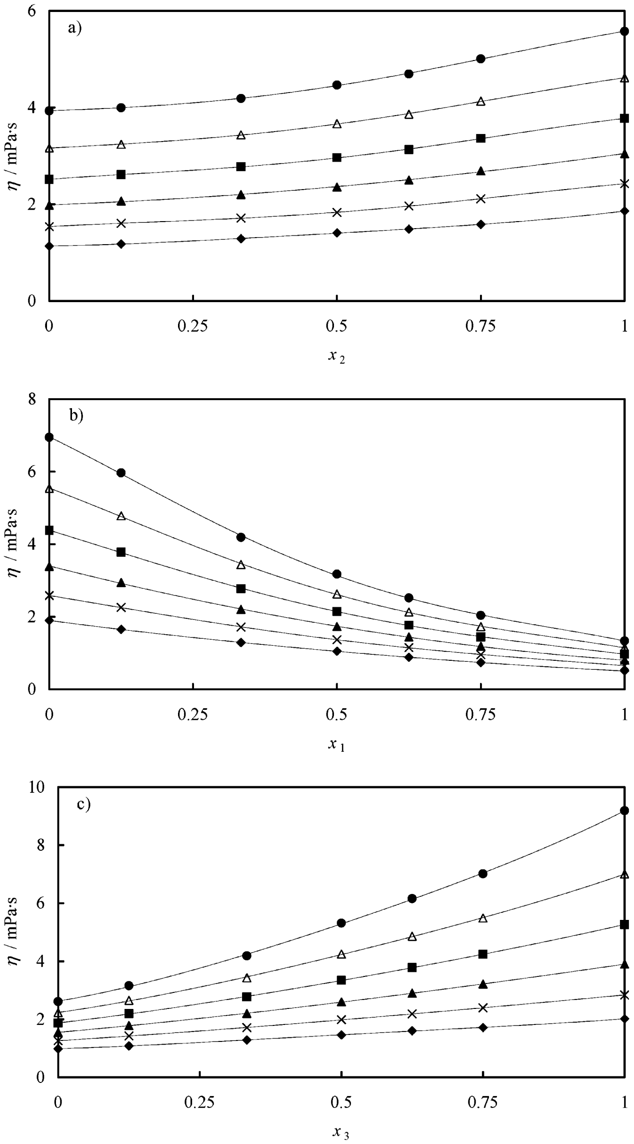

Figure 2. Dynamic viscosity η of the mixture methylcyclohexane (1) + *cis*-decalin (2) + 2,2,4,4,6,8,8-heptamethylnonane (3) with (a) $x_1 = x_3$ versus x_2 (line A in Figure 1), (b) $x_2 = x_3$ versus x_1 (line B in Figure 1), and (c) $x_1 = x_2$ versus x_3 (line C in Figure 1) at 323.15 K: ◆, 0.1 MPa; ×, 20 MPa; ▲, 40 MPa; ■, 60 MPa; △, 80 MPa; ●, 100 MPa.

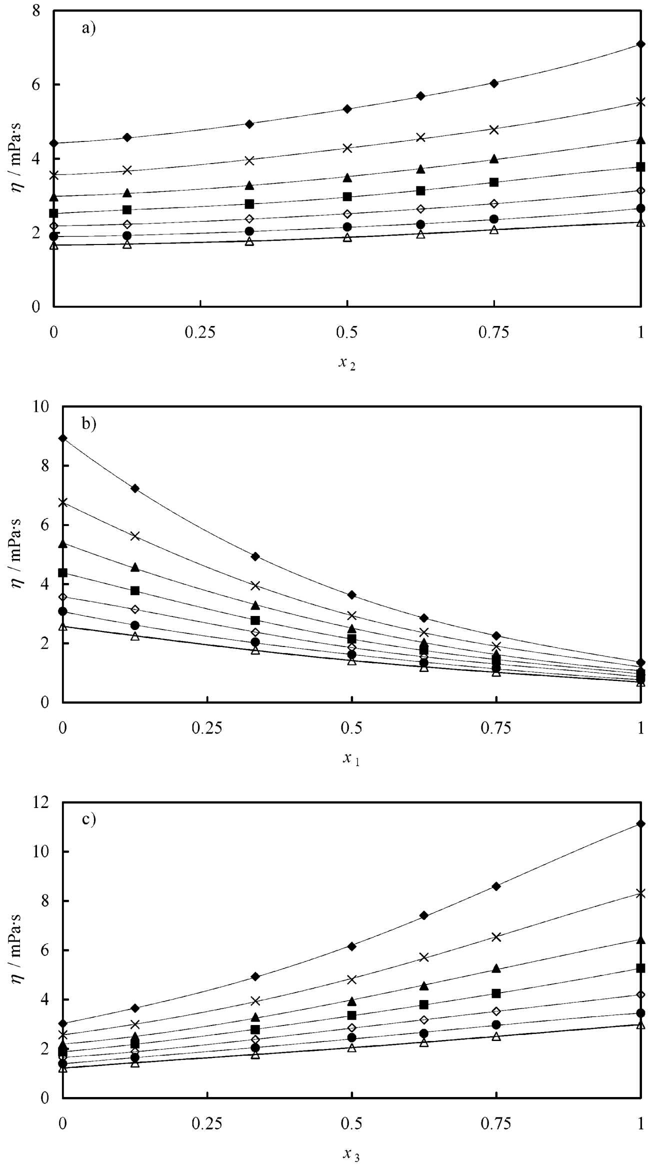

Figure 3. Dynamic viscosity η of the mixture methylcyclohexane (1) + *cis*-decalin (2) + 2,2,4,4,6,8,8-heptamethylnonane (3) with (a) $x_1 = x_3$ versus x_2 (line A in Figure 1), (b) $x_2 = x_3$ versus x_1 (line B in Figure 1), and (c) $x_1 = x_2$ versus x_3 (line C in Figure 1) at 60 MPa: ◆, 293.15 K; ×, 303.15 K; ▲, 313.15 K; ■, 323.15 K; ◇, 333.15 K; ●, 343.15 K; △, 353.15 K.

ternary samples composed of methylcyclohexane, *cis*-decalin, and 2,2,4,4,6,8,8-heptamethylnonane as a function of temperature T, pressure P, and mole fraction x. It should be stressed that for a given mixture the pressure dependence of the viscosity at constant temperature $(\partial\eta/\partial P)_T$ is greater than zero and the viscosity increases with pressure. This effect is more pronounced for mixtures with a high content of especially 2,2,4,4,6,8,8-heptamethylnonane, but also of *cis*-decalin, due to an important reduction of the fluid mobility with increasing pressure. This may be related to interlinking effects due to the molecular structure of the compounds. On the contrary, the temperature dependence of the viscosity at constant pressure $(\partial\eta/\partial T)_P$ is always less than zero. The variation of the density with pressure at constant temperature is concave with $(\partial\rho/\partial P)_T$ but is associated with a negative second derivative. The shape of the isothermal density behavior with 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 isobaric variation of the density with temperature is practically linear due to the small temperature interval (293.15 K to 353.15 K) considered in this investigation. Similar observations have previously been made by other authors and ourselves on different liquid systems.$^{1-5}$

Figure 2 shows the isobaric variation of the viscosity at 323.15 K versus the composition for each of the three lines (A, B, and C) in Figure 1. To complete this figure and the following figures, the reported data for the pure compounds and the binary mixtures$^{1-3}$ have been used. The isothermal variation of the viscosity at 60 MPa is presented in Figure 3 versus the composition for each of the three lines (A, B, and C) in Figure 1. The isobaric density behavior at 323.15 K is shown in Figure 4 versus the composition for each of the three lines (A, B, and C) in Figure 1, whereas Figure 5 presents the isothermal density variation at 60 MPa versus the composition for each of the three lines (A, B,

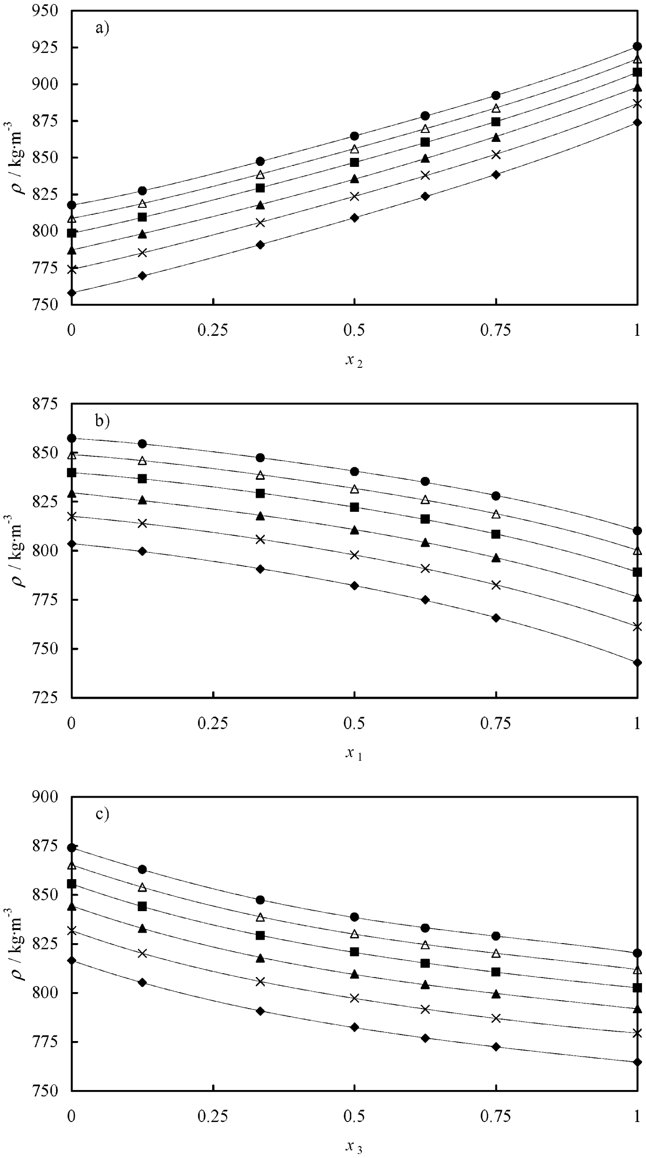

Figure 4. Density ρ of the mixture methylcyclohexane (1) + *cis*-decalin (2) + 2,2,4,4,6,8,8-heptamethylnonane (3) with (a) $x_1 = x_3$ versus x_2 (line A in Figure 1), (b) $x_2 = x_3$ versus x_1 (line B in Figure 1), and (c) $x_1 = x_2$ versus x_3 (line C in Figure 1) at 323.15 K: ◆, 0.1 MPa; ×, 20 MPa; ▲, 40 MPa; ■, 60 MPa; △, 80 MPa; ●, 100 MPa.

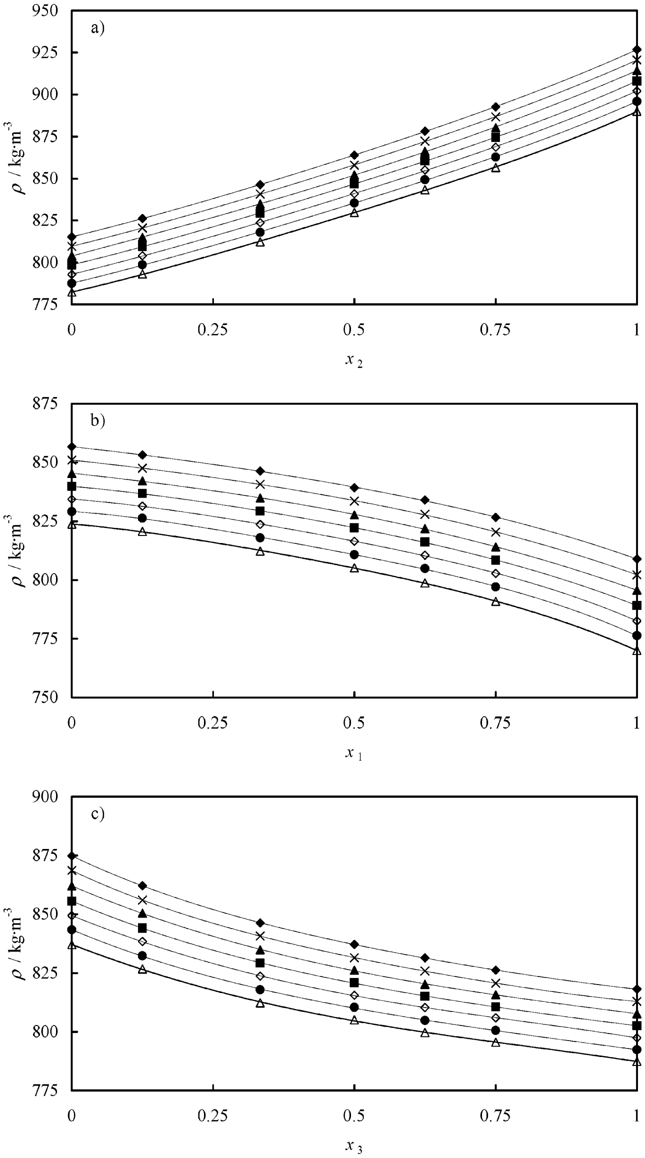

Figure 5. Density ρ of the mixture methylcyclohexane (1) + *cis*-decalin (2) + 2,2,4,4,6,8,8-heptamethylnonane (3) with (a) $x_1 = x_3$ versus x_2 (line A in Figure 1), (b) $x_2 = x_3$ versus x_1 (line B in Figure 1), and (c) $x_1 = x_2$ versus x_3 (line C in Figure 1) at 60 MPa: ◆, 293.15 K; ×, 303.15 K; ▲, 313.15 K; ■, 323.15 K; ◇, 333.15 K; ●, 343.15 K; △, 353.15 K.

and C) in Figure 1. These figures show that the viscosity increases monotonically as the more viscous components are approached. In addition, the density of the mixtures increases with increasing content of *cis*-decalin, since *cis*-decalin is the most dense fluid (higher density) of the three pure compounds. However, it should be stressed that 2,2,4,4,6,8,8-heptamethylnonane has the highest viscosity, which may be related to interlinking effects due to its molecular structure. Similar figures can be made for other temperatures and pressures.

4. Performance of Mixing Laws

The measured viscosity and density data for the 13 ternary mixtures along with the values for the pure compounds[1−3] 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 on the basis of 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,[18] which for a ternary mixture is given by

$$\ln(\eta_{\mathrm{mix}}) = \sum_{i=1}^{3} x_i \ln(\eta_i) \tag{2}$$

where x is the mole fraction and the subscripts mix and i refer to the mixture and the pure compounds, respectively. By comparing the calculated viscosities using eq 2 with the experimental values for the ternary mixtures (546 points), an overall absolute average deviation (AAD) of 3.9% is obtained with a maximum absolute deviation (MD) of 11% obtained at 343.15 K and 20 MPa for the ternary mixture composed of 43.75 mol % methylcyclohexane + 12.50 mol % *cis*-decalin + 43.75 mol % 2,2,4,4,6,8,8-heptamethylnonane. Despite the fact that the ternary mixtures are composed of two chemically different families, two naphthenes and a highly branched paraffin, 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 of the pure compounds and the composition.

The Katti and Chaudhri mixing law,[19] which in addition to the viscosity and composition also requires the molar volume, is shown below for a ternary mixture

$$\ln(\eta_{\text{mix}} v_{\text{mix}}) = \sum_{i=1}^{3} x_i \ln(\eta_i v_i) \qquad (3)$$

where $v = M_w/\rho$ is the molar volume and M_w is the molecular weight, which for a mixture is defined as $M_w = \sum x_i M_{w,i}$. In this case, using the measured densities in order to obtain v_{mix}, an AAD of 8.6% is obtained, when the viscosities calculated by eq 3 are compared with the experimental values. The resultant MD is 17.5%, obtained at 343.15 K and 100 MPa for the ternary mixture composed of 43.75 mol % methylcyclohexane + 12.5 mol % *cis*-decalin + 43.75 mol % 2,2,4,4,6,8,8-heptamethylnonane. Despite the fact that the Katti−Chaudhri mixing law also incorporates the molar volume in the viscosity calculations, the more simple Grunberg−Nissan mixing law, eq 2, gives better predictions for this ternary system.

5. Conclusion

The viscosity and density of 13 ternary mixtures composed of methylcyclohexane + *cis*-decalin + 2,2,4,4,6,8,8-heptamethylnonane have been measured in the temperature range 293.15 K to 353.15 K and up to 100 MPa (546 data points for viscosity). The uncertainty in the reported viscosity values is <2%, found at high pressure, while the uncertainty in the density is <1 kg·m^{-3}. The viscosity and density measurements reported in this work together with the measurements of the three pure compounds and the three corresponding binary systems[1−3] represent a fully comprehensive study of the ternary system methylcyclohexane + *cis*-decalin + 2,2,4,4,6,8,8-heptamethylnonane, which is described by a total of 1554 data points.

A preliminary study of two simple mixing laws (Grunberg−Nissan and Katti−Chaudhri) showed that these mixing laws, despite their simplicity, are able to adequately represent the viscosity of this asymmetrical ternary system. Finally, although, in some cases, the simple models give good results, the obtained viscosity and density data can be included in databases and used to carry out future extensive evaluations of the performance of different, more sophisticated viscosity models incorporating the effects of temperature, pressure, and composition.

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