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Density and Viscosity of Decalin, Cyclohexane, and Toluene Binary Mixtures at (283.15, 293.15, 303.15, 313.15, and 323.15) K

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Densities and viscosities for three binary systems, cyclohexane + toluene, cyclohexane + decalin, and toluene + decalin, at T = (283.15, 293.15, 303.15, 313.15, and 323.15) K have been measured over the whole composition range and atmospheric pressure along with the properties of the pure components. Viscosities deviations and excess molar volumes for the binary systems at the above-mentioned temperatures were calculated from experimental data and fitted to the Redlich−Kister expansion. In addition, the Prigogine−Flory−Patterson (PFP) model was used to correlate experimental density data. The Redlich−Kister expansion well correlated viscosity deviation and excess volume values. Shape and length asymmetries and molecular interaction asymmetries impact on viscosity deviations, but the latter had a more pronounced influence. Negative excess molar volumes were found when only shape and length asymmetries were present, while molecular interaction asymmetries led to positive values. The effects of simultaneous molecular interaction and length asymmetries were somehow additive for excess volume. The Prigogine−Flory−Patterson model well correlates density data and predicts qualitatively the excess molar volumes, but does not predict the temperature dependence on this property. Moreover, the results lead to the conclusion that the model fails when the molecular interaction term is omitted, even when the system presents only shape and length asymmetries.

Introduction

In many chemical engineering areas such as process design, oil fraction characterization, and others, accurate estimation of liquid mixture densities and viscosities as a function of composition and temperature is particularly important.[1] A considerable amount of work has been carried out on the measurement of density and viscosity of the liquid mixtures and the corresponding excess molar volumes and viscosity deviations.[2] In addition, many equations of state[3] and viscosity models[4−6] have been developed to predict liquid mixture properties.

In this work, experimental density, ρ, and viscosity, η, data are reported at T = (283.15, 293.15, 303.15, 313.15, and 323.15) K for three binary systems: cyclohexane + toluene, cyclohexane + decalin, and toluene + decalin.

All of the substances used are of industrial interest. Cyclohexane and decalin, for example, are used as solvents for vinyl and naphthalene resins,[7] respectively. Also, cyclohexane and toluene are typical naphtha molecules. In petroleum research, decalin is a reference naphthenic compound used to simulate kerosene and diesel fractions, especially as a geometrical isomeric mixture that is the more commonly found form. In this sense, studies of densities and viscosities of binary decalin mixtures with cyclohexane or toluene are intended to simulate blending of naphtha and kerosene or diesel fractions. On the other hand, these mixtures are asymmetrical in length, while decalin + toluene mixtures are also asymmetrical in chemical nature. Besides, cyclohexane + toluene mixtures are asymmetrical mainly in chemical nature.

Another aim of this work was to analyze the behavior of decalin binary mixture viscosity deviations, $\Delta\eta$, and excess molar volume, V^E, as a function of temperature and composition. In this sense, derived properties obtained here for these mixtures were modeled by a Redlich−Kister expansion,[8] aiming to help future studies involving decalin mixtures. Besides, density data were used to estimate Prigogine−Flory−Patterson (PFP) model[9] parameters, allowing the correlation of pure component and mixture data.

Experimental Section

The mass fraction purities of the components were more than 99.0 % for cyclohexane (Vetec Brazil) and toluene (Tedia Brazil), and more than 99.7 % for decalin isomer mixture (41.06 % *cis* and 58.69 % *trans* − Vetec Brazil).

Mixtures were prepared by transferring known masses of the pure liquids via pipet into stoppered bottles to prevent preferential evaporation, using a balance with a precision of $\pm 10^{-7}$ kg. The estimated uncertainty in the mole fractions was $\pm 1 \cdot 10^{-4}$. The viscosity and density data were measured experimentally for each pure component, and the results are shown together with literature values[10,11] in Table 1.

The viscosity and density were obtained using an automatic viscometer (Stabinger SVM 3000/G2). It has a measuring cell that contains a tube filled with sample, which rotates at a constant speed. In this tube floats a measuring rotor. The result is a rotational viscometer aiming to eliminate the influence of bearing friction. The rotor floats in the sample and is centered by the centrifugal forces during measurement. Shortly after the start of the measurement, the rotor reaches a steady speed determined by the brake torque of the eddy currents and the driving shear forces of the sample.[12] To

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Table 1. Experimental Density and Viscosity of Pure Liquids

		$10^{-3}\ \rho/\mathrm{kg \cdot m^{-3}}$		$\eta/\mathrm{mPa \cdot s}$	
component	T/K	exptl	literature	exptl	literature
cyclohexane	283.15	0.78795	0.78779[10]	1.18040	1.189[10]
	293.15	0.77870	0.77853[10]	0.98467	0.9769[10]
	303.15	0.76920	0.76918[10]	0.83400	0.8187[10]
	313.15	0.75965	0.75971[10]	0.71086	0.6980[10]
	323.15	0.74990	0.75011[10]	0.61937	0.6037[10]
toluene	283.15	0.87610	0.87611[10]	0.6659	0.6695[11]
	293.15	0.86675	0.86685[10]	0.5960	0.5882[11]
	303.15	0.85748	0.85754[10]	0.5368	0.5219[11]
	313.15	0.84808	0.84821[10]	0.4858	0.4670[11]
	323.15	0.83870	0.83871[10]	0.4400	0.4208[11]
cis-decalin	283.15		0.9044[14]		4.092[14]
	293.15		0.8968[15]		3.355[15]
	303.15		0.8891[15]		2.704[15]
	313.15		0.8815[15]		2.214[15]
	323.15		0.8739[15]		1.861[15]
trans-decalin	283.15		0.8774[14]		2.578[14]
	293.15		0.8697[15]		2.107[15]
	303.15		0.8620[15]		1.760[15]
	313.15		0.8544[15]		1.499[15]
	323.15		0.8472[15]		1.283[15]

Table 2. Densities, Viscosities, Viscosity Deviations, and Excess Molar Volumes of the Binary Mixture Cyclohexane (1) + Toluene (2)

x_1	$\dfrac{10^{-3} \cdot \rho}{\mathrm{kg \cdot m^{-3}}}$	$\dfrac{\eta}{\mathrm{mPa \cdot s}}$	$\dfrac{\Delta\eta}{\mathrm{mPa \cdot s}}$	$\dfrac{10^{6} \cdot V^{\mathrm{E}}}{\mathrm{m^3 \cdot mol^{-1}}}$
		283.15 K		
0.0000	0.87610	0.66568	0.000	0
0.0958	0.86615	0.67120	−0.044	0.168
0.1960	0.85585	0.66229	−0.104	0.339
0.2986	0.84600	0.67917	−0.140	0.436
0.3988	0.83650	0.69481	−0.176	0.520
0.4974	0.82765	0.72175	−0.200	0.546
0.5989	0.81880	0.76347	−0.210	0.541
0.6977	0.81010	0.82031	−0.204	0.552
0.7998	0.80250	0.91032	−0.167	0.382
0.8994	0.79480	0.99942	−0.129	0.254
1.0000	0.78795	1.18023	0.000	0
		293.15 K		
0.0000	0.86675	0.59580	0.000	0
0.0958	0.85690	0.59946	−0.034	0.160
0.1960	0.84660	0.59084	−0.081	0.334
0.2986	0.83670	0.60509	−0.107	0.441
0.3988	0.82720	0.61713	−0.134	0.528
0.4974	0.81835	0.63783	−0.151	0.555
0.5989	0.80940	0.66996	−0.159	0.565
0.6977	0.80070	0.71372	−0.153	0.579
0.7998	0.79310	0.78375	−0.123	0.407
0.8994	0.78550	0.84724	−0.098	0.264
1.0000	0.77870	0.98467	0.000	0
		303.15 K		
0.0000	0.85748	0.53676	0.000	0
0.0958	0.84750	0.53948	−0.025	0.175
0.1960	0.83720	0.53063	−0.064	0.350
0.2986	0.82730	0.54295	−0.081	0.455
0.3988	0.81780	0.55242	−0.101	0.541
0.4974	0.80890	0.56832	−0.114	0.572
0.5989	0.80000	0.59348	−0.119	0.573
0.6977	0.79130	0.62735	−0.114	0.584
0.7998	0.78365	0.68237	−0.088	0.413
0.8994	0.77610	0.72712	−0.073	0.258
1.0000	0.76920	0.82948	0.000	0
		313.15 K		
0.0000	0.84808	0.48594	0.000	0
0.0958	0.83815	0.48788	−0.019	0.169
0.1960	0.82780	0.47762	−0.051	0.351
0.2986	0.81790	0.48697	−0.065	0.456
0.3988	0.80840	0.49711	−0.077	0.541
0.4974	0.79945	0.50951	−0.086	0.578
0.5989	0.79050	0.52935	−0.088	0.584
0.6977	0.78180	0.55526	−0.084	0.594
0.7998	0.77415	0.59870	−0.063	0.418
0.8994	0.76650	0.63733	−0.047	0.272
1.0000	0.75965	0.70609	0.000	0
		323.15 K		
0.0000	0.83870	0.44080	0.000	0
0.0958	0.82865	0.44276	−0.013	0.183
0.1960	0.81835	0.43096	−0.041	0.356
0.2986	0.80845	0.44258	−0.045	0.456
0.3988	0.79890	0.44913	−0.054	0.545
0.4974	0.78995	0.45885	−0.060	0.577
0.5989	0.78100	0.47349	−0.061	0.578
0.6977	0.77225	0.48861	−0.062	0.591
0.7998	0.76450	0.52922	−0.037	0.421
0.8994	0.75690	0.55831	−0.024	0.260
1.0000	0.74990	0.59778	0.000	0

calculate the kinematic viscosity from the measured dynamic viscosity, the density value must be known. For this reason, the SVM 3000 also has a density cell using the well-known oscillating U-tube principle: an appropriate amount of sample is used to fill the U-shaped tube, and a periodic perturbation was applied by means of an electronic system. Usually, the densimeter is assumed to behave as an oscillator without damping.[13] In the measurement, the samples were transferred to the equipment by syringe, and all physical properties were obtained in the same injection. The viscometer was factory-calibrated against standard Canon oils.

In the calculation of averages for each state condition, each sample had at least two injections, and the outliers were discarded. To identify outliers, the data points were analyzed following some criteria: (1) viscosity repeatability should not be worse than 1 % (expected fluctuation according to equipment manufacturer); (2) variations expected for density data at the same composition and temperature should be, at most, 0.2 $\mathrm{kg \cdot m^{-3}}$; and (3) for each composition, a linear trend to $\ln(\eta/\rho)$ versus T^{-1} was expected presenting a coefficient of determination (R^2) higher than 0.9994. When one experimental data point (average of two runs) did not attend one of these criterions, additional measurements were done, by preparing a new sample. After removal of outliers, a new average was calculated for this data point. Fluctuations are attributed to bubble formation during the run that disturbed the measurement.

Results and Discussion

The experimental densities and viscosities of pure cyclohexane and toluene, for each temperature investigated in this work, are presented in Table 1 along with literature values.[10,11] As can be seen by the results presented in Table 1, the agreement between our data and the literature values is quite good.

The experimental densities, viscosities, viscosity deviations, and excess molar volumes of the binary mixtures cyclohexane (1) + toluene (2), cyclohexane (1) + decalin (2), and toluene (1) + decalin (2) for each composition and temperature are presented in Tables 2, 3, and 4, respectively. In this work, mixtures involving volatile liquids have been studied (not oils), so uncertainties were estimated using the more volatile liquid, cyclohexane, the viscosity and density measurement of which would present higher uncertainties due to bubble formation. Ten different injections (different operators and days) were performed to measure viscosity and density for cyclohexane at 313.15 K. The estimated relative uncertainty in dynamic viscosity measurements is 0.82 %, higher than that observed for oils (e.g., 0.35 %).[16] The uncertainty in density is ± 0.1 $\mathrm{kg \cdot m^{-3}}$. The uncertainty in the temperature is ± 0.01 K and in the V^{E} due to the estimated uncertainty in ρ (± 0.1 $\mathrm{kg \cdot m^{-3}}$) is ± $0.02 \cdot 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$. Viscosities deviations ($\Delta\eta$) and excess molar volume (V^{E}) were derived, respectively, from:

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i\eta_i \qquad (1)$$

$$V^{\mathrm{E}} = V - \sum_{i=1}^{2} x_i\left(\frac{M_i}{\rho_i}\right) \qquad (2)$$

where η_i, ρ_i, M_i, and x_i are the absolute viscosity, density, molecular weight, and the molar fraction of i component, respectively, and η and V are the mixture absolute viscosity and molar volume, respectively. The derived properties were fitted in the Redlich−Kister polynomial equation with parameters represented by a second-order reciprocal temperature polynomial:

$$Y^{\mathrm{E}} = x_i x_j[(A_0 + A_1{\cdot}T^{-1} + A_2{\cdot}T^{-2}) + (B_0 + B_1{\cdot}T^{-1} + B_2{\cdot}T^{-2})(x_i - x_j)] \qquad (3)$$

where Y^{E} is $\Delta\eta$ or V^{E}, and A_i and B_i are the fitting parameters. The least-squares method was used to determine the values of the parameters. The coefficients A_i and B_i along

Table 3. Densities, Viscosities, Viscosity Deviations, and Excess Molar Volumes of the Binary Mixture Cyclohexane (1) + Decalin (2)

x_1	$\frac{10^{-3}\cdot\rho}{\mathrm{kg\cdot m^{-3}}}$	$\frac{\eta}{\mathrm{mPa\cdot s}}$	$\frac{\Delta\eta}{\mathrm{mPa\cdot s}}$	$\frac{10^{6}\cdot V^{\mathrm{E}}}{\mathrm{m^3\cdot mol^{-1}}}$
		283.15 K		
0.0000	0.88780	3.09742	0.000	0
0.0979	0.88090	2.86953	−0.040	−0.003
0.1958	0.87355	2.65384	−0.068	−0.007
0.2988	0.86550	2.44132	−0.083	−0.047
0.3970	0.85710	2.25829	−0.078	−0.058
0.5057	0.84725	2.06876	−0.059	−0.096
0.5974	0.83820	1.90992	−0.042	−0.115
0.7062	0.82675	1.72208	−0.021	−0.162
0.7999	0.81560	1.55521	−0.009	−0.137
0.8978	0.80275	1.37443	−0.002	−0.082
1.0000	0.78795	1.18023	0.000	0
		293.15 K		
0.0000	0.88025	2.50378	0.000	0
0.0979	0.87330	2.32612	−0.029	−0.019
0.1958	0.86570	2.15668	−0.050	−0.004
0.2988	0.85750	1.98490	−0.065	−0.046
0.3970	0.84895	1.83598	−0.065	−0.059
0.5057	0.83885	1.68262	−0.053	−0.087
0.5974	0.82965	1.55265	−0.044	−0.108
0.7062	0.81790	1.40180	−0.029	−0.141
0.7999	0.80650	1.27020	−0.019	−0.105
0.8978	0.79360	1.13151	−0.008	−0.070
1.0000	0.77870	0.98467	0.000	0
		303.15 K		
0.0000	0.87270	2.06586	0.000	0
0.0979	0.86560	1.92410	−0.021	−0.021
0.1958	0.85790	1.78688	−0.037	−0.018
0.2988	0.84950	1.64718	−0.049	−0.057
0.3970	0.84075	1.52373	−0.051	−0.067
0.5057	0.83045	1.39372	−0.047	−0.096
0.5974	0.82105	1.28946	−0.038	−0.115
0.7062	0.80905	1.16463	−0.028	−0.145
0.7999	0.79750	1.06083	−0.016	−0.116
0.8978	0.78430	0.94806	−0.008	−0.067
1.0000	0.76920	0.82948	0.000	0
		313.15 K		
0.0000	0.86515	1.73385	0.000	0
0.0979	0.85790	1.61864	−0.015	−0.024
0.1958	0.85010	1.50544	−0.027	−0.033
0.2988	0.84150	1.38991	−0.037	−0.071
0.3970	0.83260	1.28612	−0.040	−0.087
0.5057	0.82205	1.17734	−0.037	−0.111
0.5974	0.81245	1.08994	−0.030	−0.128
0.7062	0.80020	0.98501	−0.023	−0.155
0.7999	0.78840	0.89660	−0.015	−0.118
0.8978	0.77500	0.80526	−0.006	−0.071
1.0000	0.75965	0.70609	0.000	0
		323.15 K		
0.0000	0.85765	1.47722	0.000	0
0.0979	0.85020	1.38115	−0.010	−0.023
0.1958	0.84230	1.28623	−0.019	−0.050
0.2988	0.83350	1.18890	−0.026	−0.091
0.3970	0.82445	1.10147	−0.027	−0.118
0.5057	0.81370	1.00557	−0.027	−0.149
0.5974	0.80380	0.93426	−0.018	−0.152
0.7062	0.79130	0.84467	−0.011	−0.181
0.7999	0.77930	0.76251	−0.011	−0.149
0.8978	0.76560	0.68994	0.002	−0.093
1.0000	0.74985	0.59774	0.000	0

Table 4. Densities, Viscosities, Viscosity Deviations, and Excess Molar Volumes of the Binary Mixture Toluene (1) + Decalin (2)

x_1	$\frac{10^{-3}\cdot\rho}{\mathrm{kg\cdot m^{-3}}}$	$\frac{\eta}{\mathrm{mPa\cdot s}}$	$\frac{\Delta\eta}{\mathrm{mPa\cdot s}}$	$\frac{10^{6}\cdot V^{\mathrm{E}}}{\mathrm{m^3\cdot mol^{-1}}}$
		283.15 K		
0.0000	0.88780	3.09742	0.000	0
0.0994	0.88630	2.52494	−0.331	0.117
0.2007	0.88470	2.08553	−0.524	0.231
0.2995	0.88335	1.75436	−0.615	0.291
0.4029	0.88190	1.46241	−0.655	0.343
0.4973	0.88075	1.26392	−0.624	0.350
0.5986	0.87960	1.07879	−0.563	0.332
0.6998	0.87860	0.94322	−0.452	0.280
0.8059	0.87745	0.82588	−0.312	0.226
0.9025	0.87665	0.73838	−0.164	0.133
1.0000	0.87610	0.66568	0.000	0
		293.15 K		
0.0000	0.88025	2.50378	0.000	0
0.0994	0.87860	2.07415	−0.240	0.123
0.2007	0.87690	1.73740	−0.383	0.232
0.2995	0.87540	1.48585	−0.447	0.295
0.4029	0.87390	1.24863	−0.487	0.331
0.4973	0.87255	1.09147	−0.463	0.345
0.5986	0.87120	0.93837	−0.423	0.330
0.6998	0.87000	0.82830	−0.340	0.277
0.8059	0.86865	0.73108	−0.235	0.220
0.9025	0.86760	0.65738	−0.124	0.129
1.0000	0.86675	0.59580	0.000	0
		303.15 K		
0.0000	0.87270	2.06586	0.000	0
0.0994	0.87090	1.73575	−0.178	0.130
0.2007	0.86910	1.47171	−0.287	0.236
0.2995	0.86745	1.27287	−0.335	0.302
0.4029	0.86580	1.08060	−0.369	0.338
0.4973	0.86435	0.95187	−0.354	0.344
0.5986	0.86270	0.82547	−0.325	0.348
0.6998	0.86135	0.73366	−0.262	0.289
0.8059	0.85975	0.65215	−0.181	0.234
0.9025	0.85850	0.58971	−0.096	0.140
1.0000	0.85748	0.53676	0.000	0
		313.15 K		
0.0000	0.86515	1.73385	0.000	0
0.0994	0.86320	1.47495	−0.135	0.136
0.2007	0.86130	1.26415	−0.219	0.236
0.2995	0.85955	1.10272	−0.257	0.295
0.4029	0.85775	0.94576	−0.285	0.330
0.4973	0.85605	0.83857	−0.275	0.351
0.5986	0.85430	0.73215	−0.255	0.341
0.6998	0.85265	0.65565	−0.205	0.296
0.8059	0.85085	0.58582	−0.142	0.236
0.9025	0.84940	0.53224	−0.075	0.136
1.0000	0.84808	0.48594	0.000	0
		323.15 K		
0.0000	0.85765	1.47722	0.000	0
0.0994	0.85560	1.26997	−0.104	0.132
0.2007	0.85350	1.09848	−0.171	0.244
0.2995	0.85160	0.95802	−0.209	0.304
0.4029	0.84955	0.83406	−0.226	0.352
0.4973	0.84775	0.74561	−0.216	0.363
0.5986	0.84580	0.65876	−0.198	0.354
0.6998	0.84400	0.58891	−0.163	0.300
0.8059	0.84195	0.52897	−0.113	0.242
0.9025	0.84025	0.48247	−0.059	0.143
1.0000	0.83870	0.44080	0.000	0

Table 5. Fitted Values for the Redlich−Kister Equation Coefficients and Root-Mean-Square Deviations

system	derived property	A_0	$(10^{-3}\cdot A_1)/(K)$	$(10^{-5}\cdot A_2)/(K^2)$	B_0	$(10^{-3}\cdot B_1)/(K)$	$(10^{-5}\cdot B_2)/(K^2)$	δ_{rms}[a]
cyclohexane + toluene	$\Delta\eta$/mPa·s	3.855	−1.318		2.464	−0.807		0.008
	$V^E\cdot 10^6/m^3\cdot mol^{-1}$	3.4440	−0.3305		0.9794	−0.1421		0.023
cyclohexane + decalin	$\Delta\eta$/mPa·s	5.415	−3.030	4.040	16.61	−10.53	16.76	0.002
	$V^E\cdot 10^6/m^3\cdot mol^{-1}$	−1.8613	0.4233		0.6185	−0.3399		0.014
toluene + decalin	$\Delta\eta$/mPa·s	−31.950	22.205	−39.292	−0.9564	−0.8331	3.9144	0.010
	$V^E\cdot 10^6/m^3\cdot mol^{-1}$	1.9510	−0.1605		0.2825	−0.0920		0.007

[a] *n* equal to 45 data points for all systems.

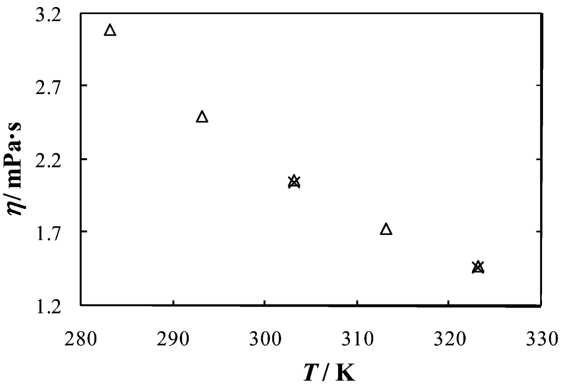

Figure 1. Dynamic viscosity as a function of temperature for △, a mixture with 41.06 % of *cis*-isomer and 58.69 % *trans*-isomer, and ×, interpolated values from a polynomial adjustment of literature data.[17]

with root-mean-square deviation (δ_{rms}) are reported in Table 5.

$$\delta_{rms} = \left[\sum (Y^E_{exptl} - Y^E_{calcd})^2/n\right]^{1/2} \qquad (4)$$

Here, *n* is the number of experimental data points in the range *T* = (283.15 to 323.15) K and over the whole composition range for each binary mixture, and the subscripts "exptl" and "calcd" denote experimental and calculated from eq 3, respectively.

Figure 1 shows the comparison of the dynamic viscosity versus temperature between the experimental values of decalin isomer mixture used in this work and a polynomial interpolation from literature data.[17] As it can be seen, there is a quite good agreement between our data and the interpolated data.

Parts (a), (b), and (c) of Figure 2 show viscosity deviations versus the mole fraction for binary mixtures of cyclohexane (1) + toluene (2), cyclohexane (1) + decalin (2), and toluene (1) + decalin (2), respectively. Further, a comparison between cyclohexane (1) + toluene (2) literature data[18] and those obtained in this work at 313.15 K is also presented in part (a). A good agreement is found between the two data sets within their uncertainties. In this figure, we can observe that the absolute values of viscosity deviations decrease with temperature, and all values are negative.

The lowest absolute deviations are found for cyclohexane (1) + decalin (2), presenting only asymmetry in chain length and shape. The cyclohexane (1) + toluene (2) system, presenting mainly asymmetry in molecular interaction, presents intermediate deviations, while the system with asymmetries in length, shape, and molecular interactions presents the highest values. Thus, $\Delta\eta$ are functions of interactions as well as the size and shape of the participating molecules,[19] and these effects lead to negative viscosity deviations for the nonassociating hydrocarbon systems studied here.

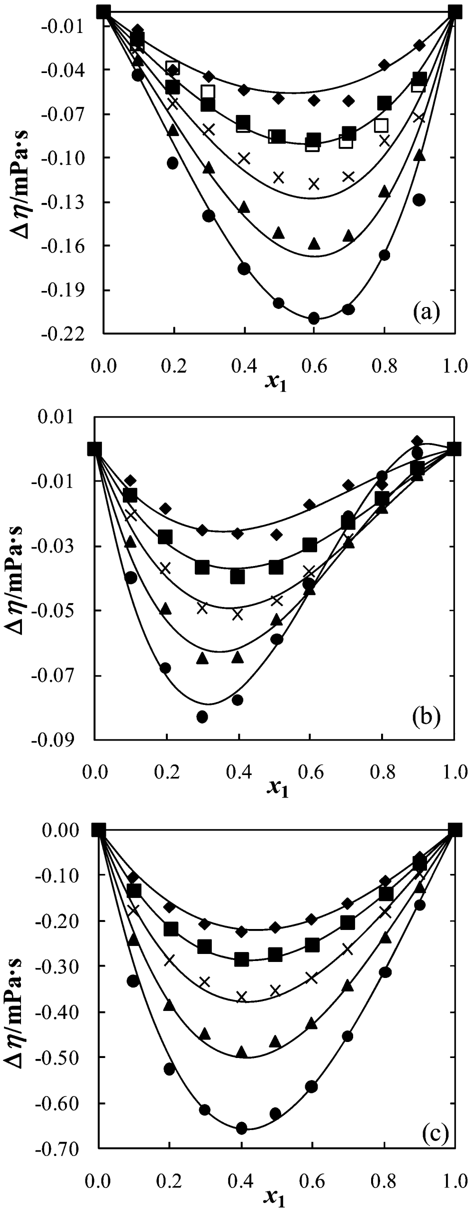

Figure 2. Viscosities deviations, $\Delta\eta$, versus the mole fraction at ●, 283.15 K; ▲, 293.15 K; ×, 303.15 K; ■, 313.15 K; □, 313.15 K;[18] and ◆, 323.15 K for binary mixtures: (a) cyclohexane (1) + toluene (2); (b) cyclohexane (1) + decalin (2); and (c) toluene (1) + decalin (2). The solid curves have been derived from eq 3.

In this Article, experimental densities have been correlated by the Prigogine−Flory−Patterson (PFP) model. The relevant equations are given elsewhere.[9,20,21] The method of least-squares has been used to fit the values of the characteristic parameters for pure components and binary mixture interaction parameters. PFP characteristic parameters for each substance were fitted to their respective experimental density obtained in this work. Initial guesses for these parameters were obtained elsewhere.[9,21] Equation 4 (with Y^E denoting ρ) is also used to calculate δ_{rms} for densities calculated by the PFP model. The correlation led to δ_{rms} satisfactorily close to experimental uncertainty (± 0.1 kg·m^{-3}). Binary interaction parameters (X_{12}) were estimated

Table 6. Fitted Values for the Prigogine−Flory−Patterson (PFP) Model Characteristic Parameters and Root-Mean-Square Deviations

	p_1[a]	T_1[a]	$10^6 \cdot v_1$[a]	p_2[a]	T_2[a]	$10^6 \cdot v_2$[a]	X_{12}	δ_{rms}
system	MPa	K	$\mathrm{m^3 \cdot mol^{-1}}$	MPa	K	$\mathrm{m^3 \cdot mol^{-1}}$	MPa	$\mathrm{kg \cdot m^{-3}}$[a]
cyclohexane (1) + toluene (2)	$5.3 \cdot 10^2$	4719.0	84.193	$5.6 \cdot 10^2$	5049.0	84.662	36.2	0.3
cyclohexane (1) + decalin (2)	$5.3 \cdot 10^2$	4719.0	84.193	$2.2 \cdot 10^2$	5737.8	129.596	−57.3	0.2
toluene (1) + decalin (2)	$5.6 \cdot 10^2$	5049.0	84.662	$2.2 \cdot 10^2$	5737.8	129.596	−26.8	0.2

[a] n equal to 55 data points for all systems. Here, Y^E denotes ρ in eq 4.

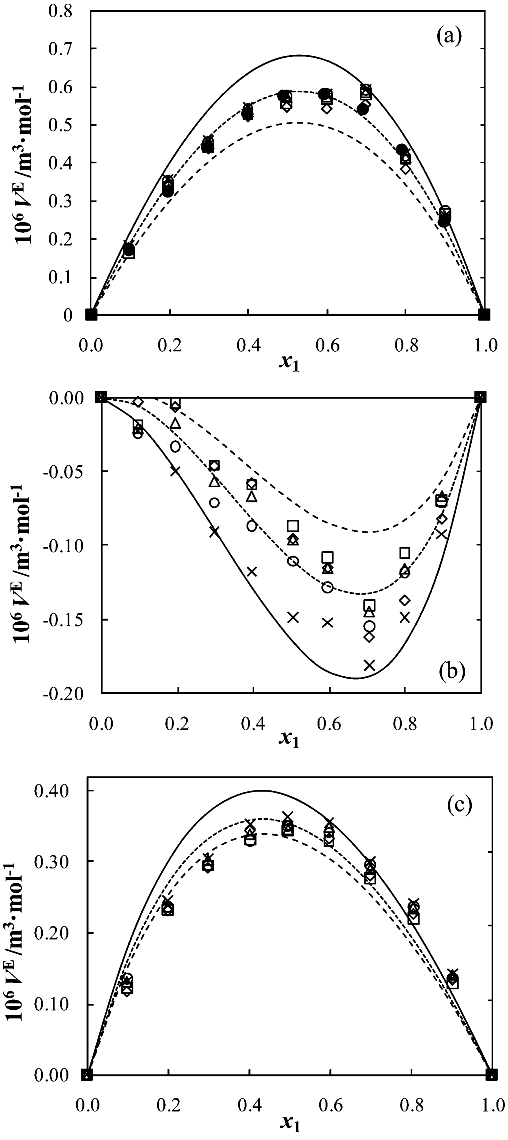

Figure 3. Excess molar volumes, V^E, versus the mole fraction at ◇, 283.15 K; □, 293.15 K; △, 303.15 K; ○, 313.15 K; ●, 313.15 K;[18] and ×, 323.15 K for binary mixtures: (a) cyclohexane (1) + toluene (2); (b) cyclohexane (1) + decalin (2); and (c) toluene (1) + decalin (2). Lines denote PFP model correlations: − − −, 283.15 K; - - -, 303.15 K; −, 323.15 K.

using all density data for each binary mixture. The fitted values for the characteristic parameters and overall mean absolute square deviations (eq 4) are summarized in Table 6.

Parts (a), (b), and (c) of Figure 3 show excess molar volume for binary mixtures cyclohexane (1) + toluene (2), cyclohexane (1) + decalin (2), and toluene (1) + decalin (2), respectively, in the range T = (283.15 to 323.15) K versus the mole fraction over the whole composition range. Moreover, the calculated values in T = (283.15, 303.15, and 323.15) K (for the sake of clarity), obtained by means of the Prigogine−Flory−Patterson (PFP) model, are also represented in Figure 3. Again, a comparison between cyclohexane (1) + toluene (2) literature data[18] and those obtained in this work at 313.15 K is also presented in part (a). A good agreement is found between the two data sets within their uncertainties.

As it can be seen in Figure 3, the model describes qualitatively the excess volume experimental data, but misses the temperature effect on this property. The mixtures with toluene are subjected to asymmetries in chemical nature leading to a repulsive behavior, lowering the proximity of the molecules and also lowering the effective attraction. For the cyclohexane + decalin mixture, which is asymmetrical only in chain length, the excess volumes are negative and small in modulus, probably due to the effect of mixing substances with different free volumes. Also, it is noticeable that Figure 3c can be roughly obtained by the addition of curves on Figure 3a and b. The effects of molecular interaction and length asymmetries are somehow additive for excess volume.

Analyzing the work of Gepert et al.,[20] one can see that the cyclohexane + benzene interaction parameter is close enough to the one obtained in this work for cyclohexane + toluene, although we used densities at five temperatures as input data, whereas they used densities and excess enthalpies at 298.15 K as input data. Gepert et al.[20] also studied other hydrocarbons mixtures and showed that shape asymmetry leads to an increase in the correlated interaction parameters with more intensity than does asymmetry in chain length. Yet, the interaction parameter should be mainly sensitive to molecular interaction asymmetry and not to asymmetries in length or shape. This result points to an important lack of performance of PFP theory for substances of more complex structure, as is the case for decalins. One should expect a value near zero for the cyclohexane + decalin interaction parameter. Besides, positive interaction parameters are expected from PFP theory. Instead, our results led to a negative value for this system, also with a modulus greater than that found for the cyclohexane + toluene (involving molecular interaction asymmetry) mixture, indicating that the interaction parameter for cyclohexane + decalin as a matter of fact sums all nonidealities altogether. To illustrate this problem, in Figure 4 the excess volume prediction (without interaction parameter) for cyclohexane + decalin system is shown. Once again following the additive-like asymmetry behavior for volume, the interaction parameter for toluene + decalin can roughly be obtained through the addition of the parameters for the other systems.

Conclusions

In this Article, we have experimentally determined the density and viscosity for three binary systems: cyclohexane + toluene, cyclohexane + decalin, and toluene + decalin. Data are reported at T = (283.15, 293.15, 303.15, 313.15, and 323.15) K. To analyze the experimental results, we have calculated the viscosity deviations and excess molar volume for the above binary mixtures over the temperature interval.

A Redlich−Kister-type model was used to correlate viscosity deviations and excess molar volumes for the studied binary systems at all studied temperatures and in the whole composition

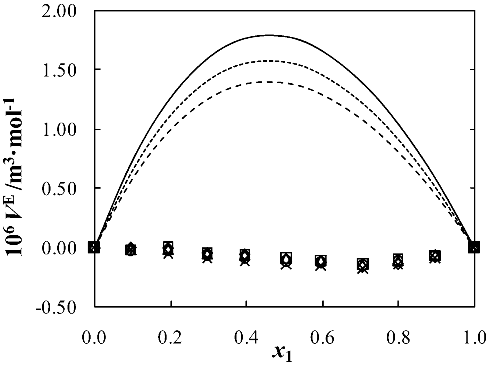

Figure 4. Excess molar volumes, V^E, versus the mole fraction at ◇, 283.15 K; □, 293.15 K; △, 303.15 K; ○, 313.15 K; and ×, 323.15 K for cyclohexane (1) + decalin (2) mixture. Lines denote PFP model predictions (neglected interaction parameter): − − −, 283.15 K; - - -, 303.15 K; −, 323.15 K.

range, with good results been reached. We have noticed that shape and length asymmetries and molecular interaction asymmetries are important to explain viscosity deviations, but the latter has a more pronounced influence.

Negative excess molar volumes were found when only shape and length asymmetries were present, while molecular interaction asymmetries led to positive values. The effects of simultaneous molecular interaction and length asymmetries were somehow additive for excess volume.

The Prigogine−Flory−Patterson (PFP) equation of state was used to correlate densities. The model correlates densities with deviation from experimental data compatible to experimental uncertainties. Also, it predicts satisfactorily the excess volume data, but misses the temperature effect on this property. Moreover, the results lead to the conclusion that the model fails when the molecular interaction term is omitted, even when the system presents only shape and length asymmetries.

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