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High-Pressure Viscosity Measurements for the Binary System Cyclohexane + *n*-Hexadecane in the Temperature Range of (318.15 to 413.15) K[†]

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The viscosities of binary mixtures of cyclohexane and *n*-hexadecane at high pressures were measured for six different compositions with an electromagnetic viscometer in the range of (6.90 to 62.05) MPa at temperatures varying from (318.15 to 413.15) K, extending the data of Tanaka et al. with a vibrating crystal viscometer and that of Wakeham and co-workers utilizing a vibrating wire viscometer, for higher temperatures. The data were correlated with the molar additive mixing rule using temperature-dependent Gaussian functions in pressure for pure component viscosities. At higher temperatures, the curvature of the viscosity−pressure function changes significantly with composition for this asymmetric mixture.

1. Introduction

The viscosity has been traditionally used in the characterization of complex mixtures[1] of hydrocarbons like petroleum containing long chain alkanes as well as naphthenic and aromatic compounds. In asymmetric mixtures, large differences in molecular shape, size, or flexibility could cause deviations in physical properties from ideal mixture properties, even for mixtures of nonpolar substances.[3]

Using a torsionally vibrating crystal viscometer, Tanaka et al.[4] measured viscosities for asymmetric mixtures of cyclohexane and *n*-hexadecane at pressures up to 150 MPa at (298.15, 323.15, and 348.15) K, with estimated uncertainties of ± 2 %. Professor Wakeham and co-workers (Pádua et al.[5]) validated the use of a vibrating wire instrument for viscosity measurements at high pressures and obtained an estimated accuracy of ± 2 % for viscosities of pure cyclohexane. Using a commercially available electromagnetic viscometer with oscillating piston, high-pressure viscosities of cyclohexane + *n*-hexadecane mixtures were measured up to 62.05 MPa for a wider range of temperatures of (318.15 to 413.15) K, at the same conditions used by Amorim et al.[6] in their density measurements. The widening of the temperature range allows a better experimental and modeling evaluation of pressure and mixing effects on the physical properties. The data were successfully correlated with the molar additive mixing rule using an empirical model for pure component viscosities as a function of pressure and temperature.

2. Experimental Methods and Materials

The mixtures were prepared at ambient temperature and pressure by weighing desired amounts of the cyclohexane (TEDIA, USA, 99 %) and *n*-hexadecane (TEDIA, USA, 99 %) which were purchased from VETEC, Brazil, and were used without further purification.

The viscosities were measured using a VISCOlab PVT high-pressure viscometer of Cambridge Viscosity described previously by Ahosseini et al.[7] and Lundstrum et al.[8] However, the pump and the bath differ. The temperature can be controlled within 0.2 K of the selected temperature using a Julabo F12 thermostatic bath and control system. The pressure meter is the Omega DP41-B ultra high precision input meter. The pressure measurement is accurate to 0.003 MPa or 0.005 % full-scale, and the system can be readily controlled within 0.035 MPa of selected pressure. For the present study, two pistons were selected, in the range (0.2 to 2.0) mPa·s and (0.5 to 10) mPa·s. The apparatus was factory calibrated, with each of these two pistons separately calibrated with deviations up to 0.05 % in the range (0.5 to 10) mPa·s and 0.48 % in the range (0.2 to 2) mPa·s, using two certified standard calibration fluids for each piston. When the variance of measurements was small and constant, the value of the measured value η and its standard deviation δ were recorded. The repeatability of the experiments was found in the range (0.1 to 1.0) %.

Ahosseini et al.[7] have indicated a 3 % uncertainty for the Cambridge viscometer where the temperature is controlled by an air oven. In this work, the temperature is controlled to a high precision by a circulating silicon oil bath, and Lundstrum et al.[8] observed a 7 % error as an upper bound when a generic piston recommended by the manufacturer for the range (2 to 50) mPa·s was used. They have reported an uncertainty of 2 % over the viscosity range from (6.1 to 45) mPa·s and repeatability of 1 % in the temperature range studied, similar to the manufacturer's claim. In our work, we have observed reproducibility in the range (1.8 to 3.0) %, with 2.4 % as the average using different samples of pure fluid.

3. Results and Discussion

Measured viscosities of cyclohexane (1), *n*-hexadecane (2), and their mixtures are presented in Table 1.

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Table 1. Experimental Viscosity (η/mPa·s) Data for the System Cyclohexane (1) + *n*-Hexadecane (2) as a Function of Pressure (p/MPa) and Composition (Mole Fraction x_1) at Several Temperatures (T/K)

	$x_1 = 1$		$x_1 = 0.9$		$x_1 = 0.7$		$x_1 = 0.3$		$x_1 = 0.1$		$x_1 = 0$	
p/MPa	η/mPa·s	$10^2\delta$	η/mPa·s	$10^2\delta$	η/mPa·s	$10^2\delta$	η/mPa·s	$10^2\delta$	η/mPa·s	$10^2\delta$	η/mPa·s	$10^2\delta$
$T = 318.15$ K												
6.90	0.671	0.3	0.864	0.4	1.213	0.4	1.638	0.4	1.986	0.3	2.151	0.5
13.79	0.726	0.2	0.941	0.5	1.315	0.5	1.772	0.2	2.160	0.4	2.331	0.2
20.68	0.785	0.4	1.016	0.2	1.424	0.3	1.928	0.3	2.332	0.3	2.538	0.3
27.58	0.839	0.4	1.095	0.4	1.525	0.3	2.080	0.4	2.521	0.2	2.728	0.3
34.47	0.906	0.2	1.225	0.7	1.645	0.3	2.247	0.4	2.717	0.3	2.920	0.4
41.37	0.974	0.2	1.319	0.3	1.748	0.3	2.410	0.4	2.917	0.2	3.169	0.4
48.26	1.049	0.4	1.408	0.4	1.880	0.5	2.602	0.2	3.136	0.3	3.413	0.4
55.16	1.149	0.3	1.508	0.6	2.000	0.5	2.789	0.2	3.364	0.2	3.641	0.3
62.05	1.216	0.3	1.635	0.8	2.128	0.5	2.980	0.2	3.595	0.3	3.901	0.6
$T = 333.15$ K												
6.90	0.546	0.2	0.665	0.2	0.927	0.4	1.291	0.2	1.588	0.700	1.705	0.5
13.79	0.595	0.2	0.720	0.2	1.005	0.3	1.408	0.5	1.706	0.300	1.827	0.5
20.68	0.642	0.2	0.778	0.3	1.096	0.4	1.525	0.5	1.839	0.500	1.951	0.4
27.58	0.698	0.2	0.833	0.2	1.182	0.2	1.642	0.5	1.984	0.300	2.101	0.5
34.47	0.750	0.2	0.899	0.2	1.280	0.4	1.766	0.7	2.124	0.300	2.246	0.4
41.37	0.808	0.3	0.969	0.2	1.364	0.1	1.893	0.3	2.266	0.400	2.406	0.2
48.26	0.855	0.2	1.035	0.3	1.462	0.4	2.015	0.3	2.426	0.500	2.582	0.3
55.16	0.916	0.4	1.096	0.4	1.548	0.4	2.148	0.4	2.579	0.500	2.761	0.3
62.05	0.951	0.3	1.189	0.3	1.659	0.5	2.272	0.2	2.737	0.300	2.990	0.4
$T = 348.15$ K												
6.90	0.458	0.4	0.556	0.4	0.763	0.2	1.056	0.5	1.251	0.6	1.329	0.2
13.79	0.495	0.3	0.606	0.3	0.823	0.2	1.145	0.6	1.352	0.7	1.450	0.5
20.68	0.536	0.3	0.645	0.3	0.905	0.9	1.234	0.9	1.462	0.7	1.571	0.9
27.58	0.579	0.4	0.698	0.4	0.980	0.4	1.325	0.5	1.572	0.5	1.670	0.5
34.47	0.624	0.4	0.747	0.4	1.051	0.2	1.425	0.7	1.670	0.3	1.788	0.4
41.37	0.670	0.3	0.789	0.4	1.116	0.2	1.506	0.5	1.788	0.6	1.938	0.7
48.26	0.717	0.3	0.849	0.3	1.194	0.2	1.610	0.5	1.895	0.5	2.084	0.3
55.16	0.769	0.2	0.887	0.2	1.249	0.2	1.709	0.6	2.039	0.5	2.234	0.6
62.05	0.814	0.2	0.945	0.2	1.329	0.3	1.814	0.5	2.155	0.3	2.364	0.3
$T = 363.15$ K												
6.90	0.386	0.7	0.471	0.5	0.631	0.2	0.897	0.2	1.026	0.8	1.145	0.5
13.79	0.420	0.4	0.508	0.3	0.679	0.3	0.973	0.2	1.109	0.5	1.236	0.4
20.68	0.455	0.3	0.550	0.4	0.736	0.2	1.048	0.2	1.197	0.3	1.338	0.4
27.58	0.493	0.3	0.587	0.3	0.787	0.3	1.129	0.3	1.294	0.9	1.428	0.4
34.47	0.530	0.3	0.628	0.3	0.840	0.2	1.206	0.2	1.382	0.6	1.528	0.5
41.37	0.568	0.2	0.667	0.3	0.896	0.3	1.289	0.2	1.481	1.0	1.621	0.5
48.26	0.618	2.0	0.713	0.3	0.950	0.3	1.369	0.2	1.577	0.5	1.714	0.6
55.16	0.658	0.3	0.750	0.2	1.011	0.2	1.453	0.2	1.682	0.8	1.833	0.2
62.05	0.699	0.3	0.797	0.2	1.073	0.3	1.537	0.2	1.779	0.5	1.929	0.5
$T = 388.15$ K												
6.90	0.301	0.4	0.386	0.6	0.497	0.3	0.668	0.2	0.790	0.3	0.831	0.4
13.79	0.328	0.4	0.406	0.4	0.534	0.9	0.724	0.2	0.844	0.2	0.899	0.7
20.68	0.356	0.5	0.431	0.6	0.565	0.2	0.778	0.2	0.902	0.3	0.968	0.2
27.58	0.384	0.4	0.463	0.4	0.609	0.5	0.835	0.2	0.965	0.4	1.042	0.3
34.47	0.412	0.5	0.494	0.3	0.656	0.6	0.890	0.2	1.031	0.3	1.160	0.6
41.37	0.441	0.6	0.527	0.3	0.700	0.8	0.949	0.2	1.086	0.4	1.177	0.5
48.26	0.469	0.4	0.565	0.4	0.738	0.7	1.006	0.2	1.179	0.4	1.264	0.7
55.16	0.498	0.2	0.597	0.4	0.779	0.5	1.067	0.2	1.242	0.2	1.331	0.4
62.05	0.528	0.3	0.625	0.2	0.830	0.7	1.127	0.2	1.311	0.3	1.396	0.3
$T = 413.15$ K												
6.90	0.245	0.6	0.308	0.60	0.402	0.6	0.530	0.3	0.567	0.4	0.621	0.8
13.79	0.273	0.7	0.332	0.40	0.440	0.8	0.578	0.3	0.625	0.5	0.673	0.7
20.68	0.293	0.4	0.362	0.40	0.477	0.5	0.622	0.3	0.679	0.2	0.733	1.4
27.58	0.316	0.7	0.387	0.40	0.515	0.5	0.664	0.2	0.723	0.2	0.790	1.7
34.47	0.342	0.4	0.423	0.40	0.542	0.7	0.715	0.3	0.774	0.3	0.813	0.3
41.37	0.367	0.6	0.433	0.50	0.582	0.5	0.752	0.7	0.824	0.3	0.879	1.2
48.26	0.396	0.5	0.459	0.30	0.608	0.7	0.796	0.3	0.888	0.5	0.935	1.2
55.16	0.415	0.5	0.486	0.20	0.639	0.6	0.847	0.4	0.926	0.2	0.972	1.8
62.05	0.438	0.5	0.513	0.50	0.678	1.8	0.888	0.4	0.974	0.2	1.014	0.6

The measured viscosities for pure cyclohexane at (298.15, 323.15, and 333.15) K and for pure *n*-hexadecane at 348.15 K at pressures up to 55 MPa are compared to data in Figure 1 as fractional deviations from our values, $\Delta\eta/\eta$ (i.e., $(\eta_{\text{calculated}} - \eta_{\text{experimental}})/\eta_{\text{experimental}}$). Table 2 presents additional measurements of cyclohexane. Our results are comparable to the literature[4,5] data within experimental uncertainty. The precise data of Pádua et al.[5] are very close to our values.

The viscosities as a function of pressure at (318.15 and 413.15) K are presented in Figures 2(a) and 2(b), respectively. The viscosities increase with pressure increasing for all temperatures. The viscosity of *n*-hexadecane varies less

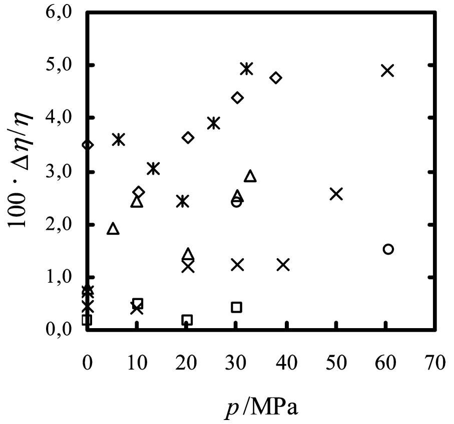

Figure 1. Fractional deviations of experimental viscosity data for cyclohexane and n-hexadecane obtained in this work with literature values, at several pressures and temperatures: ○, n-hexadecane at 348.15 K, ref 4; Δ, cyclohexane at 298.15 K, ref 5; *, cyclohexane at 298.15 K, ref 4; □, cyclohexane at 323.15 K, ref 5; ×, cyclohexane at 323.15 K, ref 4; ◇, cyclohexane at 333.15 K, ref 5.

Table 2. Additional Experimental Viscosity (η/mPa·s) Data for Cyclohexane Measured at Pressures (p/MPa) up to 55 MPa and at the Same Temperatures (T/K) as the Literature Data

T = 298.15 K		T = 323.15 K		T = 333.15 K	
p/MPa	η/mPa·s	p/MPa	η/mPa·s	p/MPa	η/mPa·s
0.10	0.888	0.10	0.606	0.10	0.512
4.02	0.903	7.24	0.667	3.79	0.538
7.58	0.962	14.23	0.721	7.31	0.563
13.71	1.037	21.10	0.776	14.07	0.609
20.86	1.129	27.70	0.835	20.63	0.657
27.70	1.222	39.96	0.952	27.83	0.709
34.67	1.309	48.19	1.035	34.66	0.757
		50.88	1.061	41.99	0.815
		52.32	1.072	49.01	0.876
		54.27	1.091	53.48	0.904
				54.95	0.915

linearly with pressure than that of cyclohexane. At higher temperature, the curvature of viscosity−pressure function changes with increasing mole fraction of n-hexadecane, partly due to the asymmetry of mixtures. The viscosity decreases with the enhancement of cyclohexane in the mixture at constant pressure in Figure 3. The curvature increases with an increase in temperature. A quasi-linear behavior for the logarithm of viscosity against the reciprocal of absolute temperature at constant pressure is found for all compositions, as presented in Figure 4.

The following model is proposed for viscosity as a function of pressure (p/MPa) and temperature (T/K) for calculation of pure component viscosities and the linear molar additivity mixing rule, eq 5, for calculation of mixture viscosities for a given composition

$$\ln(\eta) = A(T) + B(T)p + C(T)p^2 \qquad (1)$$

where

$$A(T) = A_0 + A_1/T \qquad (2)$$

$$B(T) = B_0 + B_1/T \qquad (3)$$

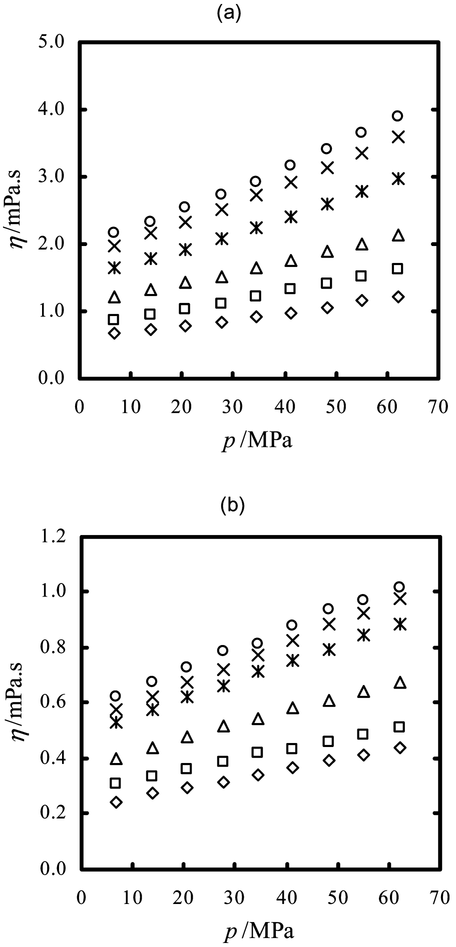

Figure 2. Experimental viscosity of cyclohexane (1)/n-hexadecane (2) binary mixtures as a function of pressure at 318.15 K (a) and 413.15 K (b): ○, x_1 = 0.0; ×, x_1 = 0.1; *, x_1 = 0.3; Δ, x_1 = 0.7; □, x_1 = 0.9; ◇, x_1 = 1.0.

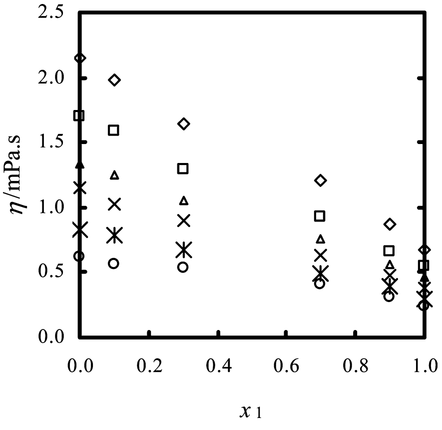

Figure 3. Experimental viscosity of cyclohexane (1)/n-hexadecane (2) binary mixtures as a function of composition at 6.90 MPa: ◇, 318.15 K; □, 333.15 K; Δ, 348.15 K; ×, 363.15 K; *, 388.15 K; ○, 413.15 K.

$$C(T) = C_0 + C_1/T \qquad (4)$$

Approximating the logarithm of viscosity as a quadratic function of pressure preserves the essence of this relation,

Table 3. Parameters in Equations 1 to 4 for Pure Components

component	A_0	$10^{-3}A_1$/K	10^2B_0/MPa^{-1}	B_1/K·MPa^{-1}	10^4C_0/MPa^{-2}	10^2C_1/K·MPa^{-2}
(1) cyclohexane	−4.6616	1.3277	1.2422	0.2231	−0.9507	1.8111
(2) n-hexadecane	−4.4024	1.6072	−0.2848	5.6098	0.9197	−4.8997

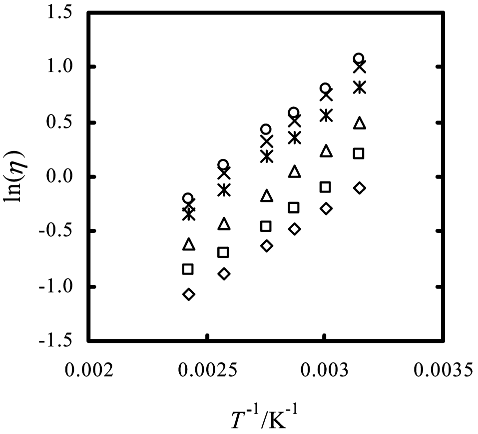

Figure 4. Variation of the logarithmic viscosity of cyclohexane (1)/*n*-hexadecane (2) binary mixtures with the inverse temperature at 34.47 MPa: ○, $x_1 = 0.0$; ×, $x_1 = 0.1$; *, $x_1 = 0.3$; Δ, $x_1 = 0.7$; □, $x_1 = 0.9$; ◇, $x_1 = 1.0$.

allowing the study of the curvature of logarithm of viscosity versus pressure.

$$\eta = \sum_i x_i \eta_i \tag{5}$$

The pure component parameters in eqs 2 to 4 are presented in Table 3. They were estimated by minimization of the objective function (f^{obj}) defined in eq 6 using all available data, so that the regression can be robust and the pure component parameters can best fit all the data

$$f^{\text{obj}} = \frac{1}{\text{ND}} \sum_{i=1}^{\text{ND}} \left(\frac{\eta_{\text{calc},i} - \eta_{\text{exp},i}}{\delta_i} \right)^2 \tag{6}$$

where δ is the standard deviation of repetitions of each measurement and the number of measurements ND used in the calculation.

The root-mean-square fractional deviation of the proposed correlation is 3.3 %, which is quite close to the experimental uncertainty. The average $\Delta\eta/\eta$ is close to zero, indicating the error does not have a bias.

4. Conclusions

The absolute viscosities of cyclohexane, *n*-hexadecane, and their mixtures were measured with a commercial electromagnetic viscometer, with measured viscosities and uncertainties comparable to those previously reported with different techniques.

The proposed correlation with six parameters for each pure component when used with the molar additivity mixing rule provides a satisfactory route to calculate viscosities of this asymmetric mixture from pure component viscosities.

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