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Viscosity and Density of Binary Mixtures of Cyclohexane with *n*-Octane, *n*-Dodecane, and *n*-Hexadecane Under High Pressures

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The viscosity and density of three binary mixtures of cyclohexane with *n*-octane, *n*-dodecane, and *n*-hexadecane have been measured at 298, 323, and 348 K at pressures up to 150 MPa or freezing pressures. The measurements of the viscosity were performed by a torsionally vibrating crystal viscometer on a relative basis using benzene and cyclohexane as reference materials. The density was measured using a high-pressure burette apparatus. The uncertainties of the measurements are estimated to be less than 2% for viscosity and 0.1% for density, respectively. The effects of temperature, pressure, density, and composition on the viscosity are discussed. Applicabilities of several empirical correlating equations to the viscosity data were examined.

KEY WORDS: alkanes; cyclohexane; density; dodecane; hexadecane; mixtures; octane; Tait equation; viscometer; viscosity.

1. INTRODUCTION

It is essential to have accurate transport properties data over wide ranges of temperature and pressure for liquids and liquid mixtures in order to develop methods of correlation and prediction and theories of transport properties. In earlier papers [1–4], we have reported measurements of the viscosity of binary aqueous alcohol solutions at elevated pressure using a falling-cylinder viscometer. This paper extends the investigation to mixtures of cyclohexane with *n*-octane, *n*-dodecane, and *n*-hexadecane at pressures up to 150 MPa or the freezing pressures at 298, 323, and 348 K, employing a torsionally vibrating crystal viscometer. The experimental results have been used to test the applicability of several empirical correlation methods.

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2. EXPERIMENTAL

2.1. Viscosity Measurements

The viscosity was measured using a torsionally vibrating crystal viscometer described in detail previously [5]. The operating procedures of the apparatus and the method of data reduction also remained unchanged. The viscosity η is derived from the measured resonant frequency of the crystal, f, and the frequency bandwidth of the resonant curve Δf, using the following equation:

$$\eta\rho = (W/S)^2(\pi f)(\Delta f/f - \Delta f_0/f_0)^2 \tag{1}$$

where ρ is the density of the fluid, and W and S are the mass and surface area of the crystal, respectively. The subscript zero denotes a loss terms due to the internal friction of the crystal and its suspension. The value $\Delta f_0/f_0$ was calibrated at atmospheric pressure for each isotherm using benzene and cyclohexane [5] as reference materials. The uncertainty of the electrical measuring system is less than 0.5%. The viscometer was thermostatically controlled within ± 20 mK. The temperature was measured with a platinum resistance thermometer within ± 10 mK. The pressure was measured with a Bourdon tube gauge within ± 0.1%. Considering all of these error sources, the overall uncertainty of the viscosity obtained is estimated to be less than 2%.

2.2. *PVT* Measurements

The density was measured with a high-pressure burette apparatus which has been described in detail elsewhere [1, 6]. The piezometer was thermostatically controlled to within ± 10 mK in a liquid bath. The temperature was measured with standard mercury thermometers within an accuracy of ± 50 mK. The pressure was measured by Heise Bourdon-tube gauges within ± 0.10 MPa. The overall uncertainty of the density obtained is estimated to be less than 0.1%.

2.3. Materials

All the sample liquids were supplied as the reagent-grade from commercial sources. The purities of cyclohexane, *n*-octane, *n*-dodecane, and *n*-hexadecane are 99.8, 98.0, 99.0, and 98.0%, respectively. They were used after desiccation by calcium hydride. The mixtures were prepared by weighing.

3. EXPERIMENTAL RESULTS

3.1. Density

As shown in Eq. (1), a precise value of the density is necessary to determine the viscosity by the torsionally vibrating crystal method. The density was measured for three binary mixtures of cyclohexane at every 0.2 mole fraction under pressures up to 180 MPa or the freezing pressures along three isotherms of 298, 323, and 348 K. More than 180 data points were obtained for each mixture.[2]

The pressure dependence of the density can be represented satisfactorily with the Tait equation:

$$(\rho - \rho_0)/\rho = C \ln[(B + P)/(B + P_0)] \tag{2}$$

where ρ and ρ_0 are the densities at pressure P and at the atmospheric pressure P_0, and B and C are the empirical coefficients. The optimum values of the coefficients were determined by the nonlinear regression method and are listed in Table I together with the deviations of experimental data from Eq. (2). The value of density was calculated by Eq. (2) in order to determine the viscosity.

3.2. Comparison of Viscosity with Literature Values

Prior to measuring the viscosity of mixtures at high pressures, the experimental data obtained at atmospheric pressure for the pure components were compared with the data obtained with an Ubellohde viscometer and some literature values [9–12]. It was confirmed that the present results agreed with the experimental data obtained with the Ubellohde viscometer within 1.5%, and the API reference viscosity values [9] within 0.8–2.0%. The present data obtained at high pressures for the pure components are also found to agree within 2% with the data of Dymond et al. [10–12] measured with a falling-body viscometer.

As for the cyclohexane + *n*-alkane mixtures studied in this work, the present results are in good agreement with the experimental data of Awwad and Salman [13] obtained with an Ubellohde viscometer at atmospheric pressure within 1.6%, which are the only experimental data found in the literature.

[2] The experimental raw data are available from Y. Tanaka on request.

Table I. Coefficients B, C, and ρ_0 in Eq. (2)

Mole fraction of cyclohexane	Temp. (K)	ρ_0 (kg · m^{-3})	B (MPa)	C	Avg. dev. (%)	Max. dev. (%)
		Cyclohexane + *n*-octane mixture				
0	298.15	698.2	69.6	0.08895	Cited from Ref. 7	
	323.15	678.6	57.5	0.08895		
	348.15	657.4	46.7	0.08895		
0.2	298.15	708.5	65.6	0.08436	0.04	0.13
	323.15	687.7	57.2	0.08803	0.01	0.03
	348.15	667.0	45.3	0.08708	0.02	0.03
0.4	298.15	720.0	67.7	0.08540	0.03	0.14
	323.15	699.0	59.4	0.08927	0.02	0.06
	348.15	677.1	47.4	0.08872	0.03	0.09
0.6	298.15	734.0	70.8	0.08641	0.02	0.10
	323.15	712.5	58.9	0.08770	0.02	0.05
	348.15	691.0	47.7	0.08782	0.02	0.06
0.8	298.15	751.6	68.9	0.08278	0.01	0.03
	323.15	729.4	60.5	0.08697	0.01	0.03
	348.15	707.3	47.3	0.08597	0.02	0.03
1	298.15	773.8	77.9	0.08634	0.01	0.01
	323.15	749.8	61.6	0.08634	0.01	0.05
	348.15	724.8	49.3	0.08634	0.03	0.06
		Cyclohexane + *n*-dodecane mixture				
0	298.15	745.3	81.9	0.08356	Cited from Ref. 7	
	323.15	727.0	76.8	0.08926		
	348.15	708.6	65.5	0.08869		
0.2	298.15	747.3	77.8	0.08000	0.01	0.02
	323.15	728.6	67.4	0.08129	0.09	0.68
	348.15	709.7	57.4	0.08203	0.00	0.01
0.4	298.15	750.1	71.4	0.07620	0.02	0.03
	323.15	731.0	63.7	0.08002	0.01	0.03
	348.15	711.7	53.9	0.08093	0.01	0.02
0.6	298.15	754.4	73.0	0.07880	0.01	0.03
	323.15	734.6	62.0	0.08067	0.01	0.04
	348.15	714.7	51.0	0.08074	0.01	0.04
0.8	298.15	761.2	55.5	0.06526	0.01	0.01
	323.15	740.2	59.8	0.08120	0.01	0.02
	348.15	719.3	49.0	0.08190	0.01	0.03
		Cyclohexane + *n*-hexadecane mixture				
0	298.15	770.3	45.3	0.04653	Cited from Ref. 8	
	323.15	753.1	83.2	0.08447		
	348.15	735.9	70.9	0.08490		
0.2	298.15	769.8	71.2	0.06736	0.01	0.02
	323.15	752.1	77.2	0.08081	0.01	0.05
	348.15	734.6	69.3	0.08477	0.13	0.46
0.4	298.15	769.2	81.1	0.07646	0.02	0.07
	323.15	751.0	63.9	0.07477	0.03	0.07
	348.15	733.0	60.3	0.07957	0.03	0.18
0.6	298.15	768.6	71.5	0.07224	0.00	0.01
	323.15	749.8	64.5	0.07850	0.02	0.07
	348.15	731.1	58.3	0.08116	0.01	0.02
0.8	298.15	769.1	74.7	0.07851	0.01	0.01
	323.15	748.9	63.6	0.08055	0.01	0.02
	348.15	729.0	54.1	0.08239	0.00	0.01

3.3. Pressure and Density Dependences of Viscosity

The experimental results for the mixtures of cyclohexane with *n*-octane, *n*-dodecane, and *n*-hexadecane, as functions of temperature, pressure, and composition are summarized in Tables II–IV, respectively.

The pressure dependence of the viscosity of the cyclohexane + *n*-hexadecane mixture is shown in Fig. 1. The behavior of the viscosity of the other two systems is quite similar. The viscosity at constant temperature and composition increases monotonously with increasing pressure, with a small positive curvature in each mixture. The pressure coefficient of the viscosity, $(\partial\eta/\partial P)_{T,x}$, is always positive and the temperature coefficient $(\partial\eta/\partial T)_{P,x}$ is negative.

The isothermal density dependence of the viscosity of *n*-dodecane, *n*-hexadecane, and (cyclohexane + *n*-octane) mixtures is shown in Fig. 2. In order to make the viscosity isotherms discrete, $\text{kmol} \cdot \text{m}^{-3}$ was used for the unit of density instead of $\text{kg} \cdot \text{m}^{-3}$. The viscosity increases with increasing density, with a small positive curvature similar to the pressure dependence.

3.4. Composition Dependence of Viscosity

The variation of the viscosity with composition at constant temperature and pressure for the cyclohexane + *n*-octane mixture is shown in Fig. 3. The isobaric composition dependences of the viscosity at 0.1 MPa and 298.15 K for the three mixtures studied in this work are also plotted in Fig. 4 together with those of several benzene + *n*-alkane mixtures [14] at saturation pressure for comparison.

The composition dependence of the viscosity of the cyclohexane mixtures is quite simple. No viscosity extreme is observed in the entire experimental range. The viscosity of the mixture in the *n*-octane system is always lower than the simple mole-fraction average value as shown in Fig. 3. The deviation of the viscosity of the mixture from the mole-fraction average value increases with increasing pressure. This behavior differs from that of monohydric alcohol + water solutions [1–3]. In aqueous monohydric alcohol solutions, the viscosity of the mixture is always much larger than the mole-fraction average value and the deviations between them decrease with increasing pressure.

As for the *n*-dodecane mixture, the viscosity changes almost linearly with composition, as shown in Fig. 4. On the other hand, it should be noted that the viscosity of the mixtures with *n*-hexadecane is always a little greater than the mole-fraction average value. This behavior is rather unique for nonpolar binary solutions. As shown in Fig. 4, the positive deviation from simple additivity is never observed in benzene solutions.

Table II. Viscosity and Density of Cyclohexane + *n*-Octane Mixtures

P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)
	Cyclohexane, 0%			Cyclohexane, 20%	
	298.15 K			348.15 K	
0.1	698.2	0.5107	0.1	667.0	0.3240
9.9	706.5	0.5702	10.1	678.7	0.3626
20.4	714.5	0.6293	20.8	689.5	0.4055
29.9	721.0	0.6874	30.0	697.7	0.4485
61.2	739.6	0.8907	41.2	706.6	0.4917
102.1	759.1	1.210	61.5	720.6	0.5760
149.6	777.4	1.680	79.6	731.4	0.6564
			102.1	743.2	0.7633
	323.15 K		120.9	751.9	0.8487
0.1	678.6	0.3850	140.2	760.1	0.9630
20.1	697.1	0.4745			
52.2	719.8	0.6376		Cyclohexane, 40%	
79.4	735.2	0.7809		298.15 K	
100.8	745.6	0.8965	0.1	720.0	0.5777
151.0	766.3	1.224	9.9	728.4	0.6489
			20.5	736.6	0.7156
	348.15 K		29.6	743.0	0.7861
0.1	657.4	0.3031	40.4	749.9	0.8637
20.0	678.8	0.3796	50.6	756.0	0.9474
50.9	703.3	0.5055	60.6	761.5	1.030
80.3	721.4	0.6250	80.3	771.5	1.211
100.2	731.8	0.7052	101.8	781.2	1.412
150.4	753.8	0.9351	120.1	788.7	1.625
			152.6	800.6	2.023
	Cyclohexane, 20%				
	298.15 K			323.15 K	
0.1	708.5	0.5398	0.1	699.0	0.4326
10.2	717.1	0.6053	10.6	709.3	0.4930
20.4	725.0	0.6652	20.9	718.2	0.5411
30.4	731.9	0.7319	30.4	725.7	0.5962
41.2	738.8	0.8005	40.9	733.1	0.6514
50.9	744.4	0.8751	60.3	745.5	0.7643
80.3	759.6	1.110	79.9	756.4	0.8887
100.6	768.7	1.283	100.5	766.6	1.024
120.1	776.6	1.481	120.6	775.6	1.187
161.5	791.3	1.934	141.0	784.0	1.345
			160.1	791.2	1.513
	323.15 K				
0.1	687.7	0.4103		348.15 K	
13.4	700.6	0.4786	0.1	677.9	0.3331
20.7	706.8	0.5110	20.4	700.0	0.4215
30.1	714.2	0.5611	40.4	717.0	0.5046
39.1	720.7	0.6075	60.8	731.3	0.5975
60.1	734.0	0.7148	80.3	743.1	0.6879
80.3	745.1	0.8320	103.9	755.6	0.8158
101.6	755.5	0.9630	120.9	763.6	0.9101
120.8	764.0	1.088	140.1	772.0	1.023
140.5	771.9	1.232	163.0	781.1	1.168

Table II. (*Continued*)

P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)
	Cyclohexane, 60%			Cyclohexane, 80%	
	298.15 K			348.15 K	
0.1	734.0	0.6273	0.1	707.2	0.3900
10.0	742.4	0.7069	20.4	729.6	0.4943
20.6	750.4	0.7887	40.6	746.9	0.6070
30.1	757.1	0.8710	60.4	761.0	0.7233
40.8	763.9	0.9601	80.3	773.1	0.8506
49.5	769.1	1.044	100.8	784.1	0.9929
100.2	794.4	1.581	120.1	793.3	1.153
137.7	809.4	2.101	140.2	802.1	1.319
			160.7	810.3	1.510
	323.15 K				
0.1	712.5	0.4655		Cyclohexane, 100%	
10.2	722.4	0.5182		298.15 K	
21.1	732.0	0.5820	0.1	773.8	0.8918
30.7	739.5	0.6395	6.2	778.9	0.9702
41.3	747.1	0.7049	13.1	784.2	1.059
60.4	759.4	0.8381	19.0	788.6	1.136
81.2	770.9	0.9907	25.6	793.1	1.240
102.5	781.4	1.160	32.1	797.4	1.337
139.9	797.4	1.497			
161.9	805.7	1.722		323.15 K	
			0.1	749.8	0.6089
	348.15 K		9.9	759.5	0.6902
0.1	691.0	0.3564	20.2	768.6	0.7788
9.8	702.4	0.3968	30.3	776.6	0.8690
19.6	712.4	0.4378	39.5	783.2	0.9596
40.1	730.0	0.5338	50.2	790.4	1.081
71.3	751.2	0.6953	60.7	796.9	1.193
102.4	768.2	0.8835	70.1	802.3	1.326
120.6	776.9	0.9920	80.1	807.8	1.459
140.1	785.4	1.127			
161.2	793.9	1.284		348.15 K	
			0.1	724.8	0.4382
	Cyclohexane, 80%		10.0	736.5	0.4997
	298.15 K		20.0	746.7	0.5640
0.1	751.5	0.7162	30.0	755.7	0.6292
18.4	766.5	0.8936	40.0	763.9	0.6978
29.3	774.1	1.011	50.1	771.4	0.7757
40.6	781.5	1.139	60.4	778.5	0.8514
50.1	787.1	1.249	70.0	784.6	0.9386
79.3	802.3	1.614	80.4	790.7	1.033
			90.3	796.3	1.126
	323.15 K		100.0	801.4	1.222
0.1	729.4	0.5138			
20.0	747.9	0.6495			
40.6	763.3	0.7998			
59.7	775.5	0.9619			
79.9	786.9	1.145			
99.7	796.7	1.335			
121.2	806.4	1.572			
139.7	814.0	1.783			
160.2	821.7	2.024			

Table III. Viscosity and Density of Cyclohexane + *n*-Dodecane Mixtures

P (MPa)	ρ (kg · m^{-3})	η (mPa · s)	P (MPa)	ρ (kg · m^{-3})	η (mPa · s)
	Cyclohexane, 0% 298.15 K			Cyclohexane, 20% 323.15 K	
0.1	745.3	1.352	0.1	728.6	0.8615
19.5	758.8	1.707	20.6	744.6	1.096
39.7	770.7	2.144	40.6	757.6	1.350
50.0	776.1	2.388	59.9	768.2	1.608
81.1	790.7	3.236	81.9	778.9	1.957
92.4	795.4	3.567	102.0	787.5	2.322
	323.15 K		121.5	795.1	2.704
0.1	727.0	0.9146	140.7	802.0	3.101
20.8	742.8	1.159	161.7	809.0	3.599
49.7	760.8	1.553	179.9	814.6	4.086
80.6	776.6	2.046		348.15 K	
100.2	785.4	2.397	0.1	709.7	0.6372
120.3	793.6	2.827	20.6	727.9	0.8071
149.9	804.6	3.490	42.2	743.2	0.9989
	348.15 K		59.5	753.5	1.173
0.1	708.6	0.6654	80.6	764.6	1.389
20.0	725.7	0.8342	101.0	774.0	1.612
40.6	740.2	1.022	121.5	782.5	1.883
60.2	752.0	1.213	140.4	789.7	2.155
80.6	762.8	1.439	160.8	796.9	2.470
100.5	772.2	1.685	180.7	803.3	2.801
121.5	781.2	1.965		Cyclohexane, 40% 298.15 K	
150.8	792.5	2.393	0.1	750.1	1.171
	Cyclohexane, 20% 298.15 K		20.7	764.8	1.486
			40.6	776.7	1.852
0.1	747.3	1.263	60.9	787.0	2.287
19.9	761.1	1.603	80.4	795.7	2.751
39.7	772.7	1.990	100.8	804.0	3.324
60.2	783.1	2.447			
81.1	792.5	3.007			
101.0	800.5	3.600			

Table III. (*Continued*)

P (MPa)	ρ (kg · m^{-3})	η (mPa · s)	P (MPa)	ρ (kg · m^{-3})	η (mPa · s)
	Cyclohexane, 40 % 323.15 K			Cyclohexane, 60 % 348.15 K	
0.1	731.0	0.8075	0.1	714.7	0.5585
20.0	747.3	1.003	29.8	742.1	0.7778
40.2	760.7	1.247	60.6	762.8	1.035
61.3	772.6	1.504	99.9	783.2	1.422
81.1	782.3	1.800	119.6	791.8	1.660
101.3	791.1	2.149	149.7	803.5	2.054
120.3	798.7	2.494	170.2	810.6	2.354
140.1	805.9	2.896			
161.7	813.1	3.404		Cyclohexane, 80 % 298.15 K	
181.0	819.1	3.880			
200.2	824.7	4.438	0.1	761.2	0.9790
			9.6	769.1	1.114
	348.15 K		20.7	777.1	1.260
0.1	711.7	0.5992	30.5	783.5	1.415
21.0	731.1	0.7567	41.3	789.7	1.586
41.0	745.7	0.9166	48.5	793.6	1.726
61.1	758.1	1.102			
80.8	768.6	1.291		323.15 K	
100.8	778.0	1.515	0.1	740.2	0.6736
119.9	786.0	1.749	29.4	764.9	0.9489
139.4	793.6	2.019	61.2	785.0	1.301
159.9	800.9	2.310	71.1	790.4	1.432
179.9	807.5	2.637	99.7	804.1	1.835
			121.5	813.3	2.208
	Cyclohexane, 60 % 298.15 K		150.8	824.3	2.772
				348.15 K	
0.1	754.4	1.071			
19.6	768.7	1.360	0.1	719.3	0.4981
40.8	781.7	1.723	29.5	748.0	0.7022
60.8	792.2	2.121	60.3	769.7	0.9388
80.9	801.4	2.549	101.4	791.9	1.320
			122.3	801.3	1.554
	323.15 K		149.9	812.4	1.914
			179.6	823.0	2.353
0.1	734.6	0.7427			
29.9	758.6	1.042			
61.3	777.6	1.414			
80.6	787.4	1.684			
100.9	796.6	2.001			
121.5	804.9	2.365			
150.6	815.5	2.959			
180.4	825.3	3.641			

Table IV. Viscosity and Density of Cyclohexane + *n*-Hexadecane Mixtures

P (MPa)	ρ (kg·m^{-3})	η (mPa·s)	P (MPa)	ρ (kg·m^{-3})	η (mPa·s)
	Cyclohexane, 0% 298.15 K			Cyclohexane, 20% 323.15 K	
0.1	770.3	3.061	0.1	752.1	1.632
9.9	777.4	3.490	29.4	772.2	2.360
20.7	784.0	3.967	60.6	789.0	3.269
29.8	788.8	4.463	92.2	803.0	4.414
			120.6	813.9	5.675
	323.15 K		149.8	823.8	7.225
0.1	753.1	1.829			
20.9	767.6	2.379		348.15 K	
61.1	789.7	3.649	0.1	734.6	1.132
102.3	807.7	5.353	29.8	757.1	1.606
123.3	815.7	6.450	62.0	775.9	2.216
147.9	824.1	7.920	91.6	790.0	2.872
			121.1	802.1	3.649
	348.15 K		150.8	812.8	4.557
0.1	735.9	1.231	180.3	822.3	5.642
30.3	758.7	1.759			
60.9	776.7	2.380		Cyclohexane, 40% 298.15 K	
102.2	796.1	3.380			
120.8	803.7	3.931	0.1	769.2	2.239
150.5	814.5	4.977	10.7	776.5	2.596
			21.2	783.0	2.936
	Cyclohexane, 20% 298.15 K		30.3	788.3	3.310
			41.5	794.2	3.745
0.1	769.8	2.654	50.3	798.6	4.182
9.6	776.4	3.018			
20.1	782.8	3.438		323.15 K	
39.8	793.5	4.347	0.1	751.0	1.399
			30.7	773.6	2.049
			60.6	790.3	2.783
			80.7	799.7	3.392
			101.3	808.3	4.059
			120.4	815.5	4.841
			141.5	822.7	5.727

Table IV. (*Continued*)

P (MPa)	ρ (kg · m^{-3})	η (mPa · s)	P (MPa)	ρ (kg · m^{-3})	η (mPa · s)
	Cyclohexane, 40%			Cyclohexane, 80%	
	348.15 K			298.15 K	
0.1	733.0	0.9867	0.1	769.1	1.326
29.4	756.8	1.384	10.5	777.1	1.542
61.1	776.1	1.906	20.7	784.1	1.735
91.7	791.1	2.514	30.2	790.1	1.968
120.6	803.1	3.145	40.6	796.2	2.199
150.8	814.0	3.955		323.15 K	
180.8	823.7	4.882	0.1	748.9	0.8848
	Cyclohexane, 60%		29.8	772.7	1.269
	298.15 K		60.6	791.5	1.743
0.1	768.6	1.790	80.0	801.4	2.100
11.2	776.7	2.082	101.1	811.0	2.558
20.4	782.7	2.339	120.1	818.7	3.037
40.9	794.5	2.978		348.15 K	
50.3	799.3	3.320	0.1	729.0	0.6415
	323.15 K		29.5	756.0	0.9109
0.1	749.8	1.154	60.6	777.0	1.237
30.2	773.0	1.668	91.6	793.7	1.632
60.4	790.7	2.272	119.3	806.3	2.044
81.0	800.8	2.779	150.4	818.6	2.608
101.7	809.9	3.357			
120.8	817.4	3.949			
	348.15 K				
0.1	731.1	0.8234			
29.1	755.9	1.164			
60.6	775.9	1.585			
91.5	791.6	2.086			
120.3	804.0	2.648			
149.8	815.2	3.309			
179.9	825.2	4.115			

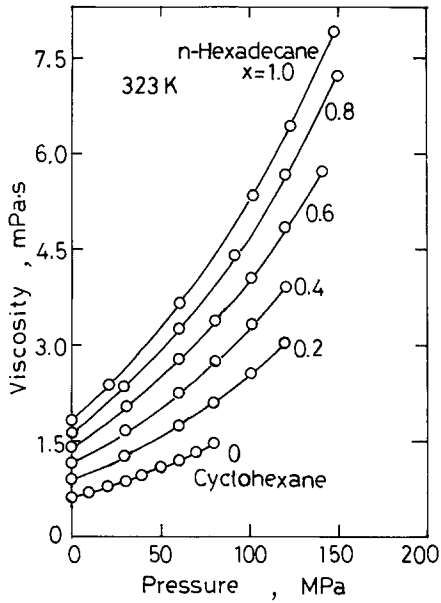

Fig. 1. Pressure dependence of the viscosity of cyclohexane + *n*-hexadecane mixtures at 323 K.

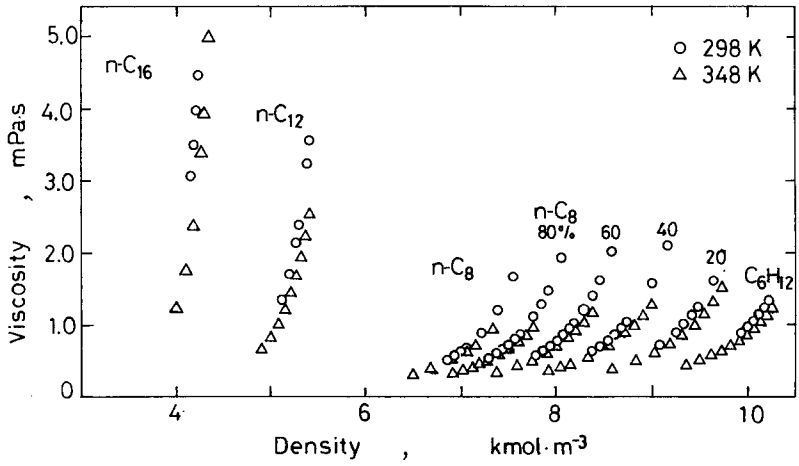

Fig. 2. Density dependence of the viscosity of *n*-dodecane, *n*-hexadecane, and cyclohexane + *n*-octane mixtures.

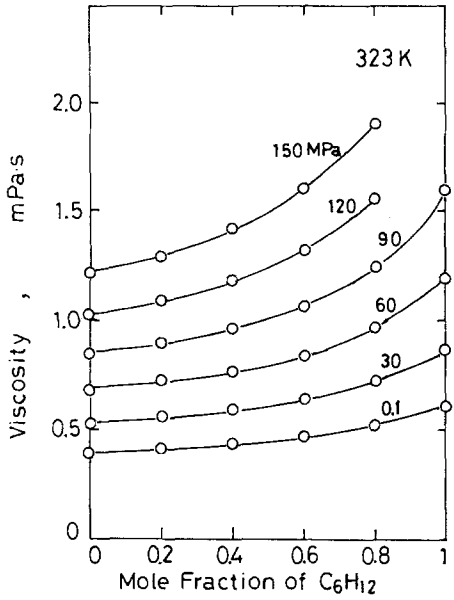

Fig. 3. Composition dependences of the viscosity of cyclohexane + *n*-octane mixtures at 323 K.

4. CORRELATION OF VISCOSITY DATA

The viscosity data obtained have been correlated with pressure, density, and composition with the aid of some empirical methods.

4.1. Correlation with Pressure

An empirical expression similar to the Tait equation, Eq. (2), which is one of the simple and most successful equations to represent the isothermal variation of liquid density under high pressure, was applied to correlate the viscosity data obtained with pressure at a constant temperature and composition:

$$\ln(\eta/\eta_0) = E \ln[(D + P)/(D + P_0)] \tag{3}$$

where η and η_0 are the viscosities at pressure P and P_0 ($=0.1$ MPa), and D and E are the empirical coefficients, respectively. The optimum values of the coefficients were determined from the experimental data by the nonlinear regression method; they are listed in Table V together with the deviations of the experimental data from Eq. (3). The equation is found to represent 359 sets of viscosity data obtained with a mean deviation of 0.7%

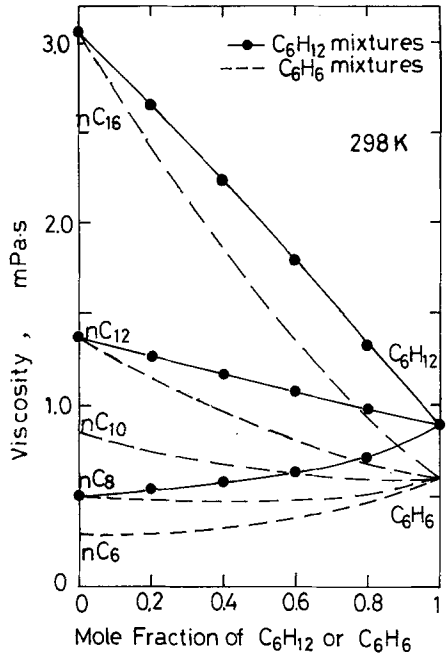

Fig. 4. Composition dependences of the viscosity of (cyclohexane + *n*-alkane) and (benzene + *n*-alkane) mixtures at 298 K. Cyclohexane + *n*-alkane mixtures, at 0.1 MPa; benzene + *n*-alkane mixtures, at saturation pressure.

and a maximum deviation of 1.7%. However, it should be noted that the deviations are found to be systematic for the *n*-hexadecane mixtures, the calculated values are a bit too low at low and high pressures and too high at moderate pressures. This may be due to the fact that the second derivative of Eq. (3) with respect to pressure is always negative. Therefore, this equation is not suitable for liquids whose viscosity increases significantly with increasing pressure with a large positive curvature.

4.2. Correlation with Density

The viscosity of organic liquids and liquid mixtures has been correlated very satisfactorily with molar volume with the aid of the free-volume equation proposed by Dymond and Brawn [15]:

$$\ln \eta_r = F + GV_0/(V - V_0) \tag{4}$$

Table V. Coefficients D, E, and η_0 in Eq. (3)

Mole fraction of cyclohexane	Temp. (K)	η_0 (mPa · s)	D (MPa)	E	Avg. dev. (%)	Max. dev. (%)
		Cyclohexane + *n*-octane mixture				
0	298.15	0.5107	167.5	1.8085	0.2	0.4
	323.15	0.3850	141.4	1.5885	0.3	0.7
	348.15	0.3031	95.2	1.1866	0.4	0.9
0.2	298.15	0.5398	213.3	2.2602	0.5	1.0
	323.15	0.4103	135.6	1.5360	0.6	1.0
	348.15	0.3240	113.9	1.3449	0.5	1.2
0.4	298.15	0.5777	205.5	2.2485	0.5	1.2
	323.15	0.4326	161.4	1.8082	0.7	1.7
	348.15	0.3331	136.2	1.5878	0.5	1.5
0.6	298.15	0.6273	191.2	2.2194	0.5	1.0
	323.15	0.4655	188.2	2.1064	0.1	0.2
	348.15	0.3532	181.9	2.0326	0.4	1.1
0.8	298.15	0.7162	136.7	1.7809	0.2	0.3
	323.15	0.5138	161.7	1.9965	0.2	0.4
	348.15	0.3900	167.1	2.0026	0.5	1.0
1	298.15	0.8921	176.0	2.3950	0.2	0.3
	323.15	0.6090	262.0	3.2740	0.3	0.6
	348.15	0.4382	165.0	2.1590	0.5	0.9
		Cyclohexane + *n*-dodecane mixture				
0	298.15	1.3515	208.6	2.6550	0.4	0.8
	323.15	0.9146	210.0	2.4868	0.6	1.0
	348.15	0.6654	183.3	2.1305	0.5	1.0
0.2	298.15	1.2634	250.7	3.0936	0.2	0.4
	323.15	0.8615	211.3	2.5202	0.4	0.8
	348.15	0.6372	185.4	2.1673	0.6	1.3
0.4	298.15	1.1708	281.8	3.4149	0.1	0.3
	323.15	0.8075	270.8	3.0744	0.4	1.1
	348.15	0.5992	220.7	2.4808	0.4	0.9
0.6	298.15	1.0708	184.1	2.3881	0.2	0.3
	323.15	0.7427	240.2	2.8384	0.3	0.7
	348.15	0.5585	202.1	2.3504	0.4	1.0
0.8	298.15	0.9790	187.8	2.4576	0.4	0.7
	323.15	0.6736	232.3	2.8253	0.3	0.7
	348.15	0.4981	210.0	2.5008	0.8	1.6
		Cyclohexane + *n*-hexadecane mixture				
0	298.15	3.0608	352.9	4.6044	0.3	0.4
	323.15	1.8288	235.8	3.0031	0.5	0.9
	348.15	1.2306	203.1	2.5057	0.8	1.0
0.2	298.15	2.6542	194.6	2.6565	0.1	0.2
	323.15	1.6316	214.5	2.8032	0.5	1.0
	348.15	1.1320	208.1	2.5659	0.5	0.8
0.4	298.15	2.2386	235.4	3.2163	0.5	0.7
	323.15	1.3993	213.1	2.7650	0.5	1.1
	348.15	0.9867	206.5	2.5383	0.3	0.7
0.6	298.15	1.7898	185.7	2.5778	0.1	0.2
	323.15	1.1544	214.7	2.7550	0.3	0.7
	348.15	0.8234	214.6	2.6358	0.5	1.2
0.8	298.15	1.3264	117.1	1.7041	0.4	0.7
	323.15	0.8848	248.3	3.1180	0.4	0.8
	348.15	0.6403	203.1	2.5194	0.5	1.0

η_r is reduced viscosity defined as

$$\eta_r = \eta V^{2/3}/(MT)^{1/2} \tag{5}$$

where η is the viscosity in mPa·s, V is the molar volume in $cm^3 \cdot mol^{-1}$, and M is the molecular weight in 10^{-3} kg·mol^{-1}. The applicability of this equation has been examined. The empirical coefficients F, G, and V_0 were determined by the regression method. Although the optimum values could be determined for each isotherm, it is more convenient to treat F as a constant independent of mixtures, composition, and temperature. Therefore, F was fixed at -5.3 and G and V_0 were redetermined. The coefficients thus obtained are listed in Table VI. Equation (4) was found to represent all experimental data within the experimental uncertainty. The variation of V_0 with composition is quite systematic. The composition dependence of V_0 is found to be correlated satisfactorily with the mole fraction x by the following equation:

$$V_0 = \sum_{i=1}^{4} a_i x^{i-1} \tag{6}$$

Using the value of V_0 calculated from Eq. (6), G was redetermined again. It is found that the variation of the final value of G thus obtained with composition is quite systematic and can be represented by the following equation:

$$G = \sum_{i=1}^{4} b_i x^{i-1} \tag{7}$$

The values of a_i and b_i are given in Table VII. The viscosity at any composition and density can be calculated by Eqs. (4), (6), and (7) within the experimental uncertainty, when the value of η_0 is known.

4.3. Correlation with Composition

The Grunberg and Nissan equation [16] has been applied to correlate the viscosity of mixture η to the viscosities of the pure components η_1 and η_2 at the same temperature and pressure:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 H \tag{8}$$

where H is a characteristic constant for each mixture. This equation has been applied to the binary mixtures studied, and H was found to depend on composition and pressure as

$$H = c_1 + c_2 P + c_3 P^2 + d x_1 \tag{9}$$

Table VI. Coefficients G and V_0 in Eq. (4) with $F = -5.3$

Mole fraction of cyclohexane	Temp. (K)	V_0 ($cm^3 \cdot mol^{-1}$)	G	Avg. dev. (%)	Max. dev. (%)
		Cyclohexane + *n*-octane mixture			
0	298.15	104.8	1.5774	0.3	0.5
	323.15	103.8	1.5642	0.7	1.2
	348.15	102.8	1.5649	1.2	1.7
0.2	298.15	98.9	1.5485	0.3	0.7
	323.15	97.2	1.5827	0.4	0.7
	348.15	96.1	1.5861	0.5	0.9
0.4	298.15	92.4	1.5532	0.3	0.5
	323.15	91.3	1.5590	0.4	0.9
	348.15	91.2	1.5093	0.4	0.7
0.6	298.15	87.3	1.4807	0.4	0.6
	323.15	86.0	1.5006	0.4	0.8
	348.15	86.1	1.4436	0.5	0.9
0.8	298.15	82.2	1.4090	0.6	0.9
	323.15	80.5	1.4578	0.8	1.6
	348.15	80.5	1.4076	0.2	0.4
1	298.15	77.9	1.2878	0.2	0.4
	323.15	76.3	1.3386	0.5	0.7
	348.15	75.8	1.3322	0.3	0.6
		Cyclohexane + *n*-dodecane mixture			
0	298.15	155.0	1.8068	0.3	0.4
	323.15	151.3	1.8643	0.5	0.8
	348.15	150.4	1.8291	0.6	0.9
0.2	298.15	140.6	1.6991	0.2	0.4
	323.15	138.5	1.7136	0.3	0.7
	348.15	136.1	1.7538	0.5	0.8
0.4	298.15	125.1	1.6178	0.5	0.7
	323.15	123.2	1.6342	0.5	1.3
	348.15	121.4	1.6581	0.7	1.2
0.6	298.15	109.1	1.5466	0.2	0.4
	323.15	107.5	1.5618	0.3	0.6
	348.15	105.8	1.5945	0.6	0.9
0.8	298.15	93.8	1.4181	0.6	0.7
	323.15	92.0	1.4584	0.3	0.5
	348.15	91.0	1.4594	0.6	0.9
		Cyclohexane + *n*-hexadecane mixture			
0	298.15	196.2	2.3142	0.6	0.9
	323.15	199.2	2.0944	0.3	0.4
	348.15	195.0	2.1339	0.4	0.6
0.2	298.15	176.5	2.0494	0.2	0.3
	323.15	176.3	1.9618	0.3	0.6
	348.15	173.3	1.9923	0.2	0.4
0.4	298.15	154.1	1.8440	0.4	0.6
	323.15	151.0	1.8738	0.6	0.9
	348.15	148.9	1.8897	0.4	0.8
0.6	298.15	128.4	1.7321	0.1	0.2
	323.15	125.2	1.7917	0.4	0.8
	348.15	124.8	1.7522	0.3	0.6
0.8	298.15	103.1	1.5554	0.5	0.6
	323.15	101.9	1.5521	0.4	0.6
	348.15	99.8	1.5744	0.3	0.6

Table VII. Coefficients a_i and b_i in Eqs. (6) and (7)

Mixture	Temp. (K)	a_1	a_2	a_3	a_4	b_1	b_2	b_3	b_4
Cyclohexane + *n*-octane	298.15	104.8651	−31.3955	1.21032	3.24074	1.57429	−0.052905	−0.013673	−0.221197
	323.15	103.7548	−33.2480	5.02976	6.94444	1.56657	0.114839	−0.330757	−0.007350
	348.15	102.6786	−33.3393	1.25893	−6.25000	1.57040	0.133944	−0.810070	0.445023
Cyclohexane + *n*-dodecane	298.15	155.0556	−70.5542	−13.5813	7.06019	1.81302	−0.325159	−0.278365	0.829618
	323.15	151.3913	−60.4768	−29.9206	15.3935	1.86212	−0.876800	0.981343	−0.622652
	348.15	150.4048	−69.4206	−11.0417	5.90278	1.83101	−0.412354	0.082431	−0.162122
Cyclohexane + *n*-hexadecane	298.15	196.1563	−86.2533	−61.0317	29.0509	2.31877	−1.79103	2.18691	−1.42593
	323.15	199.4040	−114.876	−18.9484	10.9954	2.08856	−0.666741	0.601746	−0.678009
	348.15	195.0683	−104.430	−32.0734	17.2454	2.13187	−0.746477	0.541650	−0.589354

Table VIII. Coefficients c_i and d in Eq. (9)

Mixture	Temp. (K)	$c_1 \times 10$	$c_2 \times 10^3$	$c_3 \times 10^5$	d
Cyclohexane + *n*-octane	298.15	−2.44098	−0.857043	−0.478443	−0.501
	323.15	−0.730763	−1.74532	−1.33900	−0.501
	348.15	0.419237	−4.07309	1.50175	−0.501
Cyclohexane + *n*-dodecane	298.15	1.02496	−1.28085	2.30673	−0.043
	323.15	1.62721	−1.52400	0.157217	−0.043
	348.15	2.95154	−2.78267	1.26860	−0.043
Cyclohecane + *n*-hexadecane	298.15	5.62976	4.10433	−5.27683	0.467
	323.15	5.59606	1.08301	−1.05368	0.467
	348.15	6.53769	−1.27272	0.905823	0.467

where c_i and d are the characteristic constants for mixture, and d is independent of temperature and pressure. The optimum values of the coefficients are given in Table VIII. Equation (8) was found to represent the composition dependence of the viscosity at a given pressure within the maximum deviation of 2.5%. In making this correlation, the viscosities of the mixture and the pure components at a given pressure were calculated from Eq. (3).

5. CONCLUSIONS

As a continuation of the study of the thermophysical properties of organic liquids under pressure, the viscosity and density of binary mixtures of cyclohexane with *n*-octane, *n*-dodecane, and *n*-hexadecane have been measured with an estimated accuracy of better than 2% using a torsionally vibrating crystal viscometer at 298, 323, and 348 K at pressures up to 150 MPa or the freezing pressures. Previously proposed method of correlation and representation of the data are shown to apply satisfactorily to these mixtures. An expression similar to the Tait equation, Eq. (3), gives a good representation of the pressure dependence of the viscosity. The free-volume equation, Eq. (4), and the Grunberg and Nissan equation, Eq. (8), are found to reproduce the experimental data within the uncertainty of the measurements.

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