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Isotope Effect on the Viscosity of Benzene and Cyclohexane Mixtures Under High Pressures

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Viscosities of binary mixtures of cyclohexane with protiobenzene, C_6H_6, or deuteriobenzene, C_6D_6, have been measured at 298 and 323 K and at pressures up to 50 MPa using a capillary viscometer. The viscosities of these mixtures obtained were represented by a empirical Tait-type equation within the experimental uncertainty of $\pm 2\%$. The effect of the isotopic substitution on the viscosity has been discussed.

KEY WORDS: benzene; cyclohexane; deuteriobenzene; isotope effect; molar volume; viscosity.

1. INTRODUCTION

The thermophysical properties of the simple fluids, which are in general governed by their molecular sizes and intermolecular force fields, are frequently reduced by their intermolecular force constants, ε and σ. It is of interest, therefore, to compare the properties of isotopic species which have the negligible effect on the values of ε and σ. But most of the accurate measurements of the isotope effects are restricted only at atmospheric or saturated pressures because of the technical difficulties in making the measurements under high pressures.

In the previous study [1], the densities of the binary mixtures of cyclohexane with protiobenzene, C_6H_6, or deuteriobenzene, C_6D_6, have been measured at 288, 298, and 313 K and at pressures up to 35 MPa. Based on the densities obtained at high pressures, the isotope effects on their compressibilities have been interpreted in terms of a statistical model which partitions the temperature and pressure effects on the

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compressibilities into hard-sphere, internal vibration, libration, and intermolecular attractive parts.

As an extension of the previous study, the isotope effects on the viscosities of these mixtures have been measured at 298 and 323 K and at pressures up to 50 MPa. For pure cyclohexane, the measurement at 298 K was restricted at pressures up to 23 MPa to avoid solidification of the sample. The measurements have been performed with a high-pressure capillary viscometer and the estimated uncertainty of the viscosity obtained is ±2%.

2. EXPERIMENTAL

Viscosities at high pressures were measured with a capillary viscometer described in detail elsewhere [2]. In this study, the viscometer was used on a relative basis and the instrument constant has been calibrated against pure water in the entire range of the temperature and pressure. Therefore, neglecting the small contribution rising from the acceleration and the deceleration effects at the ends of the capillary, we can determine the sample viscosity by measuring the ratio of the time intervals in which a given volume of the sample fluid or pure water passes through the capillary. The capillary prepared for the present measurement is made of stainless steel with a length of 105 mm and with outer and inner diameters of 1.59 and 0.080 mm, respectively. Temperatures and pressures are measured with a quartz thermometer to within ±10 mK and with a digitized Bourdon gauge to within ±0.2 MPa, respectively.

Protiobenzene and cyclohexane were obtained from Nakalai Tesque Inc. with guaranteed purities more than 99.5%. Deuteriobenzene, whose inverting ratio with deuterium is more than 99.5%, was obtained from Aldrich Chemical Company, Inc. These pure materials were dried over sodium for more than 48 hr before preparing the sample mixtures gravimetrically. Besides the impurities of the samples, the additional uncertainty of the composition of each mixture arising from the preparation procedure should be accurate to within ±0.01%. For each binary mixture, the viscosity measurements at high pressures were performed at each 0.25 nominal mole fraction. And the extra measurements have been performed at atmospheric pressure with an Ubbelohde viscometer in order to elucidate the composition dependences.

Judging from the precisions of the instruments, the purities of samples and the reproducibility of measurements, we estimate the uncertainties of the viscosities obtained to be within ±2%.

3. RESULTS AND DISCUSSION

3.1. Viscosity at Atmospheric Pressure

The viscosities obtained at atmospheric pressure with an Ubbelohde viscometer are presented in Table I and are shown in Fig. 1 as a function of concentration. As is evident from this figure, the viscosities of these mixtures are considerably lower than the mole-fraction averaged values and it is observed that each isotherm has a shallow minimum at the lower concentration of cyclohexane.

The following empirical equation was adopted to correlate these experimental viscosities as a function of concentration:

$$\eta_0 = (1-x_c)\,\eta_{b,0} + x_c\eta_{c,0} + x_c(1-x_c)\sum_{i=1}^{3} d_i(1-2x_c)^{i-1} \tag{1}$$

where η_0 is the viscosity at atmospheric pressure in mPa · s and x_c is the mole fraction of cyclohexane. The subscript b indicates pure protiobenzene or pure deuteriobenzene and c pure cyclohexane. The empirical coefficients d_i, determined from the best fit to the experimental viscosities, are presented in Table II together with the average and maximum deviations.

The viscosity of pure protiobenzene obtained at 298 K agrees with the literature values within the combined experimental uncertainties; i.e., 0.18% higher than that of Grunberg and Nissan [3], 0.40 and 0.35% lower than those of Kashiwagi and Makita [4], and Dymond [5, 6], respectively. For pure cyclohexane at the same temperature, our datum is

Table I. Viscosities, in mPa · s, of Protiobenzene + Cyclohexane Mixtures and Deuteriobenzene + Cyclohexane Mixtures at Atmospheric Pressure

$C_6H_6 + C_6H_{12}$			$C_6D_6 + C_6H_{12}$		
x_c	298.15 K	313.15 K	x_c	298.15 K	313.15 K
0	0.6015	0.4891	0	0.6392	0.5187
0.1130	0.5844	0.4798	0.1261	0.6146	0.5047
0.2788	0.5858	0.4800	0.2320	0.6081	0.5011
0.3934	0.5941	0.4892	0.3618	0.6124	0.5039
0.4840	0.6105	0.5008	0.5055	0.6320	0.5185
0.6277	0.6509	0.5311	0.6416	0.6687	0.5457
0.7507	0.7020	0.5672	0.7430	0.7109	0.5747
0.8313	0.7502	0.6015	0.8733	0.7861	0.6260
0.9186	0.8154	0.6463	1.0	0.8909	0.6980
1.0	0.8909	0.6980			

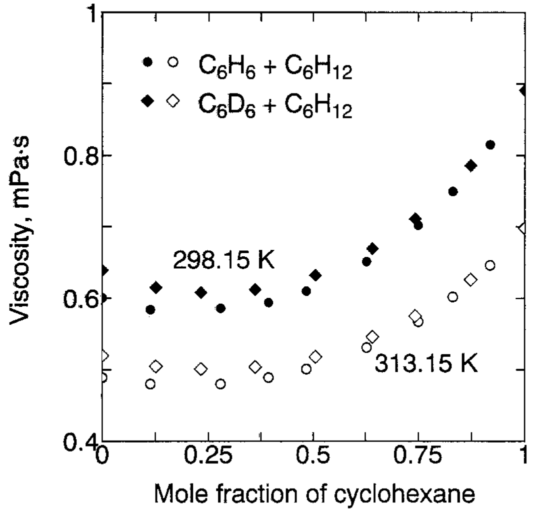

Fig. 1. Composition dependence of the viscosity of the protiobenzene and cyclohexane mixtures and the deuteriobenzene and cyclohexane mixtures at atmospheric pressure.

0.55 % higher than that of Grunberg and Nissan and 0.13 and 0.58 % lower than those of Kashiwagi and Makita and of Dymond, respectively. For the protiobenzene and cyclohexane mixtures, the present results at 298 K agree with those of Grunberg and Nissan within 0.9 % in the entire range of composition.

Table II. Coefficients d_i in Eq. (1)

Temp. (K)	$\eta_{b,0}$	$\eta_{c,0}$	d_1	d_2	d_3	Dev. (%)	
						Ave.	Max.
			($C_6H_6 + C_6H_{12}$)				
298.15	0.6015	0.8909	−0.52819	0.13186	−0.09526	0.11	0.31
313.15	0.4891	0.6980	−0.35967	0.08272	−0.05606	0.05	0.18
			($C_6D_6 + C_6H_{12}$)				
298.15	0.6392	0.8909	−0.53481	0.10401	−0.08645	0.05	0.11
313.15	0.5187	0.6980	−0.36065	0.07268	−0.04479	0.06	0.10

3.2. Viscosity at High Pressures

The viscosities obtained at high pressures with a capillary viscometer are presented in Tables III, IV, and V. A small correction, less than 0.5%, was applied to the data collected by this viscometer so that the viscosities at atmospheric pressure reported in these tables agree with those calculated from Eq. (1). Pressure effects on the viscosities of the protiobenzene and cyclohexane mixtures at 313 K are typically shown in Fig. 2. As shown in this figure, the viscosity at each composition increases monotonously with increasing pressure. The viscosity of pure protiobenzene is slightly lower than that of the 0.25 nominal mole fraction mixuture ($x_c = 0.2530$) in the low-pressure range. Due to the increase in the pressure coefficient with the mole fraction of cyclohexane, the viscosity values of the pure protiobenzene and the 0.25 nominal mole fraction mixture are reversed around 40 MPa and the viscosities are arranged according to the mole fraction at the

Table III. Viscosities, in mPa · s, of Pure Components at Elevated Pressures

C_6H_6		C_6D_6		C_6H_{12}	
P (MPa)	η_P (mPa · s)	P (MPa)	η_P (mPa · s)	P (MPa)	η_P (mPa · s)
		298.15 K			
0.10	0.6015	0.10	0.6392	0.10	0.8909
6.12	0.6359	6.18	0.6720	1.26	0.9051
12.22	0.6722	12.18	0.7067	4.73	0.9401
18.19	0.7055	18.20	0.7490	8.13	0.9838
24.19	0.7406	24.20	0.7851	11.08	1.0252
30.18	0.7738	30.15	0.8259	14.22	1.0620
37.10	0.8127	36.17	0.8586	17.15	1.0969
43.12	0.8486	42.16	0.9018	20.22	1.1411
49.07	0.8912	49.12	0.9598	23.11	1.1880
		313.15 K			
0.10	0.4891	0.10	0.5187	0.10	0.6980
6.12	0.5139	6.21	0.5484	5.21	0.7402
12.22	0.5409	12.18	0.5760	12.16	0.8172
18.19	0.5749	18.17	0.6131	18.89	0.8835
24.19	0.6041	24.17	0.6402	24.13	0.9394
30.18	0.6302	30.15	0.6680	30.23	0.9968
37.10	0.6597	36.11	0.6955	35.97	1.0741
43.12	0.6911	42.12	0.7277	42.18	1.1508
49.07	0.7206	49.12	0.7668	47.85	1.2281

Table IV. Viscosities, in mPa · s, of Protiobenzene + Cyclohexane Mixtures at Elevated Pressures

$x_c = 0.2530$		$x_c = 0.5036$		$x_c = 0.7479$	
P (MPa)	η_P (mPa · s)	P (MPa)	η_P (mPa · s)	P (MPa)	η_P (mPa · s)
		298.15 K			
0.10	0.5828	0.10	0.6150	0.10	0.7016
6.12	0.6140	6.22	0.6531	6.19	0.7506
12.21	0.6472	12.24	0.6941	12.21	0.8033
18.21	0.6872	18.23	0.7329	18.20	0.8598
24.21	0.7212	24.25	0.7777	24.16	0.9139
30.17	0.7640	30.15	0.8243	30.28	0.9707
36.15	0.8047	36.28	0.8728	36.24	1.0322
42.16	0.8444	42.11	0.9290	42.18	1.0942
48.08	0.8899	49.99	0.9936	49.15	1.1701
		313.15 K			
0.10	0.4791	0.10	0.5042	0.10	0.5672
6.17	0.5102	6.05	0.5373	6.18	0.6080
12.15	0.5303	12.10	0.5714	12.19	0.6523
18.16	0.5664	18.21	0.6005	18.19	0.6950
24.16	0.5936	24.15	0.6376	24.21	0.7390
30.21	0.6187	30.14	0.6746	30.21	0.7815
36.10	0.6569	36.04	0.7086	36.20	0.8312
42.11	0.6920	40.08	0.7417	42.17	0.8754
49.02	0.7352	48.97	0.7977	49.17	0.9449

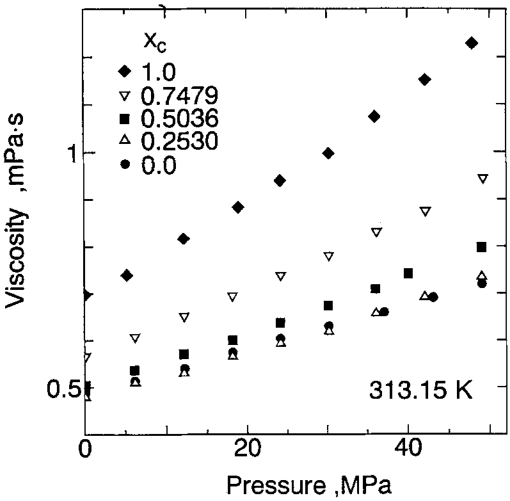

Fig. 2. Viscosity of protiobenzene and cyclohexane mixture at 313.15 K as a function of pressure.

Table V. Viscosities, in mPa · s, of Deuteriobenzene + Cyclohexane Mixtures at Elevated Pressures

$x_c = 0.2383$		$x_c = 0.5130$		$x_c = 0.7519$	
P (MPa)	η_P (mPa · s)	P (MPa)	η_P (mPa · s)	P (MPa)	η_P (mPa · s)
		298.15 K			
0.10	0.6077	0.10	0.6340	0.10	0.7148
6.17	0.6428	6.18	0.6759	6.21	0.7675
12.18	0.6777	12.18	0.7196	12.23	0.8210
18.20	0.7124	18.17	0.7669	18.20	0.8713
24.19	0.7587	24.29	0.8080	24.18	0.9363
30.23	0.7970	30.25	0.8548	30.14	0.9883
36.18	0.8408	36.19	0.9023	36.16	1.0529
42.15	0.8815	42.20	0.9544	42.26	1.1192
49.17	0.9400	49.12	1.0144	49.22	1.2047
		313.15 K			
0.10	0.5006	0.10	0.5201	0.10	0.5773
6.22	0.5324	6.18	0.5589	6.18	0.6191
12.20	0.5608	12.17	0.5933	12.18	0.6663
18.22	0.5947	18.20	0.6306	18.14	0.7080
24.20	0.6273	24.15	0.6596	24.18	0.7548
30.22	0.6574	30.21	0.6982	30.18	0.7961
36.21	0.6843	36.16	0.7384	36.19	0.8473
42.20	0.7203	42.15	0.7754	42.20	0.8958
49.17	0.7599	49.14	0.8240	49.18	0.9614

highest pressure of the measurement. A similar behavior is also observed for deuteriobenzene and cyclohexane mixtures.

The viscosity at high pressures was satisfactorily correlated in terms of the following Tait-type equation:

$$\eta_P^{-1} = \eta_0^{-1}\left(1 - C\ln\frac{B+P}{B+P_0}\right) \qquad (2)$$

where η_P and η_0 are the viscosity in mPa · s at pressure P and at atmospheric pressure P_0 in MPa. The empirical coefficients B and C were determined from the smoothed values of η_0 calculated from Eq. (1). A concentration dependence of C was not observed. Furthermore, it was found that the value of C does not vary from the protiobenzene and cyclohexane mixtures to the deuteriobenzene and cyclohexane mixtures within the experimental uncertainty. B was therefore redetermined at each temperature, with the average value taken for C. The empirical coefficients B

and C are given in Table VI together with the average and maximum deviations.

The present results for pure protiobenzene and pure cyclohexane at 298 K agree with the data of Kashiwagi and Makita [4] within 0.64 and 0.74%, respectively. Since the recent measurement of Assael et al. [7] for pure protiobenzene was performed at different temperatures of 303 and 323 K, a direct comparison with the present data cannot be made. But the relative viscosities η_P/η_0, i.e., the ratios of the viscosities at high pressures to those at atmospheric pressure, have the same dependence on temperature. Reference data at high pressures for the viscosities of present mixtures are not available.

3.3. Isotope Effect on the Viscosity

In this subsection, the isotope effects on the viscosities of the present mixtures are discussed. Rowlinson [8] has suggested that the viscosity ratio of isotope species equals the square root of their mass ratio.

$$\frac{\eta_i}{\eta}=\left(\frac{m_i}{m}\right)^{1/2} \tag{3}$$

Table VI. Coefficients B and C in Eq. (2)

	298.15 K			313.15 K		
		Dev. (%)			Dev. (%)	
x_c	B (MPa)	Ave.	Max.	B (MPa)	Ave.	Max.
			($C_6H_6+C_6H_{12}$)			
	$C=0.6884$			$C=0.5461$		
0.0	79.637	0.55	0.86	60.201	0.43	0.83
0.2530	73.777	0.23	0.56	56.101	0.50	1.13
0.5036	67.263	0.18	0.66	50.945	0.28	0.66
0.7479	61.010	0.31	0.88	45.683	0.22	0.59
1.0	53.395	0.22	0.53	39.968	0.35	0.92
			($C_6D_6+C_6H_{12}$)			
	$C=0.6884$			$C=0.5461$		
0.0	78.731	0.33	0.52	59.731	0.40	1.16
0.2383	73.212	0.20	0.58	55.675	0.37	0.72
0.5130	66.409	0.36	0.95	50.151	0.41	0.87
0.7519	60.764	0.36	1.19	45.357	0.24	0.57

Here i refers to the isotopically substituted species. According to the principle of corresponding states, the viscosity can be reduced as follows with the aid of the intermolecular force constants, ε and σ:

$$\eta^* = \frac{\eta\sigma^2}{(m\varepsilon)^{1/2}} \tag{4}$$

where η^* is the reduced value of the viscosity. It is known that the isotopic substitution has very little effect on their intermolecular force constants. The principle of corresponding states, therefore, supports the square root law proposed by Rowlinson. But the square-root law is not always satisfied and the existence of some isotopic species, for which this law does not hold, has been reported [9–11]. These inconsistencies can be explained on the basis of a theoretical approach proposed by Pople [12]. The motion of a polyatomic molecule is governed by the following linear and angular equations of motion:

$$F = m\left(\frac{dv}{dt}\right) \tag{5}$$

$$G = I\left(\frac{d\omega}{dt}\right) \tag{6}$$

where v and ω are the linear and angular velocities, m and I are the mass and mean moment of inertia, and F and G are the force and couple acting on the molecule arising from the intermolecular field. For a monoatomic molecule, the square-root law is effective because of the absence of the couple G, except for the lower temperature range where the quantum effect becomes important. Since the inertia tensor I changes in different ratio from the molecular mass m by isotopic substitution, this square-root law cannot be applicable in general for polyatomic molecules. But if all the atomic masses in the molecule are changed in the same ratio as H_2/D_2, the molecular mass and the inertia tensor alter in the same ratio. Or if the intermolecular potential is of a central force type like CH_4/CD_4, the couple G becomes practically zero. Then the square-root law remains valid even for polyatomic molecules.

The isotope effects on the viscosities of the present mixtures have been determined as follows. A smoothing fit of the coefficient B in Table VI against the mole fraction of cyclohexane x_c has been attempted to correct for the small difference of the concentrations at which the measurements for the two systems, protiobenzene and cyclohexane mixtures and deuteriobenzene and cyclohexane mixtures, were carried out.

$$B = B_b(1 - x_c) + B_c x_c + a x_c(1 - x_c) \tag{7}$$

Table VII. Coefficients a, B_b, and B_c in Eq. (7)

Temp. (K)	C	a	B_b (MPa)	B_c (MPa)	Dev. (%) Ave.	Dev. (%) Max.
			$(C_6H_6+C_6H_{12})$			
298.15	0.6884	4.0835	79.637	53.395	0.30	1.08
313.15	0.5461	4.0488	60.201	39.968	0.36	1.24
			$(C_6D_6+C_6H_{12})$			
298.15	0.6884	3.5738	78.731	53.395	0.28	1.01
313.15	0.5461	2.7235	59.713	39.968	0.34	1.15

Here B_b and B_c are the coefficients for benzene and cyclohexane presented in Table VI. The optimum value of a is given in Table VII. A comparison of the average and maximum deviations in this table with those in Table VI assures that the smoothing operation of B has very little influence upon the reproducibility of the data. The isotope effect on the viscosity $\Delta\eta_{\text{iso}}$ defined by the following equation has been determined at the various pressures and the concentrations with the aid of Eqs. (2) and (7).

$$\Delta\eta_{\text{iso}} = \{(\eta_H - \eta_D)/\eta_H\}\, 100(\%) \tag{8}$$

Here η_H and η_D are the viscosities of the protiobenzene and cyclohexane mixtures and the deuteriobenzene and cyclohexane mixtures, respectively. As shown in Table VIII, the isotope effect $\Delta\eta_{\text{iso}}$ is negative in the entire range of the measurements and monotonously gets close to zero according

Table VIII. Isotope Effect (%) Defined by Eq. (8) at Various Pressures and Compositions

	P (MPa)					
x_c	0.1	25.0	50.0	0.1	25.0	50.0
		298.15 K			313.15 K	
0	−6.27	−6.41	−6.51	−6.05	−6.22	−6.37
0.25	−4.26	−4.35	−4.42	−4.51	−4.75	−4.97
0.50	−2.78	−2.14	−3.57	−2.90	−3.17	−3.39
0.75	−1.59	−1.91	−2.27	−1.51	−1.72	−1.91

to the mole fraction of cyclohexane. The values of $\Delta\eta_{\text{iso}}$ observed between pure protiobenzene and pure deuteriobenzene are lower than the value predicted from the square-root law by -4.7%. These inconsistencies could be due to the fact that benzene has a noncentral intermolecular-force field. As neither the ratio of the molar mass m_i/m nor that of the mean moment of inertia I_i/I depends on the pressure, no dependence of the isotope effect on pressure is expected. The isotope effect seems to become more negative with increasing pressure, but this pressure effect is within the uncertainty of the measurement and a definite statement, that any pressure effect exists, cannot be made.

4. CONCLUSION

The viscosities of protiobenzene and cyclohexane mixtures and of deuteriobenzene and cyclohexane mixtures were determined at 298 and 313 K and at pressures up to 50 MPa with a capillary viscometer. Simple empirical equations are given to represent the viscosity as a function of pressure and concentration within the experimental uncertainty. A negative isotope effect on the viscosity was discussed based on the differences of the molecular mass and the mean moment of inertia between the isotopic species.

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