

Viscosity of Twelve Hydrocarbon Liquids in the Temperature Range 298–348 K at Pressures up to 110 MPa

H. Kashiwagi¹ and T. Makita¹

Received June 22, 1982

New experimental data on the viscosity of 12 organic liquids are presented at temperatures of 25, 30, 50, and 75°C and at pressures up to 110 MPa. The liquids measured are five *n*-alkanes (C₆, C₇, C₈, C₁₀, C₁₂), cyclohexane, and six aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylenes). The measurements were performed using a torsionally vibrating crystal method on a relative basis with an uncertainty less than 2%. A linear relationship between fluidity and molar volume, which is predicted from the hard-sphere theory, fails at pressures above 50 MPa. The rough hard-sphere model proposed by Chandler provides a reasonable representation of the data for aromatic hydrocarbons, while for *n*-alkanes the agreement is not satisfactory because of an aspherical shape of molecules. The viscosity data can be correlated well with the molar volume by a free-volume expression and also can be represented as a function of pressure by a similar expression to the Tait equation.

KEY WORDS: aromatic hydrocarbons; cyclohexane; free volume expression; hard-sphere theory; high pressure; *n*-alkanes; torsionally vibrating crystal method; viscosity.

1. INTRODUCTION

In the scientific and technological fields, there is a great need to obtain accurate viscosity data of liquids over wide ranges of temperature and pressure. Even at the present time, reliable experimental values of viscosity at high pressures are limited. This is ascribed to the difficulty in measurements by use of conventional techniques under special conditions, such as low temperatures or high pressures. Therefore, it is essential to establish a

¹Department of Chemical Engineering, Kobe University, Kobe 657, Japan.

new technique for precise measurements over wide ranges of temperature and pressure.

This paper describes a precise viscometer that utilizes the torsionally vibrating crystal method on a relative basis, and presents new experimental data on the viscosity of 12 organic liquids in the temperature range from 25.00°C (298.15 K) to 75.00°C (348.15 K) at pressures up to 110 MPa. The experimental data obtained are compared with values reported in the literature and are used to examine several theories or empirical expressions on the viscosity of liquids at high pressures.

2. EXPERIMENTAL PROCEDURE

2.1. Principle of Experimental Method

In the past, various techniques have been developed in order to determine the viscosity of fluids at high pressures. In such conventional methods, it is necessary to make a relative motion between the fluid and a part of the viscometer, such as rotation, oscillation, falling, or fluid flow. The difficulties were often attributed to these macroscopic motions under the special conditions. Also, the complicated structure and use of the viscometer, as well as ambiguities in the theory of the method, presented unfavorable conditions.

In the present investigation, we chose a torsionally vibrating crystal method, in which the relative motion is microscopic. The torsional viscometer was originally developed for investigations in the rheological field. The first attempt with this method to measure viscosity of fluids was reported by Welber and Quimby [1, 2]. Subsequently, the technique has been applied to lubricant oils [3, 4], organic liquids [5], fluids in low temperature ranges [6–11], and in the critical region [12]. Elaborate and representative work using this method are the measurements for cryogenic fluids at the U.S. National Bureau of Standards [7, 10, 13]. At the present time, this method is considered to be a precise technique with many advantages compared to the other methods [14].

The torsionally vibrating crystal method is based on the “converse” piezoelectric property of quartz. A quartz crystal is cut in the form of a right circular cylinder along the x axis, and four electrodes, opposite ones of which are connected electrically, are placed in the quadrants between the y and z axes. When an alternating electric field is applied across the two pairs of the electrodes, the crystal vibrates in a torsional mode, twisting its ends to the opposite direction. When the vibrating crystal is immersed in a fluid, a shear wave generated on the surface of the crystal is propagated

into the fluid. Viscous resistivity of the fluid results in changes of the electric characteristics of the crystal, mainly the resonance frequency and conductance. Therefore, with this technique measurements of viscosity of fluids reduce to those of the equivalent electric quantities of the crystal.

The viscosity of the fluid η is derived by solving the Navier–Stokes equation with appropriate boundary conditions as follows:

$$\eta\rho = (M/S)^2(f/\pi)(\delta - \delta_0)^2 \quad (1)$$

where ρ is the density of the fluid, and M , S , and f are the mass, surface area, and resonant frequency of the crystal, respectively. δ is the logarithmic decrement of the crystal when immersed in the fluid, and subscript 0 denotes a loss term due to internal friction of the crystal and its suspension. The logarithmic decrement of the crystal oscillation can be related to its resonant properties from a fundamental electrical theory, and the following expressions are obtained:

$$\eta\rho = (M/S)^2(\pi f)\left(\frac{\Delta f}{f} - \frac{\Delta f_0}{f_0}\right)^2 \quad (2)$$

or the rearranged form is

$$(\pi f \eta \rho)^{1/2} = (R - R_0)K^{-1} \quad (3)$$

and

$$K = [S/(\pi M)](R/\Delta f) \quad (4)$$

where R is the resonant resistance of the crystal, and Δf is the frequency bandwidth, the difference in frequency at the half-conductance points of the resonant curve of the crystal. As the quantities marked by the subscript 0 are determined by measurements in vacuum, the viscosity of fluids can be calculated by the electrical measurements of R , f , Δf in the sample fluids.

2.2. Apparatus

2.2.1. Quartz Crystal and Crystal Assembly

The quartz crystal used was cut right cylindrically along the x axis within an accuracy of ± 10 min of arc, and was 50.01 mm in length and 5.000 mm in diameter. This crystal had a resonant frequency of about 39

kHz. The surface of the crystal was polished to an optical finish. Four gold electrodes were coated on the crystal surface by vacuum deposition in quadrants of 80° between the y and z axes. The phosphor-bronze wires of 0.182 mm diam were soldered at the longitudinal center of each electrode. They acted as both the electrical leads and mechanical support for the crystal.

Figure 1 shows the cross-section of the crystal-holder assembly. Four brass strips, 2, were attached, by screws, to a pair of rings made of glass fiber-reinforced polytetrafluoroethylene, 4. The quartz crystal, 1, was suspended by four electric leads, which were connected to steel springs, 3. The crystal holder was vertically mounted in the cell, which was filled with the sample liquid. The bellows, 5, made of stainless steel (SUS 304), was used to transmit the pressure to the liquid and to separate it from the hydraulic oil. This cell was placed in a high pressure vessel made of stainless steel (SUS 420), which was immersed in a water bath thermostatically controlled to within ± 10 mK. Temperature was determined with a standard thermometer calibrated by the National Research Laboratory of Metrology, Japan, and the accuracy is estimated to be better than ± 20 mK. The pressure was generated with an oil pump and measured with a Bourdon gauge calibrated against a standard pressure balance with an error of $\pm 0.1\%$.

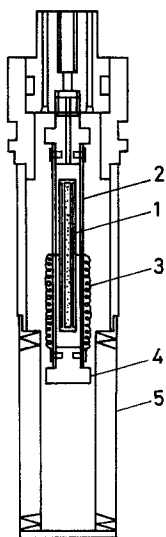


Fig. 1. The torsionally vibrating crystal viscometer: 1, quartz crystal; 2, brass strips; 3, steel springs; 4, PTFE rings; 5, stainless steel bellows.

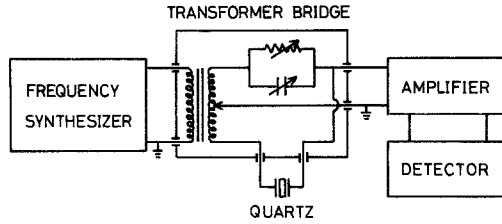


Fig. 2. Schematic diagram of the electrical measuring system.

2.2.2. Electrical System

The bridge technique was employed to measure the resonant properties of the torsional vibration of the crystal. Figure 2 shows a schematic diagram of the electric circuit. The crystal was connected in the unknown-arm of a transformer ratio-arm bridge, which could inherently eliminate the stray capacitance of the bridge and leads. The adjustable arm of the bridge consists of a variable conductor and a variable capacitor with resolutions of 0.3 nS and 0.01 pF, respectively. The bridge was driven with an eight-digit frequency synthesizer with a stability of one part in 10⁸ and a resolution of 1 mHz. The balance of the bridge was displayed as Lissajous' figure on an oscilloscope and was detected with an electronic voltmeter.

2.3. Calibration of Instrument

The viscosity of a fluid can be determined on an absolute basis using the viscometer described herein according to Eqs. (2)–(4). Although we first attempted to measure the viscosity of the liquids on an absolute basis, the viscosity data obtained were found to be 3–6% higher than values in the literature. These deviations would be ascribed partly to the uncertainty in measurements of the background damping. In the measurement of resonant properties of the crystal in a vacuum, an auxiliary conductance-capacitance box was required. However, the use of this external component would have made the measurements inaccurate. Therefore, we decided to conduct the measurements on a relative basis. Two correction factors α , β and α' , β' were introduced in Eqs. (2) and (3), respectively:

$$\eta\rho = \alpha(M/S)^2(\pi f)(\Delta f/f - \beta)^2 \tag{5}$$

$$(\pi f \eta \rho)^{1/2} = \alpha'(R - \beta')K^{-1} \tag{6}$$

where K is defined by Eq. (4). These instrument constants were determined

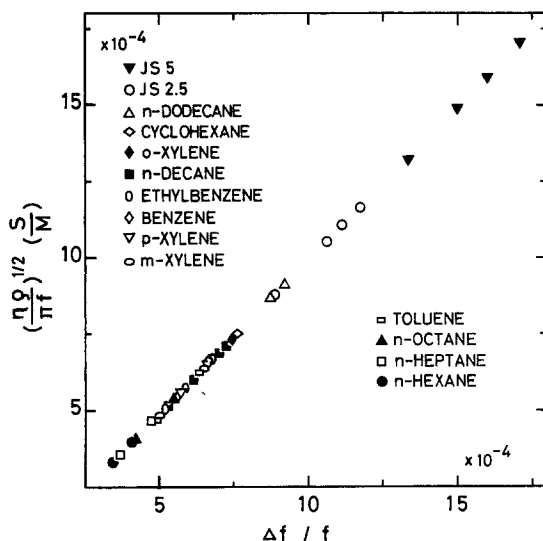


Fig. 3. Calibration curve for the viscometer on the basis of Eq. (5).

using the literature values at atmospheric pressure of the twelve liquids [15–17] and the “viscosity standard liquids” JS 2.5 and JS 5, provided from the National Research Laboratory of Metrology, Japan. The density values of the twelve liquids were cited in the literature [18–23].

The calibration curve based on Eq. (5) is shown in Fig. 3 over the entire experimental range. α and β were determined by means of the least squares method. The calibration covers the viscosity range 0.2–4.2 mPa · s. It was found that α was 1.00 within the experimental uncertainty and β was slightly dependent on temperature. β ranges from 1.1×10^{-4} at 25°C to 1.8×10^{-4} at 75°C. Another test for Eq. (6) was also attempted, and the viscosity values obtained by Eqs. (5) and (6) were found to agree well within $\pm 0.1\%$. Therefore, in the present investigation, Eq. (5) was employed to calculate viscosity.

2.4. Uncertainties of Measurements

In the torsionally vibrating crystal method, one of the assumptions in the derivation of Eq. (1) is that the flow of a fluid surrounding the crystal should be laminar. None of the earlier investigators discussed the problem of laminar-turbulent transition of the fluid flow theoretically or experimentally. Applied voltage across the crystal may be a measure of this problem [2], because the voltage relates to the velocity of the flow. Therefore, we tested several measurements at various voltages from 0.01 to 0.5 V under a

given condition. There was no evidence for the dependence of the results on the applied voltage. Since the present measurements were performed using applied voltages between 0.1 and 0.4 V, the viscosity obtained should be free from this sort of error.

It is also assumed in Eq. (1) that the propagated wave on the crystal surface should be the plane wave. The maximum amplitude in oscillation and the penetration depth, $(\pi f \rho / \eta)^{1/2}$, were within the order of 10^{-3} or 10^{-4} mm. These values were sufficiently small in comparison with the crystal radius, so that the above assumption would be valid.

The experimental results of 14 liquids used in the present calibration at atmospheric pressure were found to reproduce the literature values within $\pm 1\%$. Therefore, the uncertainty of the viscosity values obtained was estimated to be less than 2%, taking into account the accuracy of the literature values used in the calibration.

2.5. Materials

All the sample liquids used in these measurements were supplied as reagent-grade from commercial sources. Although they were used in as-received condition without further purification, their purities were in excess of 99%. The impurities should not have affected the final results.

3. EXPERIMENTAL RESULTS

3.1. Pressure Effect on the Viscosity of Liquids

The experimental data for the viscosity of 12 organic liquids were determined under pressures up to 110 MPa along four isotherms of 25, 30, 50, and 75°C. Approximately 80 data points for each liquid were obtained.² Figure 4 illustrates the typical pressure dependence of the viscosity of cyclohexane together with some literature values [5, 24–26]. The viscosity isotherms of other liquids show similar behavior, and 50°C isotherms of seven liquids are given in Fig. 5

The relative viscosity η_p/η_0 , the ratio of viscosity at high pressure to that at atmospheric pressure, of the liquids at 50°C is shown in Fig. 6. An interesting tendency was noted in the sign of the temperature coefficient of the relative viscosity $[\partial(\eta_p/\eta_0)/\partial T]_P$; that is, for *n*-alkanes, it changes from positive (C_6 , C_7) to negative (C_{10} , C_{12}) through nearly zero (C_8); for aromatic hydrocarbons, the sign is nearly zero except for *o*-xylene (negative); and for cyclohexane, the sign is positive.

²The raw data are available from T. Makita on request.

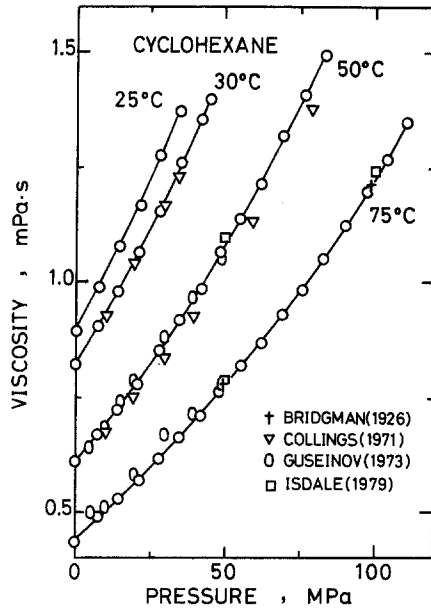


Fig. 4. Viscosity of cyclohexane as a function of pressure.

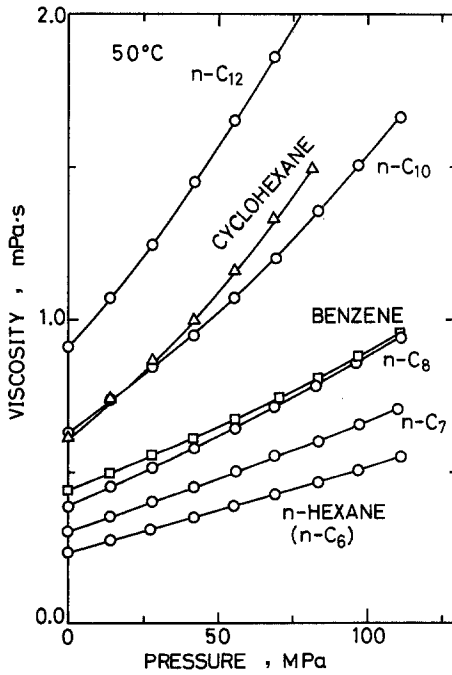


Fig. 5. Viscosity of liquids as a function of pressure at 50°C.

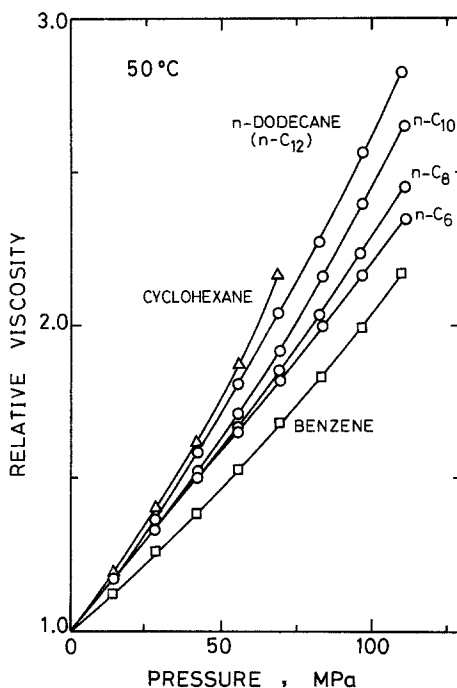


Fig. 6. Relative viscosity of liquids as a function of pressure at 50°C.

3.2. Comparison with Literature Values

Bridgman [26] measured viscosity of numerous liquids at pressures up to 1200 MPa by a falling weight method. Only a few of his data points can be compared with the present results, because he performed the measurements at pressure intervals of 50 or 100 MPa. His results agree with the present ones within the combined uncertainties, taking into account his accuracy of 2–5%, for *n*-hexane, *n*-decane, cyclohexane, benzene, toluene, and xylene isomers. Recent extensive data by Dymond and his coworkers [24, 27–29] obtained by a falling weight viscometer are in good agreement within $\pm 2\%$ with our results for *n*-octane, *n*-dodecane, cyclohexane, and benzene, except *n*-hexane at 50°C, where the maximum deviation amounts to 4%.

For *n*-hexane, *n*-heptane, and *n*-octane, the discrepancies between the present results and the values of Agaev and Golubev [30, 31] did not exceed 4%, while their pressure coefficient of viscosity is larger than that of this work. Agreements of the present results with Dickinson's data [32] by a falling weight method and with data of Brazier and Freeman [33] by a rolling ball method were not good for *n*-hexane and *n*-octane. Collings and McLaughlin [5] measured the viscosity of several organic liquids using a

torsionally vibrating crystal method. Their results agree with the present data within 4% for cyclohexane and benzene. The measurements of Guseinov et al. [25] by a transpiration method lack internal consistency as shown in Fig. 4. Data of Jobling and Lawrence [34] by a falling weight method and those of Parkhurst and Jonas [35] by a rolling ball method deviate by nearly 3% for benzene. The data of Mamedov et al. [36] for benzene and those of Akhundov et al. [37] for toluene by a transpiration method agree very well with the present results, within a maximum deviation of less than 1%. The viscosity of ethylbenzene as measured by Akhundov [38] lies far above the present data.

3.3. Empirical Representation of Viscosity with Respect to Pressure

Various empirical expressions have been proposed in order to represent viscosity data as functions of pressure and temperature. First, we attempted to fit the viscosity and the logarithm of the viscosity obtained to simple isothermal polynomial equations of pressure, and it was found that these expressions could reproduce the present results satisfactorily under the entire experimental conditions.

It is well known that the Tait equation reproduces PVT relations of many organic liquids [18, 21]. A similar expression was tested:

$$(\eta - \eta_0)/\eta = E' \ln[(D' + P)/(D' + 0.1)] \quad (7)$$

where η_0 is the viscosity at 0.1 MPa. The viscosity data of aromatic hydrocarbons and cyclohexane were fitted satisfactorily, while the fit to *n*-dodecane, which shows strong pressure dependence of the viscosity, was somewhat inferior. Some modification of the left-side term yields

$$\ln(\eta/\eta_0) = E \ln[(D + P)/(D + 0.1)] \quad (8)$$

This equation was found to give a good representation of the present results. The values of the coefficients of the equation are listed in Table I, in which the average and maximum deviations are also shown. The second derivative of Eq. (8) with respect to pressure is always negative, so it means that this expression could not be applied to liquids whose viscosity increases rapidly with pressure.

4. DISCUSSION

4.1. Linear Relation of Fluidity to Molar Volume

The fluidity, the reciprocal of viscosity, of liquids relates to the free volume, as represented by the following equation:

$$1/\eta = A' + B'(V - V_i)/V_i \quad (9)$$

Table I. Coefficients of Eq. (8)

Substance	Temp. (°C)	η_0 (mPa · s)	E	D (MPa)	Avg. dev. (%)	Max. dev. (%)
<i>n</i> -Hexane	25	0.2964	1.173	110	0.2	0.7
	30	0.2844	1.158	109	0.2	0.5
	50	0.2334	1.018	86	0.4	0.9
	60	0.2126	0.8898	69	0.4	1.1
<i>n</i> -Heptane	25	0.3905	1.477	143	0.3	0.8
	30	0.3692	1.336	125	0.3	0.9
	50	0.3019	1.159	102	0.3	1.0
	75	0.2380	0.9854	77	0.4	1.4
<i>n</i> -Octane	25	0.5094	1.840	175	0.3	1.3
	30	0.4806	1.650	154	0.3	1.1
	50	0.3862	1.361	121	0.3	1.1
	75	0.3024	1.103	90	0.4	1.4
<i>n</i> -Decane	25	0.8654	2.263	195	0.2	0.7
	30	0.8092	2.316	203	0.3	0.9
	50	0.6269	2.221	202	0.4	0.9
	75	0.4675	1.455	123	0.4	1.3
<i>n</i> -Dodecane	25	1.3587	2.978	245	0.3	0.8
	30	1.2315	2.248	176	0.5	1.4
	50	0.9100	2.011	163	0.3	0.5
	75	0.6647	1.990	169	0.5	1.1
Cyclohexane	25	0.8921	4.587	350	0.2	0.8
	30	0.8193	3.141	238	0.2	0.5
	50	0.6090	2.845	224	0.3	0.8
	75	0.4382	2.271	175	0.5	1.7
Benzene	25	0.6039	2.908	336	0.2	0.4
	30	0.5623	2.559	295	0.2	0.8
	50	0.4402	2.192	259	0.2	0.6
	75	0.3361	1.478	165	0.3	1.0
Toluene	25	0.5535	2.372	308	0.2	0.7
	30	0.5204	1.806	226	0.2	0.6
	50	0.4221	1.584	199	0.2	0.8
	75	0.3375	1.580	202	0.3	0.8
Ethylbenzene	25	0.6293	2.444	322	0.2	0.5
	30	0.5923	2.144	278	0.3	0.7
	50	0.4797	1.752	229	0.2	0.6
	75	0.3794	1.308	161	0.3	0.7
<i>o</i> -Xylene	25	0.7519	2.748	317	0.3	0.9
	30	0.7043	2.900	343	0.3	0.6
	50	0.5549	2.368	285	0.3	0.8
	75	0.4325	1.702	204	0.3	0.8
<i>m</i> -Xylene	25	0.5834	2.924	387	0.2	0.6
	30	0.5498	2.471	324	0.3	0.7
	50	0.4486	2.068	277	0.2	0.7
	75	0.3568	1.401	177	0.3	0.9
<i>p</i> -Xylene	25	0.6031	1.155	131	0.2	0.3
	30	0.5674	1.690	199	0.3	0.8
	50	0.4580	1.834	223	0.2	0.8
	75	0.3638	1.701	209	0.3	1.1

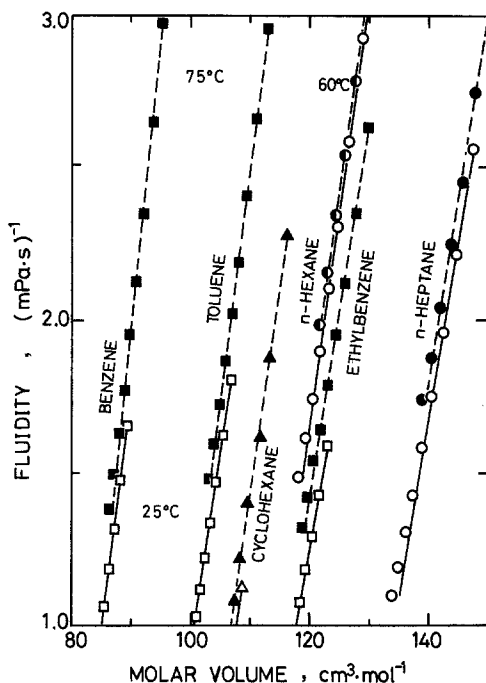


Fig. 7. Fluidity of liquids as a function of molar volume at 25 and 75°C (*n*-hexane: at 25 and 60°C).

where V is the molar volume under a given condition, and V_i is the molar volume under a condition where the molecules cannot move any longer. A linear relation between the fluidity and molar volume was also suggested from both the smooth hard-sphere model [39] and the rough hard-sphere model [40].

Figure 7 shows the dependence of the fluidity on the molar volume. As the liquids measured are not the exact hard-sphere molecules, the linear relation holds only in the limited density range, namely, at pressures up to 50–90 MPa. As pointed out by Dymond and Brawn [41], this expression provides an accurate description of viscosity in a restricted density range.

4.2. Smooth and Rough Hard-Sphere Models

One of the most successful interpretations of the viscosity of dense liquids is the rough hard-sphere theory proposed by Chandler [40], which has been examined by Jonas and his coworkers [35, 42, 43]. Based on a computer simulation [44], Chandler obtained the following expression for

the smooth hard-sphere model:

$$1/\eta_{\text{SHS}} = 0.02358(\pi mkT)^{-1/2}\sigma^2 \times [3.7043 - 6.3355n\sigma^3 + 2.6718(n\sigma^3)^2] \quad (10)$$

where η_{SHS} is in mPa · s, m is the molecular mass in 10^{-3} kg, n is the number density in cm^{-3} ($= \rho/m$), k is the Boltzmann constant, and σ is the hard-sphere diameter in cm. This equation is valid over the density range of $0.70 \leq n\sigma^3 \leq 0.97$. The viscosity by the rough hard-sphere model η_{RHS} is proportional to that by the smooth hard-sphere model η_{SHS} as

$$\eta_{\text{RHS}} = C\eta_{\text{SHS}} \quad (11)$$

where C is a parameter indicating the effect of translational-rotational coupling in this model.

The applicability of the RHS model was examined by using the present results. The adjustable parameters σ and C were simultaneously determined by statistical regression of the data along each isotherm with Eqs. (10) and (11). The RHS parameters obtained are shown in Table II, where the average and maximum deviations of the calculated values from the experimental data are also given. The RHS theory represents satisfactorily the viscosity of aromatic hydrocarbons, which have relatively rigid ring structures, while agreements of the model with the data of n -alkanes are

Table II. The Hard-Sphere Parameters of Eqs. (10) and (11)

Substance	σ^a (Å; 10^{-10} m)	C^a	Avg. dev. (%)	Max. dev. (%)
<i>n</i> -Hexane	5.683–5.701	1.434–1.239	1.1–1.3	2.1–3.3
<i>n</i> -Heptane	5.951–5.977	1.659–1.296	1.0–1.3	2.1–3.3
<i>n</i> -Octane	6.213–6.226	1.852–1.448	1.1–1.3	2.2–2.6
<i>n</i> -Decane ^b	6.677	2.447–1.867	1.0–1.9	2.4–3.6
<i>n</i> -Dodecane ^b	7.070–7.089	3.379–2.185	1.5–2.2	3.6–5.4
Cyclohexane ^b	5.538–5.526	1.669–1.459	0.4–1.1	0.7–3.1
Benzene	5.122	1.461–1.186	0.4–0.5	0.7–1.1
Toluene	5.412	1.533–1.267	0.4–0.7	0.7–1.4
Ethylbenzene	5.683	1.725–1.389	0.5–0.5	1.0–1.4
<i>o</i> -Xylene	5.702	1.653–1.320	0.6–1.2	1.3–2.0
<i>m</i> -Xylene	5.692	1.571–1.255	0.4–0.6	0.9–1.5
<i>p</i> -Xylene	5.709	1.603–1.271	0.5–0.7	1.1–1.8

^a Values at temperatures 25–75°C (*n*-Hexane: at 25–60°C).

^b Some of the data points exceed the density limit $n\sigma^3 \leq 0.97$.

unfavorable. This suggests a limitation of the RHS theory for liquids composed of aspherical molecules. (The large value of C reflects the strong coupling effect partially due to their aspherical shape.) In addition, most of the data points for n -dodecane and some of those for n -decane and cyclohexane exceeded the density limit described above.

Chandler demonstrated that σ slightly decreases with increasing temperature, that the density dependence of σ is negligible, and that C is independent of temperature and density. However, C is obviously dependent on temperature as presented in Table II. It is difficult to evaluate definitely the temperature dependence of σ from the present measurement, since the experimental range of temperature is narrow and the variation of σ with temperature is small. Jonas and his coworkers [35, 43] reported the values of σ and C using their data of self-diffusion coefficient and viscosity: $\sigma = 5.12 \sim 5.05 \text{ \AA}$ (10^{-10} m) and $C = 1.32$ (average value) at $30\text{--}160^\circ\text{C}$ for benzene, and $\sigma = 5.55 \sim 5.51 \text{ \AA}$ and $C = 1.61 \sim 1.31$ at $40\text{--}110^\circ\text{C}$ for cyclohexane. Their values are relatively in good agreement with the present results.

4.3. Free Volume Expression

The viscosity of several hydrocarbon liquids can be related to molar volume by the following equation of a free volume type:

$$\ln \eta' = A + BV_i/(V - V_i) \quad (12)$$

The quantity η' is the reduced viscosity defined [41] as

$$\eta' = 100\eta V^{2/3}/(MT)^{1/2} \quad (13)$$

where η' is in units of $\text{mPa} \cdot \text{s}$, V is in $\text{cm}^3 \cdot \text{mol}^{-1}$, and M is molecular weight in $10^{-3} \text{ kg} \cdot \text{mol}^{-1}$.

The applicability of this expression to the present results was examined. We determined the coefficients A , B , and V_i as experimentally adjustable constants dependent on temperature for each liquid by the least squares method. In the above analysis, if A is regarded as a temperature independent constant, A is equal to -1.5 for n -alkanes and -0.5 for aromatic hydrocarbons and cyclohexane. When A is assumed to be -1.0 as Dymond and his coworkers [27–29, 41] did, the fit to the data is somewhat inferior, but sufficient with a maximum deviation of 2.5%. V_i decreases linearly with increasing temperature. The optimized values of the coefficients are listed in Table III, as well as the deviations from the experimental data.

Table III. Coefficients of Eqs. (12) and (13) with $A = -1$

Substance	Temp. (°C)	V_i ($\text{cm}^3 \cdot \text{mol}^{-1}$)	B	Avg. dev. (%)	Max. dev. (%)
<i>n</i> -Hexane	25	73.1	2.057	0.4	0.8
	50	73.1	2.011	0.4	1.4
	60	73.1	1.996	0.6	2.0
<i>n</i> -Heptane	25	84.1	2.144	0.2	0.6
	50	83.8	2.104	0.4	1.0
	75	83.5	2.074	0.7	2.5
<i>n</i> -Octane	25	98.0	2.084	0.3	0.9
	50	97.0	2.073	0.3	0.7
	75	96.0	2.072	0.5	0.9
<i>n</i> -Decane	25	125.6	2.048	0.3	0.6
	50	121.9	2.152	0.5	0.9
	75	118.2	2.258	0.3	0.9
<i>n</i> -Dodecane	25	151.7	2.086	0.2	0.6
	50	148.9	2.118	0.5	0.9
	75	146.1	2.162	0.6	1.4
Cyclohexane	25	75.3	1.579	0.3	0.9
	50	73.9	1.628	0.6	1.3
	75	72.5	1.687	0.6	2.0
Benzene	25	58.2	1.642	0.3	0.6
	50	56.9	1.693	0.4	1.0
	75	55.6	1.748	0.4	0.9
Toluene	25	67.0	1.793	0.3	0.9
	50	65.8	1.822	0.2	0.8
	75	64.6	1.859	0.4	0.8
Ethylbenzene	25	76.9	1.902	0.3	0.7
	50	74.9	1.967	0.2	0.6
	75	72.9	2.047	0.2	0.6
<i>o</i> -Xylene	25	82.1	1.584	0.3	0.8
	50	80.1	1.654	0.4	0.9
	75	78.1	1.728	0.2	0.9
<i>m</i> -Xylene	25	78.6	1.762	0.4	0.9
	50	77.3	1.779	0.3	0.8
	75	76.0	1.801	0.3	0.9
<i>p</i> -Xylene	25	78.6	1.818	0.1	0.3
	50	77.6	1.809	0.2	0.7
	75	76.6	1.816	0.4	1.0

5. CONCLUSIONS

The viscosity of twelve liquids has been measured in the temperature range 25–75°C at pressures up to 110 MPa or the freezing pressure, using the torsionally vibrating crystal method on a relative basis. The experimental results are used to examine several empirical or theoretical expressions

for the viscosity of liquids:

1. A similar formula to the Tait equation, Eq. (8), gives a good representation for the present results of all the 12 liquids over the entire range of experimental conditions, as shown in Table I.
2. A linear relation between the fluidity and molar volume holds only in a limited pressure range up to 50~90 MPa.
3. The rough hard-sphere theory, Eqs. (10) and (11), represents satisfactorily the viscosity of aromatic hydrocarbons, while the agreement with the data of *n*-alkanes is unfavorable, as given in Table II.
4. Another free volume expression, Eqs. (12) and (13), is found to reproduce the present experimental data reasonably well with only two adjustable parameters, as given in Table III.

ACKNOWLEDGMENTS

Financial support for this work was provided in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan. We would like to express our appreciation to S. Nishikubo and M. Nakano for their assistance in constructing the apparatus. The valuable advice and continuing encouragement of Professors H. Kubota and Y. Tanaka are also gratefully acknowledged.

REFERENCES

1. B. Welber and S. L. Quimby, *Phys. Rev.* **107**:645 (1957).
2. B. Welber, *Phys. Rev.* **119**:1816 (1960).
3. J. K. Appeldoorn, E. H. Okrent, and W. Philippoff, *Proc. Am. Petrol. Inst.* **III 42**:163 (1962).
4. R. G. Rein, Jr., T. T. Charng, C. M. Sliepcevich, and W. J. Ewbank, *ASLE Trans.* **18**:123 (1975).
5. A. F. Collings and E. McLaughlin, *Trans. Faraday Soc.* **67**:340 (1971).
6. B. A. Lowry, S. A. Rice, and P. Gray, *J. Chem. Phys.* **40**:3673 (1964).
7. D. E. Diller, *J. Chem. Phys.* **42**:2089 (1965).
8. W. Herreman, A. Lattenist, W. Grevendonk, and A. DeBock, *Physica* **52**:489 (1971).
9. R. W. H. Webeler and G. Allen, *Phys. Rev. A* **5**:1820 (1972).
10. W. M. Haynes, *Physica* **67**:440 (1973).
11. M. P. Bertinat, D. S. Betts, D. F. Brewer, and G. J. Butterworth, *J. Low Temp. Phys.* **16**:479 (1974).
12. H. J. Strumpf, A. F. Collings, C. J. Pings, *J. Chem. Phys.* **60**:3109 (1974).
13. D. E. Diller and J. M. Saber, *Physica* **108A**:143 (1981).
14. H. J. M. Hanley, R. D. McCarty, and W. M. Haynes, *J. Phys. Chem. Ref. Data* **3**:979 (1974).
15. J. H. Dymond and K. J. Young, *Int. J. Thermophys.* **1**:331 (1980).
16. Y. Tanaka, unpublished data (obtained by correlation).
17. Selected Values in Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, API Research Project **44** (1953-).
18. H. E. Eduljee, D. M. Newitt, and K. E. Weale, *J. Chem. Soc.* 3086 (1951).
19. J. W. M. Boelhouwer, *Physica* **26**:1021 (1960).

20. P. S. Snyder, M. S. Benson, H. S. Huang, and J. Winnick, *J. Chem. Eng. Data* **19**:157 (1974).
21. H. Kashiwagi, T. Fukunaga, Y. Tanaka, H. Kubota, and T. Makita, *Rev. Phys. Chem. Japan* **49**:70 (1979).
22. Unpublished data obtained in the authors' laboratory.
23. A. M. Mamedov, T. S. Akhundov, and F. G. Abdullaev, *Inzh.-fiz. Zh.* **30**:705 (1976).
24. J. D. Isdale, J. H. Dymond, and T. A. Brawn, *High Temp.-High Press.* **11**:571 (1979).
25. S. O. Guseinov, Ya. M. Naziev, and A. K. Akhmedov, *Izv. vyssh. ucheb. Zaved., Neft' i Gaz* **16**(2):65 (1973).
26. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **61**:57 (1926).
27. J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.* **1**:345 (1980).
28. J. H. Dymond, J. Robertson, and J. D. Isdale, *Int. J. Thermophys.* **2**:133 (1981).
29. J. H. Dymond, J. Robertson, and J. D. Isdale, *Int. J. Thermophys.* **2**:223 (1981).
30. N. A. Agaev and I. F. Golubev, *Dokl. Akad. Nauk. SSSR* **151**:597 (1963).
31. N. A. Agaev and I. F. Golubev, *Gazov. Promst.* **8**(7):50 (1963).
32. E. Dickinson, *J. Phys. Chem.* **81**:2108 (1977).
33. D. W. Braizier and G. R. Freeman, *Can. J. Chem.* **47**:893 (1969).
34. A. Jobling and A. S. C. Lawrence, *Proc. Roy. Soc. London* **206A**:257 (1951).
35. H. J. Parkhurst, Jr., and J. Jonas, *J. Chem. Phys.* **63**:2705 (1975).
36. A. M. Mamedov, T. S. Akhundov, Sh. M. Ismail-Zade, and A. D. Tairov, *Izv. vyssh. ucheb. Zaved., Neft' i Gaz* **14**(2):74 (1971).
37. T. S. Akhundov, Sh. M. Ismail-Zade, and A. D. Tairov, *Izv. vyssh. ucheb. Zaved., Neft' i Gaz* **13**(2):79 (1970).
38. T. S. Akhundov, *Izv. vyssh. ucheb. Zaved., Neft' i Gaz* **16**(10):46, 74 (1973).
39. J. H. Dymond, *J. Chem. Phys.* **60**:969 (1974).
40. D. Chandler, *J. Chem. Phys.* **62**:1358 (1975).
41. J. H. Dymond and T. A. Brawn, in *Proc. 7th Symp. Thermophys. Properties* (ASME, New York, 1977), p. 660.
42. J. Jonas, D. Hasha, and S. G. Huang, *J. Chem. Phys.* **71**:3996 (1979).
43. J. Jonas, D. Hasha, and S. G. Huang, *J. Phys. Chem.* **84**:109 (1980).
44. B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.* **53**:3813 (1970).