

## **Thermophysical Properties of Liquids at High Pressures**

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Most of the thermophysical properties of fluids are greatly altered at high pressures, and the studies of these changes are of much scientific and technological importance. In this paper, the effects of temperature and pressure on the density, viscosity, and thermal conductivity of various liquids are described briefly, based on recent experimental results from the author's laboratory. The objectives of this investigation, methods of measurements, and some of the experimental results are reviewed, as well as the present aspects in this field. Several important problems to be interpreted are also pointed out from the present measurements.

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**KEY WORDS:** density; liquid; pressure; Tait-type equation; thermal conductivity; viscosity.

### **1. INTRODUCTION**

Knowledge of the thermophysical properties of fluids under pressure is of practical importance in the field of science and technology. Research on thermodynamic and transport properties at high pressures has developed vigorously in recent years. In particular, the effects of temperature and pressure on various properties have been investigated carefully for a limited number of important fluids during the past 20 years. The general behavior of these properties in the gaseous phase is well understood, and it has become possible, to some extent, to interpret theoretically and to predict empirically the effect of high pressure. Furthermore, the thermophysical properties of several industrially important gases have been critically evaluated by several data centers or groups [1], and "the most probable values"

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or "selected values" have been published in wide ranges of temperature and pressure [2].

On the other hand, the thermophysical properties of liquids under pressure have not always been interpreted both empirically and theoretically. For instance, the polarity and chemical structure of liquid molecules strongly affects their response to different temperatures and pressures. In this paper, therefore, the recent results of experimental measurements in the author's laboratory reviewed are restricted to the volumetric property (density) and the transport properties (viscosity and thermal conductivity) in the liquid phase.

## 2. OBJECTIVES OF HIGH PRESSURE RESEARCH

In consideration of the present situation of high pressure science and technology, it is essential for us to investigate the properties of fluids from the following points of view.

1. A standard method of measurements should be established for each property at each physical state, which is applicable in a wide range of temperature and pressure. As there are no standard methods of measurements of thermophysical properties of fluids, various devices have been employed for each property, and large discrepancies are often found among the results reported by different researchers.

2. Standard values of several reference fluids for each property should be determined, and these should be confirmed internationally and interdisciplinarily, as in the case of steam properties by the International Association for the Properties of Steam. The standard values should be determined by several investigators using all the available experimental methods on an absolute basis. The experimental values should be interpreted theoretically, if possible. Although various relative measurements are often made in order to avoid the theoretical difficulties of measurements, the standard values of appropriate reference fluids have not yet been established.

3. Standard values as functions of temperature and pressure with appropriate tolerances should be formulated.

4. Precise experimental data should be obtained on thermophysical properties of fluids with different chemical structures, especially polar fluids, covering wide ranges of temperature and pressure.

5. Theoretical studies should be done on the properties of polar fluids in relation to their chemical structures, as the effect of pressure is remarkably different in some cases.

6. Accurate experimental data should be obtained on various types of mixtures, and mixing rules under high pressures should be developed.

7. The anomalous phenomena of various properties under special conditions should be studied, such as the critical anomaly, the first density

coefficient of viscosity, and behavior of the excess transport properties at very high pressures. These phenomena should be observed quantitatively by precise experimental techniques.

8. The interrelation among different thermophysical properties of fluids should be investigated, for example, relations between density and transport properties from the standpoint of the pressure effect and the chemical structure of the fluids.

9. Studies on these properties should be done under high pressures beyond 1 GPa, as those regions have scarcely been explored for both gaseous and liquid states.

10. Macroscopic phenomena should be studied by means of microscopic treatments at the molecular level. Especially, the liquid structures of polar fluids should be studied in relation to their spectroscopic and electromagnetic properties.

Of course, these items are the philosophy and the final goal of our high-pressure work on fluid properties, although it will be difficult to solve even one of these problems in a short time in one laboratory.

### 3. EXPERIMENTAL METHODS

With the advancement of molecular theories and industrial technologies, more accurate data on various kinds of fluids are required over wide ranges of temperature and pressure. Consequently, several new devices for the measurement of thermophysical properties have been introduced, adding to the various traditional methods. The present methods of measurement were selected empirically from the viewpoint of good accuracy, reproducibility, and practical convenience, as described below for each property measurement.

The experimental studies at high pressure in liquid systems present no difficulty. In the pressure ranges up to 500 MPa, it is usually convenient to use thick-walled steel tubes and cylindrical pressure vessels, in which the measuring devices are installed, to generate pressure by a hand pump and an intensifier, and to measure pressure by Bourdon gauges or transducers, which are calibrated against a dead-weight gauge within an error less than 0.1%. The measuring cylinders are immersed in a liquid bath thermostatically controlled to within  $\pm 10$  mK. The temperature is determined with a standard resistance thermometer calibrated by the National Research Laboratory of Metrology, Japan.

#### 3.1. Density Measurements

The density of liquids has been measured using a high-pressure burette apparatus [3, 4], whose schematic diagram is shown in Fig. 1. The volume change with temperature and pressure of a sample liquid of known mass,

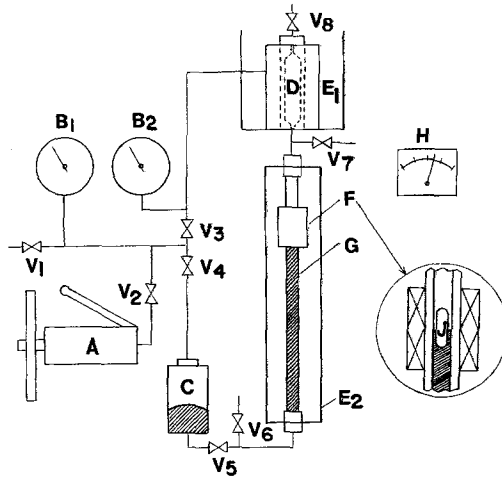


Fig. 1. Schematic diagram of the high-pressure burette apparatus: *A*, oil pump; *B*, Bourdon gauges; *C*, Hg cylinder; *D*, sample vessel; *E*, thermostats; *F*, differential transformer; *G*, burette (made of SS316); *H*, micro-ammeter; *J*, magnetic float; *V*, valves.

which is introduced into a vessel *D* and the upper part of burette *G*, is measured by the displacement of mercury level in the burette. The position of a magnetic float *J* on the surface of the mercury column is detected outside the burette by a differential linear transformer *F*. The pressure is transmitted through mercury filled in *C* and *G* by an oil pump *A*. The sample vessel *D* consists of coaxial double cylinders. The inner cylinder is a thin-walled sample cell (about 95 cm<sup>3</sup>), to the outside wall of which a somewhat lower pressure is applied separately from the oil pump in order to minimize the deformation of the cell. The burette is made of a SS316 thick-walled tube, whose inner and outer diameters are 4.742 and 14.0 mm, respectively. The inner volumes of every 10 mm length were carefully calibrated using the weight of mercury.

The density  $\rho$  is calculated by

$$\rho = W / [(W/\rho_0) - (\Delta V + \delta)] \quad (1)$$

where  $W$  is the mass of the sample liquid filled in the system,  $\rho_0$  is the density of the sample at atmospheric pressure,  $\Delta V$  is the volume change measured in the burette, and  $\delta$  is a small correction for the volume change of the burette tube with temperature and pressure. The maximum uncertainty in the measured density does not exceed 0.1% over the entire experimental range.

### 3.2. Viscosity Measurements

Difficulties encountered in the measurements of transport properties under high pressure arise out of the following technical problems: (a) establishing a constant or transient gradient in the fluid; (b) detecting the gradient precisely; (c) obtaining the theoretical solutions of the basic equation, under the measuring conditions in the apparatus employed; (d) avoiding the turbulent condition or heat convection, resulting from the existence of a gradient. In most cases, these difficulties increase with increasing pressure, especially near the critical point or the phase boundaries.

The viscosity of liquids has been measured by a falling cylinder viscometer, a falling-ball viscometer, and a torsionally vibrating-crystal method. All the measurements were performed on a relative basis, because it was difficult to realize the ideal condition required by the basic theories under high pressures. Fortunately, the viscometer calibrating liquids are available covering the wide range of viscosity values as shown in Table I, although they are effective only at atmospheric pressure.

#### 3.2.1. Falling-Cylinder Viscometer

The apparatus consists of a precisely bored Pyrex glass tube equipped coaxially in a high pressure vessel and a glass cylindrical plummet with hemispherical ends, as shown in Fig. 2 [5]. The plummet is provided with

**Table I.** Viscosity of Standard Liquids (Viscometer Calibrating Liquids) by the National Research Laboratory of Metrology, Japan

Code	Kinematic viscosity ( $\text{cSt} = 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ )		Viscosity ( $\text{cP} = \text{mPa} \cdot \text{s}$ )	
	20°C	50°C	20°C	50°C
JS 2.5	2.5	1.5	2	1.1
JS 5	5	2.5	4	2
JS 10	10	4	8	4
JS 20	20	7	17	6
JS 50	50	14	42	12
JS 100	100	25	85	20
JS 200	200	40	170	35
JS 500	500	80	450	70
JS 1000	1000	140	900	120
JS 2000	2000	250	1800	200
JS 20H	20000		(17400)	
JS 60H	60000		(52800)	
JS 200H	200000		(178000)	

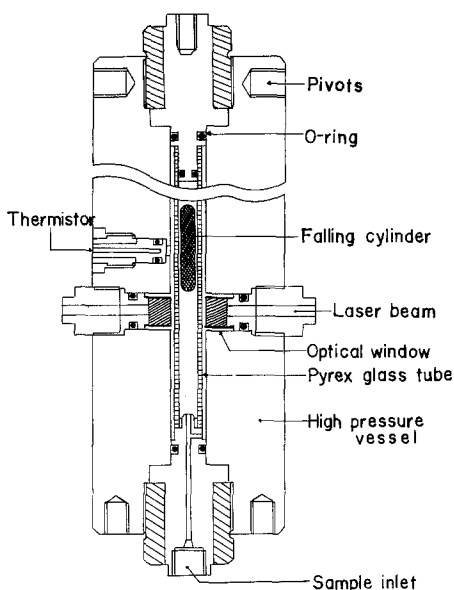


Fig. 2. Falling-cylinder viscometer.

four small projecting lugs at each end of the cylindrical part, which act as a guide to keep the plummet concentric when it falls. The falling time of the plummet was determined within 0.1 ms by an electronic timer using a He-Ne gas-laser beam passed through a pair of optical windows. The viscometer could be rotated on a horizontal axis in order to return the plummet to its starting position. The viscosity  $\eta$  was determined by

$$\eta = K(\rho_b - \rho)\theta \quad (2)$$

where  $\rho$  and  $\rho_b$  are densities of the fluid and the plummet, respectively, and  $\theta$  is the falling time. The instrument constant  $K$  and its change with temperature were determined by the calibrations using water and appropriate calibrating liquids given in Table I. It was also confirmed by the values of Reynolds numbers that all the measurements were carried out in a laminar flow region. The uncertainty in the measured viscosity was estimated to be less than 2%.

### 3.2.2. Falling-Ball Viscometer

This viscometer was constructed for engineering purposes under high pressures up to 1 GPa at temperatures up to 300° C. The viscosities of highly viscous fluids, such as lubricating oils, higher alcohols, and polyol-

esters, have been measured by this apparatus (6). The velocity of the falling ball was determined by a differential linear transformer equipped in the high pressure vessel. The viscosity was calculated from Eq. (2) by means of the same procedures as the falling-cylinder viscometer discussed above. The uncertainty of the values obtained are nearly 5%, because of the difficulty in temperature control.

### 3.2.3. *Torsionally Vibrating-Crystal Viscometer*

In most of the traditional methods for the viscosity measurements, it is necessary to generate a relative motion between the fluid and a part of viscometer, such as rotation, oscillation, falling, or fluid flow. On the other hand, in the torsionally vibrating-crystal method, the relative motion is electrically microscopic. Considering the many advantages of this method and the recent advancement of electronic devices, a new apparatus has been constructed for measurements under high pressures up to 200 MPa. The details of this viscometer were described in an earlier paper [7]. The uncertainty of the viscosity values obtained was estimated to be less than 2%.

### 3.3. Thermal Conductivity Measurements

Recent rapid progress in the electronics field has made it possible for the transient method to become a technique of high precision. The transient hot-wire method is more convenient than the various steady-state methods in view of the following features:

1. A single measurement is performed in a short time;
2. The onset of free convection is detectable immediately;
3. There is no need to account for various heat losses;
4. It is unnecessary to maintain a uniform temperature gradient for a long period of time;
5. The construction of the hot-wire cell is extremely simple, even in aiming the measurements under high pressures.

However, one of the disadvantages of this method is the inapplicability to electrically conducting fluids without the special devices. The details of a hot-wire apparatus on the relative basis and of an absolute measurement apparatus controlled by a microcomputer were reported earlier [8, 9]. The inaccuracy of the latter measurement was estimated to be less than 1%.

## 4. EXPERIMENTAL RESULTS

The present experimental results on the density, viscosity, and thermal conductivity of various liquids have been published elsewhere. The liquids, their temperature and pressure ranges, and the references are listed in

Table II. Experimental Measurements of *PVT* Relations

Fluid	<i>T</i> (°C)	<i>P</i> (MPa)	Method <sup>a</sup>	Ref.
Aniline	25, 50	0.1–70	Ad	
Aniline + benzene	25, 50	0.1–70	Ad	
Benzene	25–125	0.1–105	HPB	10, 11
Benzene + chlorobenzene	25–125	0.1–208	HPB	11
Benzene + cyclohexane	27–75	0.1–105	HPB	10
1-Butanol	25–60	0.1–150	HPB	4
2-Butanol	10–75	0.1–200	HPB	12
Castor oil	25–50	0.1–320	Ad.	13
Chlorobenzene	25–125	0.1–98	HPB	11
Cyclohexane	25–75	0.1–105	HPB	10
1, 2-Dichloroethane	10–75	0.1–130	HPB	
Ethanol	25–50	0.1–310	Ad, HPB	5
Ethanol + water	25–50	0.1–349	Ad, HPB	5
Methanol	10–75	0.1–208	HPB	3
Methanol + water	10–75	0.1–220	HPB	3
2-Methyl-1-propanol	10–75	0.1–200	HPB	12
2-Methyl-2-propanol	25–75	0.1–200	HPB	14
2-Methyl-2-propanol + water	25–75	0.1–200	HPB	14
Pentafluoropropanol	10–100	0.1–200	HPB	
1-Propanol	10–75	0.1–200	HPB	14
1-Propanol + water	10–75	0.1–200	HPB	14
R113(C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub> )	10–125	Sat.–100	HPB	15
R114(C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> )	25–125	Sat.–100	HPB	15
R114B2 (C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub> )	5–50	Sat.–192	HPB	16
R115(C <sub>2</sub> ClF <sub>5</sub> )	10–100	Sat.–120	HPB	17
R124(C <sub>2</sub> HClF <sub>4</sub> )	10–125	Sat.–100	HPB	18
Toluene	0–100	0.1–250	HPB	9
<i>o</i> -Xylene	10–125	0.1–200	HPB	

<sup>a</sup>Methods: Ad, modified Adams' piezometer; HPB, high pressure burette apparatus.

Tables II, III, and IV. The changes in these properties with temperature and pressure were expressed by appropriate empirical equations. The isotherms of the viscosity of toluene [7] and the thermal conductivity of *n*-hexane [22] are shown in Figs. 3 and 4 as examples.



Table III. Experimental Measurements of Viscosity

Fluid	$T$ (°C)	$P$ (MPa)	Method <sup>a</sup>	Ref.
Benzene	25-75	0.1-110	V-Q	7
1-Butanol	10-75	0.1-70	F-C	12
2-Butanol	10-75	0.1-70	F-C	12
Castor oil	25-150	0.1-700	F-B	18
Castor oil	25-100	0.1-500	F-B	6
Cyclohexane	25-75	0.1-110	V-Q	7
n-Decane	25-75	0.1-110	V-Q	7
1-Decanol	25-100	0.1-300	F-B	19
n-Dodecane	25-75	0.1-110	V-Q	7
1-Dodecanol	5-75	0.1-400	F-B	19
Ethanol	25-50	0.1-79	F-C	5
Ethanol + water	25-50	0.1-79	F-C	5
Ethylbenzene	25-75	0.1-110	V-Q	7
Glycerol-tri- n-caprylate	25-100	0.1-400	F-B	20, 21
Glycerol-tri- 2-ethyl-hexanoate	25-100	0.1-400	F-B	20, 21
n-Heptane	25-75	0.1-10	V-Q	7
1-Hexadecanol	25-100	0.1-400	F-B	19
n-Hexane	25-60	0.1-110	V-Q	7
1-Hexanol	1-100	0.1-350	F-B	19
Methanol	10-75	0.1-67	F-C	3
Methanol + H <sub>2</sub> O	10-75	0.1-67	F-C	3
2-Methyl-1- propanol	10-75	0.1-70	F-C	12
2-Methyl-2- propanol	10-75	0.1-70	F-C	12
2-Methyl-2- propanol + water	10-50	0.1-120	F-C	14
n-Octane	25-75	0.1-110	V-Q	7
1-Octanol	25-100	0.1-400	F-B	19
Pentaerythritol- tetra-n- caprylate	25-125	0.1-400	F-B	21
1-Propanol	25, 50	0.1-120	F-C	14
1-Propanol + water	10-50	0.1-120	F-C	14
1-Tetradecanol	25-75	0.1-350	F-B	19
Toluene	25-75	0.1-110	V-Q	7
Trimethylol- propane-tri- n-caprylate	25-125	0.1-400	F-B	21
m-Xylene	25-75	0.1-110	V-Q	7
o-Xylene	25-75	0.1-110	V-Q	7
p-Xylene	25-75	0.1-110	V-Q	7

<sup>a</sup>Methods: F-B, falling-ball; F-C, falling-cylinder; V-Q, torsionally vibrating-quartz.

Table IV. Experimental Measurements of Thermal Conductivity

Fluid	$T$ (°C)	$P$ (MPa)	Method <sup>a</sup>	Ref.
Benzene	10–100	0.1–250	H–W(II)	22
Bromobenzene	25–100	0.1	H–W	8
Chlorobenzene	25–75	0.1	H–W	8
n-Decane	30–100	0.1	H–W	8
n-Dodecane	25–100	0.1	H–W	8
Ethylbenzene	25–85	0.1	H–W	8
n-Heptane	25–85	0.1	H–W	8
n-Hexane	10–100	0.1–250	H–W(II)	22
Isopropyl- benzene	25–85	0.1	H–W	8
n-Octane	25–75	0.1	H–W	8
Toluene	0–100	0.1–250	H–W(II)	9
m-Xylene	25–85	0.1	H–W	8
o-Xylene	25–85	0.1	H–W	8
p-Xylene	25–85	0.1	H–W	8

<sup>a</sup>Methods: H–W, transient hot-wire method; H–W(II), absolute measurement.

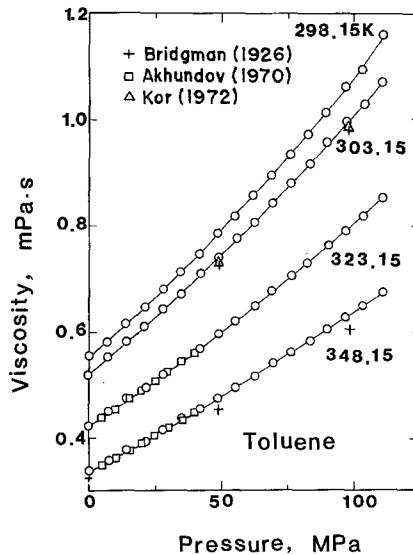


Fig. 3. Isotherms of viscosity of toluene against pressure.

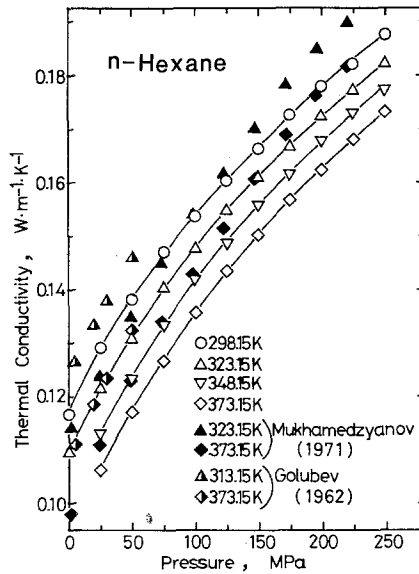


Fig. 4. Isotherms of thermal conductivity of *n*-hexane against pressure.

## 5. DISCUSSION

Using the present experimental results, several interesting phenomena and behaviors are described below from the viewpoints of the pressure effects and the chemical structures of liquids.

### 5.1. General Behavior with Temperature and Pressure

The general behavior of these properties of liquids can be summarized as follows:

1. The density  $\rho$ , viscosity  $\eta$ , and thermal conductivity  $\lambda$  of liquids increase with increasing pressure at a constant temperature, that is,  $(\partial\rho/\partial P)_T > 0$ ,  $(\partial\eta/\partial P)_T > 0$ , and  $(\partial\lambda/\partial P)_T > 0$ , with the well-known exception in the case of the viscosity of water.

2. Those pressure coefficients,  $(\partial\rho/\partial P)_T$ ,  $(\partial\eta/\partial P)_T$ , and  $(\partial\lambda/\partial P)_T$ , always decrease with increasing temperature.

3. The effect of pressure on  $\rho$  and  $\lambda$  decreases with increasing pressure, that is,  $(\partial^2\rho/\partial P^2)_T < 0$  and  $(\partial^2\lambda/\partial P^2)_T < 0$ . But the pressure effect on  $\eta$  increases with pressure,  $(\partial^2\eta/\partial P^2)_T > 0$ .

4. The effect of temperature on these properties at a constant pressure always decreases with increasing temperature, that is,  $(\partial\rho/\partial T)_P < 0$ ,  $(\partial\eta/\partial T)_P < 0$ , and  $(\partial\lambda/\partial T)_P < 0$ .

5. The change of  $\rho$  and  $\lambda$  with temperature becomes smaller with increasing pressure, while the change of  $\eta$  with temperature becomes larger with increasing pressure.

6. The temperature effect on  $\rho$  and  $\lambda$  is almost constant with increasing temperature, that is,  $(\partial^2\rho/\partial T^2)_p \doteq 0$ , and  $(\partial^2\lambda/\partial T^2)_p \doteq 0$ , while that on  $\eta$  becomes smaller with increasing temperature, that is,  $(\partial^2\eta/\partial T^2)_p < 0$ .

Although these behaviors have been observed in our measurements of various nonpolar or weak-polar liquids at conditions of 0~100°C and 0.1~300 MPa, some of these trends change under higher pressures. Nevertheless, it is noticed from the above trends that the microscopic mechanism of the viscosity of liquids should be different from that of the thermal conductivity, in contrast with the case of gases.

## 5.2. Density Dependence on the Transport Properties

The effect of pressure on the viscosity and thermal conductivity of fluids is generally represented in terms of density. For instance, isotherms of the viscosity of toluene [7] and the thermal conductivity of *n*-hexane [22] are shown in Figs. 5 and 6, respectively, where the difference between isotherms becomes smaller, in comparison with Figs. 3 and 4. Each iso-

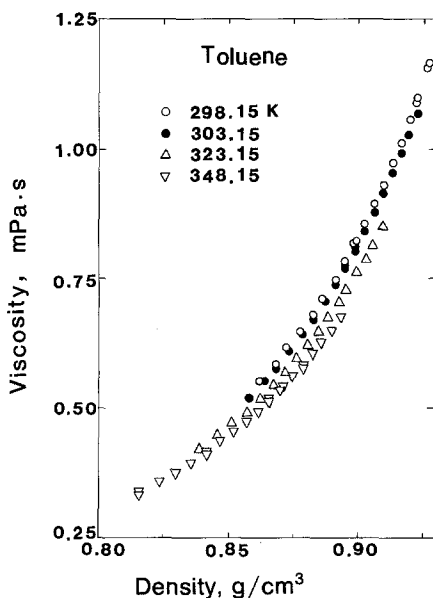


Fig. 5. Viscosity of toluene as a function of density.

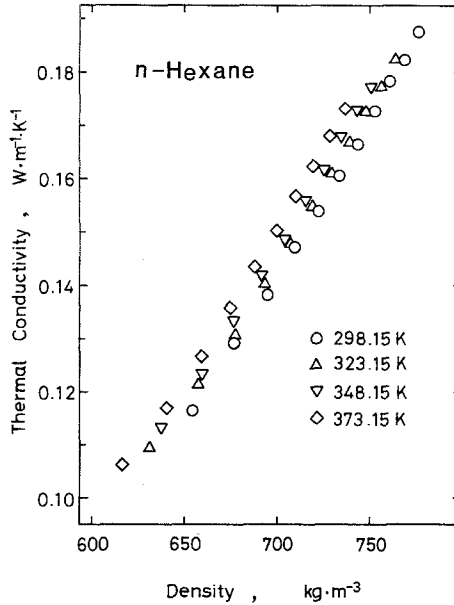


Fig. 6. Thermal conductivity of n-hexane as a function of density.

therm can be expressed by a simple empirical equation of density in both cases of viscosity and thermal conductivity. The behaviors of these properties of liquids are summarized in terms of density as follows:

1. The viscosity and thermal conductivity of liquids always increase with increasing density at a constant temperature, that is,  $(\partial\eta/\partial\rho)_T > 0$ ,  $(\partial\lambda/\partial\rho)_T > 0$ .

2. The effect of density on  $\eta$  increases with increasing density,  $(\partial^2\eta/\partial^2\rho)_T > 0$ , but the effect on  $\lambda$  is almost constant  $(\partial^2\lambda/\partial^2\rho)_T \doteq 0$ .

3. At a constant density, the viscosity decreases with increasing temperature,  $(\partial\eta/\partial T)_\rho < 0$ . In contrast, the thermal conductivity increases,  $(\partial\lambda/\partial T)_\rho > 0$ , as far as the present measurements are concerned.

In theoretical interpretations and empirical correlations, these transport properties of liquids should be treated as a function of density instead of pressure.

### 5.3. The Tait-Type Equations

Among several empirical equations used to represent isothermally the effect of pressure on compression, volume, or density of a liquid, the Tait equation is often used, because of its good fit and the simplicity having

only two constants. Using the density  $\rho$ , the equation is written

$$(\rho - \rho_0)/\rho = C \ln[(B + P)/(B + 0.1)] \quad (3)$$

where  $\rho_0$  is the density at 0.1 MPa, and  $B$  and  $C$  are constants depending on the fluid and temperature, while  $C$  appears to be almost independent of temperature. It was found that all the experimental results on the density were satisfactorily represented by Eq. (3) within the experimental error, including water and its alcohol solutions [3, 5, 14]. Since the changes in the transport properties of liquids are treated simply as a function of density, the isothermal effects of pressure on the viscosity  $\eta$  and thermal conductivity  $\lambda$  were also fitted to the Tait-type equations as follows:

$$(\eta - \eta_0)/\eta = E \ln[(F + P)/(F + 0.1)] \quad (4)$$

$$(\lambda - \lambda_0)/\lambda = G \ln[(H + P)/(H + 0.1)] \quad (5)$$

In the case of viscosity, assuming  $E$  is dependent on temperature, Eq. (4) was found to represent well the experimental data of various nonpolar or weak-polar organic liquids [7]. On the other hand, it was found that Eq. (5) reproduces satisfactorily the experimental data of thermal conductivity of toluene, benzene, and *n*-hexane [9, 22] using  $G$  independent of temperature, as in the case of density. However, the constants  $G$  and  $H$  in Eq. (5) were somewhat different from  $C$  and  $B$  in Eq. (3).

#### 5.4. Effect of Chemical Structures

Generally speaking, the properties of liquids are more sensitive to their chemical structures than those of gases. The effect of molecular structure on the compressibility and the viscosity of many higher hydrocarbons was extensively investigated [23–25], and the marked effects of a ring structure, chain length, and side-chains were found qualitatively in these nonpolar liquids. In the present measurements, although a slight effect of the chemical structure was observed on the density and thermal conductivity of various liquids, such effect on the viscosity and its pressure change was found to be remarkably large, as shown in Fig. 7, where the relative viscosity of various liquids are compared at 50°C [7, 12, 14, 19–21]. Including liquids which contain functional groups such as alcohols or esters, the influence of chemical structure, molecular weight, carbon number, and molar volume on the viscosity is now under study, based on the free volume theory, significant structure theory, and smooth-hard-sphere or rough-hard-sphere models.

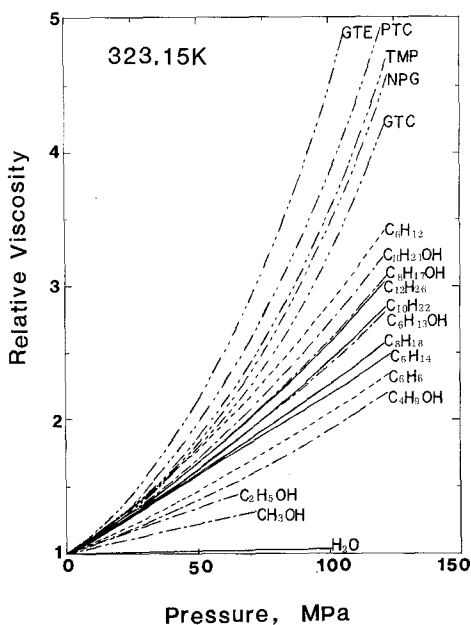


Fig. 7. Relative viscosity of various liquids at 323.15 K. GTC, glycerol-tri-n-caprylate; GTE, glycerol-tri-2-ethyl-hexanoate; NPG, neopentyl-glycol-dicaprylate; PTC, pentaerythritol-tetra-n-caprylate; TMP, trimethylol-propane-tri-n-caprylate.

### 5.5. Properties of Water + Alcohols Mixtures

The density and the viscosity of the aqueous solutions of methanol, ethanol, 1-propanol, and 2-methyl-2-propanol (tert-butanol) have been measured at temperatures from 10 to 75°C under pressures up to 320 MPa [3, 5, 14]. These polar mixtures behave anomalously resulting from the molecular associations and the liquid structures. As is well known, the viscosity of pure water at temperatures below 33°C decreases slightly with increasing pressure up to 100 MPa. It is supposed that pressure first breaks up some of the clusters, the icelike structures. In case of alcohols + water mixtures, the interaction between molecules appears to be more complicated. When the isothermal compressibility, partial molar volume, and excess volume were plotted against the composition of alcohols, definite minima appear at low temperatures and low pressures, and disappear gradually with increasing temperature or increasing pressure. On the other hand, the viscosity shows remarkable maxima at a given composition. Some of the experimental results are shown in Figs. 8 and 9, although such phenomena cannot be interpreted yet theoretically. From these figures, it

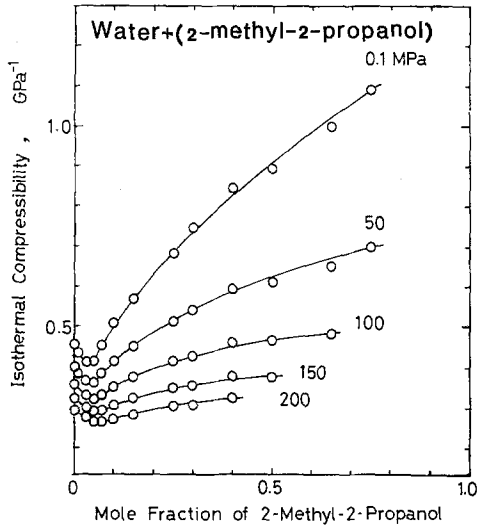


Fig. 8. Isothermal compressibility of 2-methyl-2-propanol at 298.15 K.

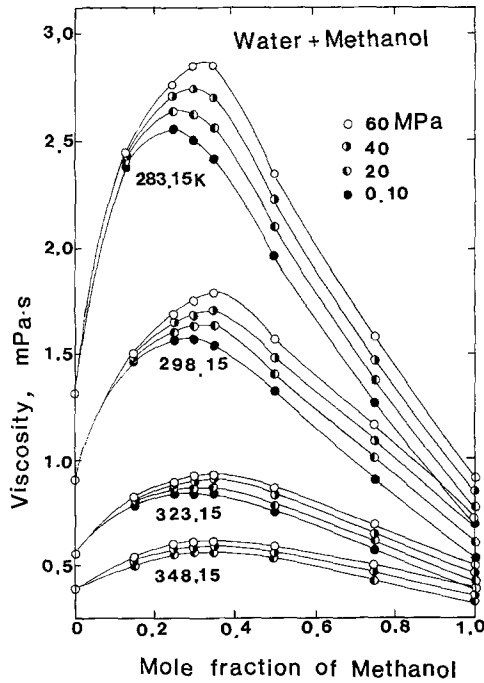


Fig. 9. Viscosity of methanol.



seems that the mixtures would approach phenomenologically to the ideal solution at higher temperatures and higher pressures.

### 5.6. On the Early Work of P. W. Bridgman

P. W. Bridgman (1882–1961), Nobel prize winner in physics in 1946, began his research at Harvard about 1906, and greatly extended the experimentally accessible pressure range. He published more than 200 papers containing large amounts of new data on high pressure physics [26, 27]. Bridgman measured the volumetric behaviors of 82 liquids up to 1.2 GPa, and in some cases, up to 5 GPa in a period 1913 through 1948. He determined the viscosity of many liquids at a few temperatures under pressures up to 1.2 GPa in 1926 [28] and 3 GPa in 1949 [29]. He also published thermal conductivity values of various liquids in 1923 [30]. His experimental data on these properties have been treated as typical behaviors of the pressure effect for a long time, nearly half a century.

Bridgman's data on the density and the viscosity are correct within a few percent, even from a standpoint of the recent advancements in experimental techniques. However, his values of thermal conductivity of liquids are questionable and are found to be nearly 15% higher than the recent experimental data. Therefore it is important to measure the thermal conductivity of various liquids and to obtain the effect of pressure on it.

## 6. CONCLUSIONS

The effects of temperature and pressure on the density, viscosity, and thermal conductivity of various liquids have been reviewed briefly. Although the necessity and the philosophy of the present investigation were described, the present aspects are far from the final goal and many problems remain unsolved. Among them, it should be specially important to study the influence of thermal radiation in measurements of the thermal conductivity, to interpret the effect of chemical structures of liquids, and to accumulate precise data for polar liquids and their mixtures. Another interesting problem is to investigate the change in the derivatives of transport properties presented in Sections 5.1 and 5.2 with pressure or characters of liquids.

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