

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 43, NO. 1, 1973

## EVALUATION AND CORRELATION OF VISCOSITY DATA

### The Most Probable Values of the Viscosity of Gaseous Methane

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The critical evaluation of the viscosity data of gaseous methane has been carried out using a number of experimental data available in literatures. All the experimental measurements under high pressure were evaluated in view of their reliability, and the data were correlated with temperature and pressure by means of two kinds of methods. The most probable values of the viscosity are presented in the forms of both a numerical table and an equation, covering the range of temperatures from 273.15 K to 473.15 K and of pressures up to  $500 \times 10^5$  Pa. The uncertainty of the tabulated values is also estimated. The relation between residual viscosity and density has been also examined over the whole range of temperature and pressure.

#### Introduction

Although a number of experimental measurements on the viscosity of gaseous methane have been reported, the discrepancy among the existing data is considerably large and, therefore, it would be important to evaluate the available data and to present the most probable values over a wide range of temperature and pressure.

This work has been performed as a part of program of "High Pressure Data Center of Japan" organized in the Society of Material Science, Japan, under the sponsorship of the Agency of Science and Technology. The following members of the Committee and researchers attended for the discussion on the present work:

J. Osugi, Y. Takezaki (Kyoto Univ.); H. Iwasaki, S. Takahashi, K. Date (Tohoku Univ.);

I. Tanishita (Nippon Univ.); K. Watanabe (Keio Univ.),

to whom the authors wish to express sincere gratitude for their valuable suggestions.

#### Survey and Evaluation of Viscosity Data

There exist sixteen different measurements on the viscosity of gaseous methane under high pressures. In Table 1, the author's names, methods of measurements, temperature ranges, and

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(Received April 14, 1973)

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Table 1 Measurements of the viscosity of methane under pressures

First author	Year	Method	Temp. range (K)	Max. press. (10 <sup>5</sup> Pa)	Ref. No.
Sage	1938	Rolling Ball	310-377	172	1)
Bicher	1943	Rolling Ball	298-498	340	2)
Comings	1944	Transpiration	298-373	137	3)
Kuss	1952	Transpiration	293-353	608	4)
Carr	1953	Transpiration	294-366	546	5)
Meshcheryakov	1954	Transpiration	258-523	811	6)
Ross	1957	Transpiration	223-298	690	7)
Pavlovich	1958	Transpiration	103-323	196	8)
Baron	1959	Transpiration	325-408	551	9)
Iwasaki	1959	Oscillating disk	298-348	507	10)
Kestin	1959	Oscillating disk	293	79	11)
Barua	1964	Transpiration	223-423	177	12)
Carmichael	1965	Rotating cylinder	277-477	340	13)
Giddings	1966	Transpiration	283-411	551	14)
Huang	1966	Falling body	103-273	340	15)
Gonzalez	1967	Transpiration	311-444	551	16)

maximum pressures are listed in the order of publishing year.

The original papers were carefully read through and examined in the viewpoint of the reliability of reported data. In the present critical evaluation, the following items were mainly taken into consideration:

- reliability of the theory of the measuring method employed,
- calibration of the apparatus used,
- precautions paid for the measuring procedures,
- experimental errors reported,
- overall accuracy estimated by the original authors,
- purity of the sample used,

- 1) Sage, B. H. and W. N. Lacey, *Am. Inst. Mining Met. Engrs.*, **127**, 118 (1938)
- 2) Bicher, L. B. Jr. and D. L. Katz, *Ind. Eng. Chem.*, **35**, 754 (1943)
- 3) Comings, E. W. and R. S. Egly, *Ind. Eng. Chem.*, **32**, 714 (1940)
- 4) Kuss, E., *Zeit. angew. Phys.*, **4**, 201 (1952)
- 5) Carr, N. L., *Inst. Gas Technol., Res. Bull.*, No. 23 (1953)
- 6) Meshcheryakov, N. V. and I. F. Golubev, *Vyazkost' Gazov i Gazovyykh Smesey*, (1959, Moskva Fizmatgiz)
- 7) Ross, J. F. and G. M. Brown, *Ind. Eng. Chem.*, **49**, 2026 (1957)
- 8) Pavlovich, N. V. and D. L. Timroth, *Teploenergetika*, **8**, 61 (1958)
- 9) Baron, J. D., J. G. Roof and F. W. Wells, *J. Chem. Eng. Data*, **4**, 283 (1959)
- 10) Iwasaki, H. and H. Takahashi, *J. Chem. Soc. Japan*, **62**, 918 (1959)
- 11) Kestin, J. and W. Leidenfrost, "Thermodynamics and Transport Properties of Gases, Liquids and Solids", p. 321, ASME (1959)
- 12) Barua, A. K., M. Afzal, G. P. Flynn and J. Ross, *J. Chem. Phys.*, **41**, 374 (1964)
- 13) Carmichael, L. T., V. Berry and B. H. Sage, *J. Chem. Eng. Data*, **10**, 57 (1965)
- 14) Giddings, J. G., J. T. F. Kao and R. Kobayashi, *J. Chem. Phys.*, **45**, 578 (1966)
- 15) Huang, E. T. S., G. W. Swift and F. Kurata, *A. I. Ch. E. J.*, **12**, 932 (1966)
- 16) Gonzalez, M. H., *Soc. Petrol. Eng. J.*, **7**, 75 (1967)

accuracy in the measurements of temperature and pressure,  
scattering of the experimental data reported, and so forth.

The final evaluation was performed by the Committee members and several researchers in this field as described above. As the results, four sets of data<sup>10, 11, 12, 14)</sup> were considered to be the most reliable and given the highest weight. The weight second to the above was given to other four sets of data<sup>3, 5, 6, 13)</sup>. No weight was given to the remainders in the present analysis.

### Methods and Results of Correlation

First, as the values of temperature, pressure and viscosity in original papers were expressed in various units, they were reduced to common units, namely, the SI units as follows:

temperature,  $T$ , in K,

pressure,  $P$ , in  $10^5$  Pa ( $=1$  bar  $=0.9869$  atm),

viscosity,  $\eta$ , in  $10^{-7}$  N·s/m<sup>2</sup> ( $10^{-6}$  poise).

In the present correlation of the viscosity of methane, two kinds of methods have been employed as described below.

#### Determination of the weighted mean values at grid-points

The first method of the correlation is the same as used in our early correlation of the  $P$ - $V$ - $T$  relations of methane<sup>17)</sup>. That is, the viscosity values at common grid-points of temperatures and pressures were obtained from the original data reported in every work. When the data reported are not at one of the common grid-points specified, the interpolation procedures were carried out along an isotherm or an isobar on a digital computer using the least squares method. The precaution was paid for this procedure in order to retain the experimental accuracy for each original work. Then, the mean value at each grid-point was calculated with the weights determined in the critical evaluation as described in the preceding section. The standard deviations were also calculated by the following equation:

$$\sigma = \sqrt{\frac{\sum [\omega_i (\eta_i - \bar{\eta})^2]}{\sum \omega_i \cdot (n-1)}} \quad (1)$$

where,  $\omega_i$  = the weight given,

$\eta_i$  = the viscosity in the original work,

$\bar{\eta}$  = the tabulated viscosity value.

$n$  = the number of sources.

The weighted mean values obtained are shown in Table 2, where the standard deviations are also given in the parentheses.

Although every tabulated value was determined independently of the adjacent values, the consistency among the determined values has been found to be rather fair. However, the original values reported along the only isotherm, whose temperature was different from one of the present common temperatures, could not be used in this method such as the data of Kestin and Leiden-frost<sup>11)</sup>.

17) Osugi, J., Y. Takezaki and T. Makita, *This Journal*, **41**, 60 (1971)

Table 2 The most probable values of the viscosity of gaseous methane in  $10^{-7}$  N.s/m<sup>2</sup>

Pressure 10 <sup>5</sup> Pa (atm)	Temperature, K (°C)								
	273.15 (0)	298.15 (25)	323.15 (50)	348.15 (75)	373.15 (100)	398.15 (125)	423.15 (150)	448.15 (175)	473.15 (200)
1.01 (1)	102.4(1.9)*	111.0(0.8)	119.0(0.5)	127.4(0.4)	134.7(0.6)	142.0(0.7)	149.1(0.6)	155.7(1.4)	162.7(1.8)
5.07 (5)	103.0(1.6)	111.5(0.7)	119.4(0.4)	127.8(0.3)	135.0(0.5)	142.2(0.8)	149.4(0.7)	156.0(1.5)	163.0(1.8)
10.13 (10)	103.9(1.3)	112.2(0.5)	120.1(0.4)	128.4(0.3)	135.5(0.5)	142.7(0.6)	149.8(0.7)	156.3(1.5)	163.3(1.8)
20.27 (20)	106.0(0.7)	113.9(0.3)	121.6(0.3)	129.7(0.3)	136.7(0.5)	143.7(0.6)	150.7(0.8)	156.9(1.7)	164.0(2.0)
30.40 (30)	108.5(0.7)	116.0(0.3)	123.4(0.3)	131.3(0.3)	138.2(0.5)	144.9(0.6)	151.7(0.9)	157.9(1.7)	164.9(2.0)
40.53 (40)	111.5(0.9)	118.4(0.3)	125.5(0.3)	133.1(0.4)	139.8(0.5)	146.3(0.5)	152.9(1.0)	159.1(1.3)	165.8(2.1)
50.66 (50)	115.0(1.3)	121.1(0.3)	127.8(0.3)	135.0(0.4)	141.5(0.4)	147.7(0.7)	154.3(1.1)	160.3(1.7)	166.8(2.2)
60.80 (60)	118.9(1.7)	124.2(0.3)	130.4(0.3)	137.1(0.4)	143.5(0.5)	149.3(0.6)	155.7(1.2)	161.5(2.0)	168.0(2.3)
70.93 (70)	123.4(1.9)	127.6(0.4)	133.3(0.3)	139.4(0.5)	145.5(0.5)	151.1(0.6)	157.2(1.3)	162.8(2.3)	169.2(2.4)
81.06 (80)	128.3(2.1)	131.4(0.4)	136.3(0.3)	141.9(0.5)	147.6(0.6)	153.2(0.8)	158.9(1.3)	164.2(2.3)	170.5(2.4)
91.19 (90)	133.7(2.3)	135.3(0.5)	139.5(0.2)	144.5(0.5)	149.9(0.6)	155.2(0.9)	160.6(1.4)	165.8(2.7)	171.9(2.5)
101.33 (100)	139.6(2.2)	139.7(0.6)	143.1(0.3)	147.3(0.5)	152.2(0.6)	157.2(0.9)	162.5(1.4)	167.4(3.0)	173.4(2.6)
121.59 (120)	152.5(2.1)	149.1(0.7)	150.3(0.4)	153.4(0.5)	157.3(0.6)	161.8(1.1)	166.4(1.5)	170.9(3.3)	176.5(2.7)
141.86 (140)	166.6(1.9)	159.4(0.8)	158.3(0.5)	160.0(0.6)	162.7(0.6)	166.5(1.0)	170.7(1.5)	174.9(3.6)	179.8(2.9)
162.12 (160)	181.3(2.0)	170.3(1.0)	166.6(0.5)	166.5(0.7)	168.3(0.9)	171.5(0.9)	175.3(1.6)	179.2(3.7)	183.4(3.1)
182.39 (180)	196.0(4.7)	182.1(1.1)	175.8(0.7)	173.9(0.9)	174.5(0.9)	177.0(1.2)	179.6(3.0)	183.7(3.5)	187.2(3.1)
202.65 (200)	211.3(5.9)	193.7(1.2)	184.9(0.7)	181.4(0.9)	181.0(0.9)	182.6(1.2)	184.7(3.1)	188.1(3.9)	191.0(3.0)
253.31 (250)		222.8(1.5)	208.9(1.1)	201.2(1.1)	197.8(0.7)	197.4(1.0)	198.0(3.1)	199.9(3.8)	201.2(3.5)
303.98 (300)		251.0(2.0)	232.0(1.4)	220.5(1.1)	215.3(0.6)	213.0(0.9)	211.7(2.7)	212.0(3.3)	211.5(3.4)
354.64 (350)		276.3(1.9)	254.7(1.4)	240.5(1.2)	232.8(0.6)	228.1(0.7)	225.5(2.4)	223.8(3.0)	221.9(3.1)
405.30 (400)		298.3(1.3)	275.1(1.3)	258.8(1.4)	249.4(0.2)	243.0(0.8)			
455.96 (450)		320.0(1.2)	295.1(1.2)	276.9(1.5)	266.0(0.0)	257.8(0.6)			
506.63 (500)		341.4(1.8)	313.7(1.3)	293.7(1.7)	282.0(0.1)	272.0(0.5)			

\* The standard deviation is shown in the parentheses

Since a number of sources of information are available for the viscosity of gaseous methane at the atmospheric pressure, the tabulated values have been compared with several sets of experimental data<sup>18-21)</sup> and two correlations<sup>22, 23)</sup>.

For the purpose of this comparison, the values at  $1.03 \times 10^5$  Pa in Table 2 were fitted to the following quartic equation as a function of temperature:

$$\eta_0 = 113.63 - 0.95579T + 5.9057 \times 10^{-3}T^2 - 1.1561 \times 10^{-5}T^3 + 8.0559 \times 10^{-9}T^4. \quad (2)$$

This equation is found to fit the tabulated values between 273.15 K and 473.15 K with a mean deviation of 0.08 percent and a maximum of 0.17 percent. The departures of the data in literatures from Eq. (2) were calculated by

$$\text{departure percent} = \frac{\eta_0(\text{lit}) - \eta_0(\text{calc})}{\eta_0(\text{calc})} \times 100, \quad (3)$$

and are plotted in Fig. 1.

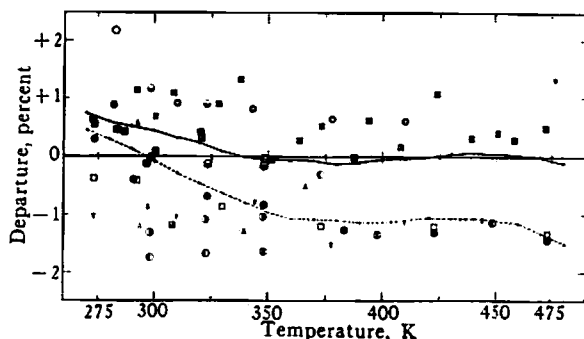


Fig. 1 Departure plots of viscosity values at the atmospheric pressure in literatures

⊗: (2), ●: (3), ○: (4),  
 △: (5), ●: (6), ⊙: (10),  
 ▲: (11), ○: (13), ⊙: (14),  
 ▽: (15), ▼: (16), □: (18),  
 ■: (19), ▣: (20), ⊠: (21),  
 ...: (22), —: (23)

### The correlation by means of an empirical equation

Another method used is the correlation utilizing an appropriate equation, in which the viscosity is expressed as a function of both temperature and pressure:

$$\eta = \sum_{j=0}^i \sum_{i=0}^j B_{ji} T^i P^j \quad (4)$$

The ranges of  $i$  and  $j$  and coefficients  $B_{ji}$  have been determined by the "trial and error" method based on the fitting of the original data at each reported temperature and pressure, so as to obtain the best consistence with the results in the former method. It has been found that the values of the viscosity covering temperatures from 273.15 K to 473.15 K and pressures up to  $500 \times 10^5$  Pa are represented by the following equation:

$$\eta = \sum_{i=0}^4 B_{0i} T^i + \left( \sum_{i=0}^2 B_{1i} T^i \right) P + \left( \sum_{i=0}^3 B_{2i} T^i \right) P^2 + \left( \sum_{i=0}^3 B_{3i} T^i \right) P^3 + \left( \sum_{i=0}^2 B_{4i} T^i \right) P^4 \quad (5)$$

The coefficients determined are given in Table 3. This equation is found to represent all the original data cited above satisfactorily. The values of the percentage standard deviation for each set of data from Eq. (5) are also shown in Table 4. Furthermore, it is also found that Eq. (5) is able to reproduce the weighted mean values given in Table 2 within the standard deviation of 0.52 percent. In Fig. 2, the percentage departures for some of the original data from Eq. (5) are plotted as a function of pressure.

This method by an empirical equation is considered to be more convenient than the former method, because all the original data reported could be used directly without any interpolation procedure and the results obtained would have been smoothed substantially over the whole region of temperature and pressure.

- 18) Trautz, M. and K. Sorg, *Ann. Phys.*, **5**(10), 81 (1931)
- 19) Johnston, H. and K. McCloskey, *J. Phys. Chem.*, **44**, 1038 (1940)
- 20) Van Itterbeek, A., *Physica*, **7**, 831 (1940)
- 21) De Rocco, A. and J. Halford, *J. Chem. Phys.*, **28**, 1152 (1958)
- 22) Zagoruchenko, V. A. and A. M. Zhuravlev, "Thermophysical Properties of Gaseous and Liquid Methane", the U. S. Department of Commerce, National Bureau of Standards and the National Science Foundation, Washington, D. C. (1970)
- 23) Thermophysical Properties Research Center, Purdue University, Indiana, U. S. A., Private Communication

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Table 3 Coefficients of Equation (5)

$B_{00} = 5.00444 \times 10^2$	$B_{20} = 5.39163 \times 10^{-2}$
$B_{01} = -5.18209$	$B_{21} = -3.33832 \times 10^{-4}$
$B_{02} = 2.30117 \times 10^{-2}$	$B_{22} = 6.91865 \times 10^{-7}$
$B_{03} = -4.19261 \times 10^{-5}$	$B_{23} = -4.75340 \times 10^{-10}$
$B_{04} = 2.8 \times 10^{-8}$	
	$B_{30} = -1.29424 \times 10^{-4}$
$B_{10} = -9.03675 \times 10^{-1}$	$B_{31} = 7.61842 \times 10^{-7}$
$B_{11} = 4.94166 \times 10^{-3}$	$B_{32} = -1.45795 \times 10^{-9}$
$B_{12} = -6.07085 \times 10^{-6}$	$B_{33} = 8.93402 \times 10^{-13}$
	$B_{40} = 7.06309 \times 10^{-8}$
	$B_{41} = -3.26629 \times 10^{-10}$
	$B_{42} = 3.75837 \times 10^{-13}$

Table 4 Percentage standard deviation from Equation (5)

	First author	Number of data points	Standard deviation (%) <sup>*</sup>
Exptl. Work	Comings	32	0.62
	Giddings	95	0.71
	Barua	26	1.08
	Iwasaki	47	1.13
	Carr	77	1.19
	Kestin	7	1.20
	Huang	9 <sup>a)</sup>	1.23
	Carmichael	101 <sup>b)</sup>	1.29
	Baron	36	1.60
	Meshcheryakov	76 <sup>c)</sup>	1.84
	Gonzalez	49	1.95
	Ross	10	3.62
	Kuss	44	4.92
	Pavlovich	15	5.16
Correlation	Bicher	45	6.34
	Sage	21 <sup>d)</sup>	9.33
	This work (Table 2)	195	0.52
	Zagoruchenko	216	2.13

\* Calculated by

$$\sigma [\%] = 100 \sqrt{\frac{1}{n} \sum \left[ \frac{(\eta_{\text{exp}} - \eta_{\text{cal}})}{\eta_{\text{cal}}} \right]^2}$$

where  $\eta_{\text{exp}}$  = original experimental values of the viscosity $\eta_{\text{cal}}$  = calculated values of the viscosity by Eq. (5) $n$  = number of data points

a) 0°C data only

b) Including 204°C data

c) Including  $506 \times 10^5$  Pa data

d) Read from the figure given

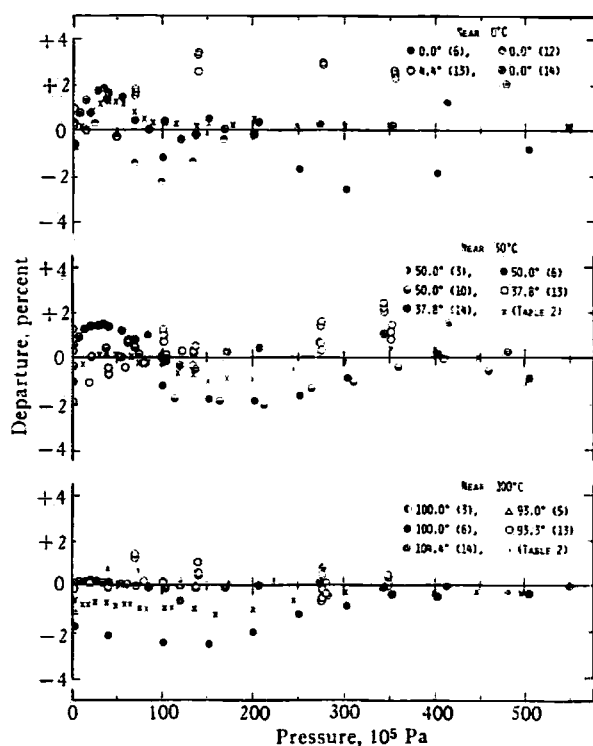


Fig. 2 Percentage departures of the original viscosity data under high pressures

### Recommended Viscosity Values

The recommended values of the viscosity for gaseous methane have been computed by Eq. (5), covering the temperatures from 250 K to 475 K and the pressures between 1 and  $500 \times 10^5$  Pa, and are given in Table 5. The tabulated values enclosed by dashed-lines in this table are substantially correct within 1.5 percent. However, the uncertainty of the values outside the lines would become larger. The values at 250 K have not been evaluated critically in this analysis and are shown merely by way of suggestion, because the reliable experimental data are scarce. Therefore, the new accurate measurements at low temperatures are desirable in future.

### Residual Viscosity Correlation

The residual viscosity  $\eta - \eta_0$  has been well correlated as a simple function of density for a number of gases. This is known as one of the most general and accurate methods of correlating the viscosity of gases under high pressure for the time being. Therefore, the present results given in Table 2 have been examined in this correlation. That is, the residual viscosities are plotted against the density in

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Table 5 Recommended values of the viscosity of gaseous methane in  $10^{-7}$  N·s/m<sup>2</sup> ( $10^{-6}$  poise)

Pressure 10 <sup>5</sup> Pa (bar)	Temperature, K									
	250	275	300	325	350	375	400	425	450	475
1	97.4	103.8	111.7	120.1	128.3	136.0	143.1	149.7	156.1	163.1
10	97.6	104.2	112.3	120.8	129.2	137.0	144.1	150.6	157.0	163.8
20	98.9	105.5	113.5	122.1	130.4	138.2	145.3	151.8	158.0	164.7
30	101.2	107.5	115.3	123.7	131.9	139.6	146.6	153.0	159.2	165.7
40	104.6	110.2	117.6	125.6	133.7	141.2	148.1	154.4	160.4	166.8
50	108.8	113.6	120.3	127.9	135.6	142.9	149.6	155.8	161.7	167.9
60	113.8	117.6	123.5	130.5	137.8	144.8	151.3	157.3	163.1	169.1
70	119.6	122.1	127.0	133.3	140.1	146.8	153.1	159.0	164.6	170.4
80	126.0	127.1	130.9	136.4	142.6	148.9	155.0	160.7	166.1	171.8
90	133.0	132.5	135.1	139.7	145.3	151.2	156.9	162.4	167.8	173.3
100	140.5	138.3	139.6	143.2	148.1	153.5	159.0	164.3	169.5	174.8
120	156.8	150.8	149.2	150.7	154.1	158.6	163.4	168.2	173.0	178.0
140	174.2	164.2	159.6	158.8	160.6	164.0	168.1	172.5	176.9	181.3
160	192.5	178.2	170.4	167.3	167.4	169.7	173.1	176.9	180.9	184.9
180	211.1	192.6	181.5	176.0	174.5	175.6	178.3	181.6	185.2	188.6
200	229.7	207.0	192.8	185.0	181.8	181.8	183.7	186.5	189.6	192.5
250	274.3	242.1	220.6	207.5	200.5	197.8	197.9	199.4	201.2	202.5
300	313.2	273.8	246.8	229.4	219.3	214.4	212.7	212.8	213.1	212.7
350	344.8	301.2	270.6	250.4	237.9	231.0	227.7	226.1	224.9	222.8
400	369.0	324.4	292.5	270.6	256.4	247.5	242.2	238.8	236.0	232.5
450	387.8	345.2	313.7	291.0	274.9	263.7	255.9	250.2	245.7	241.6
500	405.0	366.8	336.6	312.8	294.2	279.6	268.3	259.7	253.6	249.9

amagat unit, whose values were calculated from our early correlation<sup>17)</sup>. A simple relation between them has been found over the whole range of temperature and pressure in this analysis. This relation is able to be represented by the following equation:

$$\eta - \eta_0 = -0.34402 + 0.13510\rho + 1.4147 \times 10^{-3}\rho^2 - 2.8470 \times 10^{-6}\rho^3 + 6.1022 \times 10^{-9}\rho^4 \quad (6)$$

where  $\rho$  is the density in amagat unit. Eq. (6) is found to reproduce the viscosity values in this whole range within the maximum deviation of  $1.8 \times 10^{-7}$  N·s/m<sup>2</sup>. This fact proves that the viscosity is expressed more simply as a function of density than as that of pressure and temperature, as known in the case of some other physical properties.

The computation was done partly by FACOM 230-35 System at the Computation Center of Kobe University and partly by IBM 7040 System at Keio University. The authors wish to thank Miss M. Harada and Miss K. Fujishita for their help throughout the course of this work.