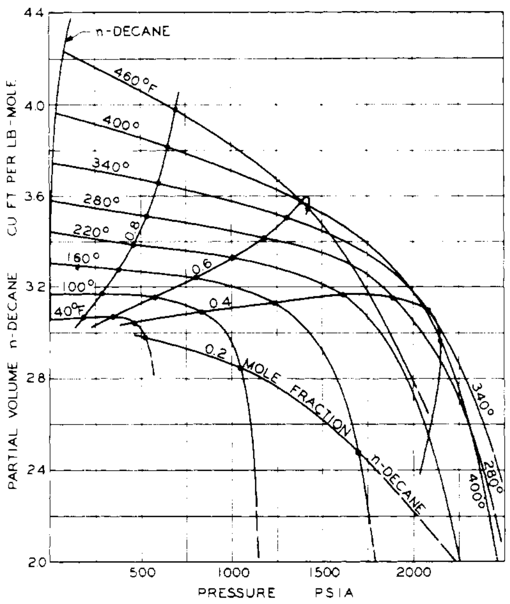

Figure 6. Partial molal volume of *n*-decane at bubble point

ACKNOWLEDGMENT

This computational effort was carried out as a part of the activities of the American Petroleum Institute Research Project 37, located at the Chemical Engineering Laboratory of the California Institute of Technology. Virginia Moore carried out the calculations associated with the volumetric data and B. Lawson Miller aided in the preparation of the manuscript.

NOMENCLATURE

d = differential operator
m_k = lb.-moles of component k
N = number of points
n_k = mole fraction of component k
V = molal volume, cu. ft./lb.-mole
$\bar{V}$ = partial molal volume, partial volume, cu. ft./lb.-mole
$\underline{V}$ = total volume, cu. ft.
Σ = summation
σ = standard error of estimate, cu. ft./lb.-mole
∂ = partial differential operator

Subscripts

gr = graphical
int = integrated
j, k = components j and k
m_i = change in state during which the weight of all components other than k remains constant
P = pressure, p.s.i.a.
T = thermodynamic temperature, ° R.

Superscript

° = pure component

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RECEIVED for review August 6, 1964. Accepted November 5, 1964. This paper was accepted as a contribution to this journal by R.L. Pigford, Editor of *Ind. Eng. Chem. Fundamentals*.

Viscosity of Hydrocarbons. Methane

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Confirmatory measurements of the viscosity of methane in the gas phase were carried out at pressures up to 5000 p.s.i.a in the temperature interval between 40° and 400° F. These measurements corroborate and extend the results reported in earlier, more extensive investigations which were carried out with entirely different types of instruments. A comparison of the current measurements with those obtained by other investigators has been included along with an analytical expression describing the effect of temperature and specific weight upon the viscosity of methane.

THE VISCOSITY of methane has been investigated extensively. However, the agreement among the several investigators leaves something to be desired. Ross and Brown (*15*) reported measurements at temperatures between 32° and 77° F., while Barua, Ross, and Afzal (*2*) extended these measurements to temperatures above 300° F. Measurements are reported with a rolling-ball viscometer (*16*) at temperatures from 100° to 220° F. Bicher and Katz (*3*) reported measurements at temperatures between 77° and 437° F., while Carr (*7*) made an investigation at temperatures up to 200° F. Comings, Mayland, and Egly (*8*) reported data from 86° to 203° F.; Baron, Roof, and Wells (*1*) reported measurements at temperatures between 125° and 275° F.; while Kestin and Leidenfrost (*10*) made measurements in the vicinity of 70° F.

The significant dispersion among these several investigators indicated the need for further confirmatory measurements with an entirely different type of instrument. For this reason, a series of measurements were carried out at temperatures between 40° and 400° F. and at pressures up to 5000 p.s.i.a. with a rotating-cylinder viscometer.

METHODS AND EQUIPMENT

The apparatus employed in this investigation is of the rotating-cylinder type. Details of the design (*13*) together with the desirable modifications (*5*), have been described. The methods employed were comparable to those used in earlier studies of ethane (*5*), propane (*4*) and *n*-butane (*6*). In principle, the apparatus consists of a rotating cylinder within which a stator is suspended on a small platinum-tungsten wire. Measurements of the angular displacement of the stator, as a result of the rotation of the outer cylinder at a predetermined angular velocity, permitted the viscosity of the fluid in the gap to be evaluated from the dimensions of the instrument and from the elastic characteristics of the suspension. The dimensions of the instrument have been checked periodically and have not undergone measurable change since the first year of operation of the instrument. It is believed that the gap is known with an uncertainty of 0.2%.

The elastic characteristics of the suspension were determined as a function of time and temperature from the natural period of the stator. Small changes in the elastic characteristics of the suspension occur with time, and there is a significant variation in the elastic characteristics with temperature (*14*). Experience indicates that the elastic characteristics of the suspension were ascertained at a given temperature within 0.1%. The angular displacement was determined by means of a transducer of the reluctance type (*5*), and the angular velocity of the outside cylinder, which was established by a predetermined rate drive, was known within 0.01%.

The temperature was determined by means of a platinum resistance thermometer whose indications were compared with a similar instrument calibrated by the National Bureau of Standards. It is believed that the temperature was known within 0.05° F. relative to the international platinum scale.

Pressures were measured with a special balance (*17*) which was calibrated against the vapor pressure of carbon dioxide, and the pressure within the instrument was known within 0.05% or 0.1 p.s.i., whichever was the larger measure of uncertainty.

MATERIAL

The methane employed in this investigation was obtained through the courtesy of Texaco, Incorporated, from a well in the San Joaquin Valley. The methane, at a pressure in excess of 500 p.s.i.a., was cooled to the temperature of dry ice and acetone and, subsequently, at room temperature passed through beds of calcium chloride, activated charcoal, ascarite, and anhydrous calcium sulfate. Mass spectrographic analysis indicated that the sample contained less than 0.0025 mole fraction of impurities. These impurities involved 0.0017 mole fraction of nitrogen and 0.0008 mole fraction of ethane.

RESULTS

The experimental results obtained in this study are reported in Table I. These results are based entirely upon the dimensions of the instrument and the elastic constant of the suspension. Measurements were made with the rotor operating first in one direction and then in the other. The results were averaged, and in no case did the individual measurements deviate from the average by more than 0.1%.

Figure 1 presents the current measurements of the viscosity as a function of pressure with temperature as a parameter. The standard error of estimate from the smooth curve was 0.96 micropoise. The data have been presented in terms of micropoise because of the widespread acceptance of this unit. However, the viscosity has also been indicated in the force length time system of dimensions, using the unit of pound-second per square foot on several of the figures.

Table I. Experimental Measurements for Methane

Pressure, P.S.I.A.	Viscosity, Micropoise	Pressure, P.S.I.A.	Viscosity, Micropoise	Pressure, P.S.I.A.	Viscosity, Micropoise	Pressure, P.S.I.A.	Viscosity, Micropoise	Pressure, P.S.I.A.	Viscosity, Micropoise
40° F.		100° F.		220° F.		340° F.		400° F.	
16.2	104.79	17.5	116.85	18.4	136.20	19.4	155.79	31.3	165.26
16.2	105.52	17.8	116.02	18.4	136.21	19.4	156.02	31.3	165.51
16.2	105.58	18.0	116.03	18.4	136.53	19.4	156.04	31.3	165.53
1010.7	124.38	18.0	116.14	1023.1	146.39	19.4	156.05	1026.8	172.42
1010.7	124.59	18.0	116.29	1023.2	146.58	1014.0	163.77	1027.2	172.53
1010.7	124.45	18.3	116.84	1023.2	146.56	1014.3	163.57	1027.7	172.14
2049.4	169.90	19.1	115.69	2012.7	163.89	1014.7	163.58	2039.8	183.38
2051.9	170.08	19.1	116.16	2039.4	163.68	2037.0	175.89	2040.2	183.54
2054.2	168.81	19.1	116.44	2040.6	163.63	2037.3	175.52	2040.2	183.89
4018.3	264.17	911.4	128.23	4013.8	208.50	2037.3	175.94	4037.4	209.09
4022.8	264.29	911.4	128.35	4015.3	209.40	4151.3	209.76	4038.8	209.21
4022.8	264.46	1480.5	142.87	4016.3	207.12	4157.1	209.18	4055.5	210.58
4023.8	264.36	1480.5	143.49	4016.3	206.41	4158.3	209.15	4055.5	211.04
5168.7	308.14	1480.4	143.28	4016.3	206.22	5049.9	222.08	4055.5	209.91
5171.3	307.70	1944.0	155.36	4047.8	207.43	5050.4	221.65	4055.5	209.39
5173.7	308.33	1944.0	155.36	4051.5	208.49	5050.4	221.79	5066.9	222.85
		1944.0	156.34	4060.4	207.76	5119.8	225.13	5069.8	223.20
		1944.0	156.42	5083.5	232.78	5123.6	224.99	5069.8	222.71
		3980.4	229.52	5083.5	234.06	5126.2	225.81		
		3983.5	229.24	5083.5	233.82				
		3983.9	227.41	5083.5	233.35				
		3990.4	226.97						
		5014.8	264.89						
		5020.2	264.54						
		5024.8	264.14						
		5103.4	264.36						
		5106.9	263.62						
		5106.9	264.34						
		5106.9	265.22						

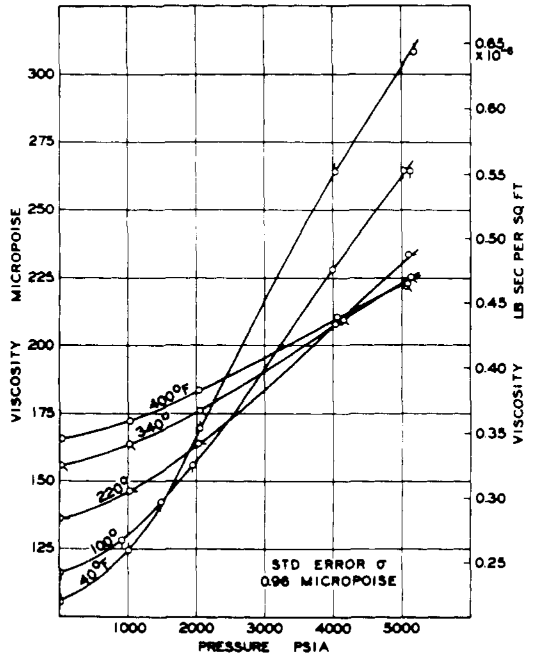

Figure 1. Viscosity of methane

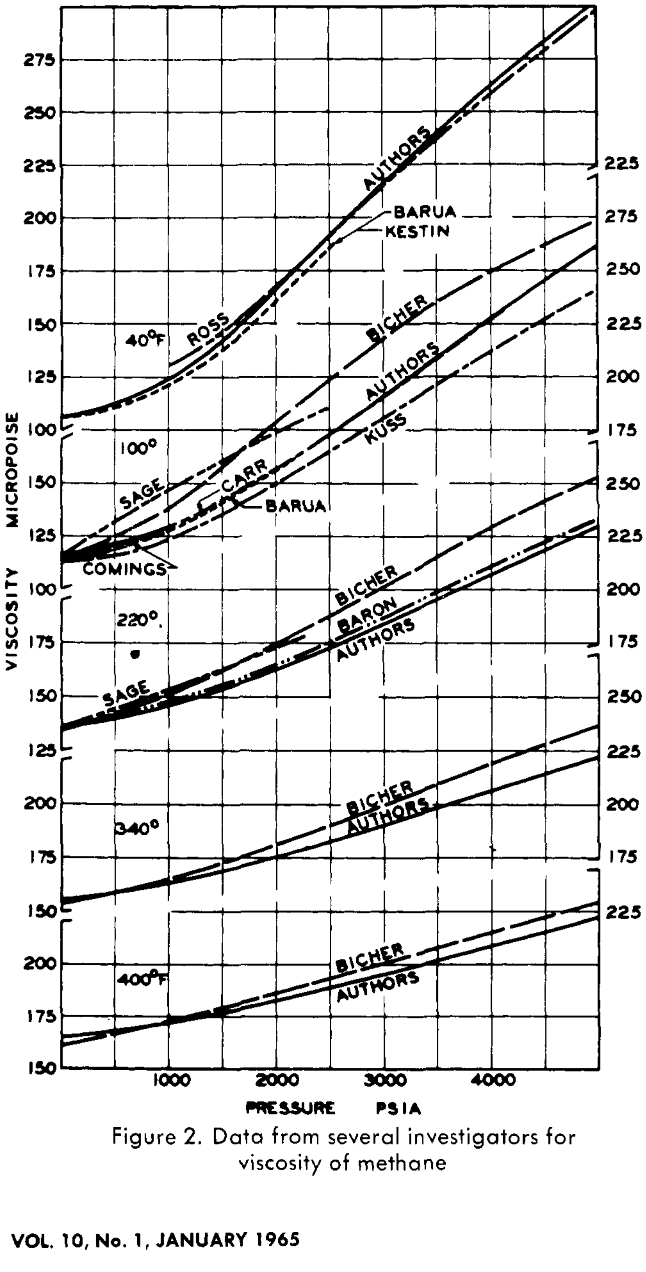

Figure 2. Data from several investigators for viscosity of methane

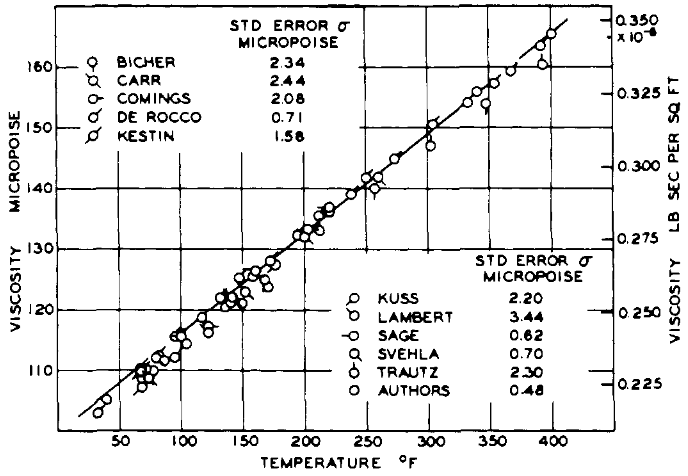

Figure 3. Data from several investigators for viscosity of methane at atmospheric pressure

A comparison of the current data with measurements of other investigators, which have in themselves been smoothed to the same temperatures as the current measurements, is shown in Figure 2. The interpolation of the data from other investigators has been sufficiently precise that uncertainties of more than one micropoise in the evaluation of the probable value from each set of measurements is unlikely.

Graphical interpolation was employed to arrive at the dashed curve at 40° F., which is based upon the data of Barua at 32° and 100° F. and upon the data of Kestin at 68° F. The current measurements were in good agreement with the measurements of Barua (*2*), Kestin (*10*), and Ross (*15*) at this temperature.

At 100° F., Bicher (*3*) and the earlier measurements for the rolling-ball viscometer (*16*) are higher than the current measurements while Kuss (*11*) is lower. Excellent agreement with the measurements of Carr (*7*), Comings (*8*), and Barua (*2*) was obtained.

At 220° F., the author's data are in good agreement with Baron (*1*) but, again, the earlier rolling-ball data (*16*) and the measurements of Bicher (*3*) indicate a somewhat higher viscosity. For comparison, only the measurements of Bicher (*3*) at temperatures of 340° and 400° F. were available. On the whole, the measurements of other investigators, shown in Figure 2, are somewhat higher than the present data except at low pressures. However, the agreement becomes more satisfactory at the higher temperatures.

Table II. Viscosity of Methane

Pressure, P.S.I.A.	Temperature, ° F.				
	40	100	220	340	400
14.7	106.2[a]	116.1	135.9	155.6	165.4
200	108.2	118.0	137.2	156.6	166.4
400	111.3	120.2	139.1	158.1	167.7
600	115.0	122.8	141.1	159.5	169.0
800	119.0	126.2	143.4	161.1	170.4
1000	124.1	130.0	146.0	163.0	172.0
1500	141.6	143.0	153.8	168.6	176.8
2000	166.6	157.4	163.0	175.2	182.6
2500	191.4	173.4	173.0	182.6	188.8
3000	215.8	191.4	183.7	190.4	195.4
3500	240.6	210.1	195.0	198.4	202.1
4000	263.3	228.8	207.0	206.8	209.0
4500	283.3	245.5	218.5	215.0	215.5
5000	303.0	262.8	230.4	223.3	222.5
σ[b]	0.92	0.99	0.92	0.96	0.98

[a] Viscosity expressed in micropoise.

[b] Standard error of estimate expressed in micropoise and defined as:

$$\sigma = [\{\sum_{1}^{N} (\eta_e - \eta_s)^2\}/N]^{1/2}$$

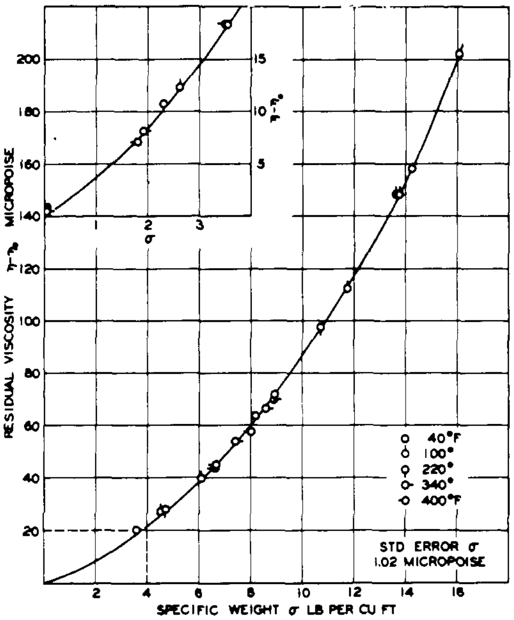

Figure 4. Residual viscosity of methane

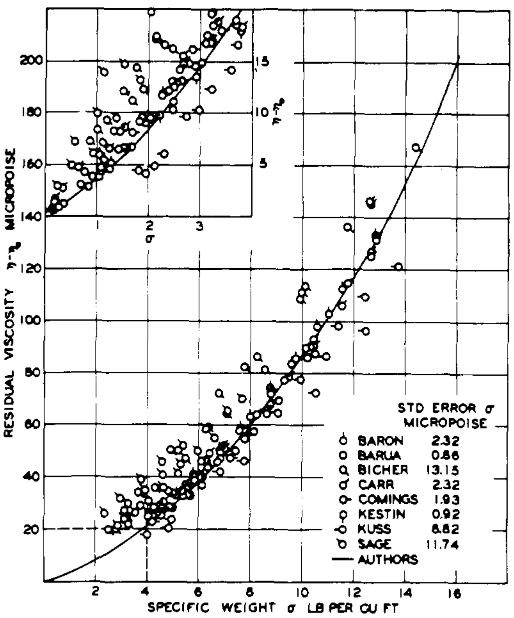

Figure 5. Residual viscosity of methane from data of several investigators

Figure 3 shows measurements at atmospheric pressure as a function of temperature. In addition to the current measurements, data from ten different investigators (*3*, *7*-*12*, *16*, *18*, *19*) have been included.

Figure 4 shows the present measurements in terms of residual viscosity as a function of specific weight. The data near atmospheric pressure have been shown on an enlarged scale. The curve yielded a standard error of estimate for the experimental data of 1.02 micropoises. This is comparable to the standard error of estimate found for the deviation of the data from the smooth curve shown in Figure 1.

Figure 5 presents a comparison of the measurements of eight different investigators, (*1*, *2*, *3*, *7*, *8*, *10*, *11*, *16*), along with the current measurements in terms of the residual viscosity for all data available above 40° F. Data at lower temperatures were not included. The standard error of estimate varies from values of less than 1 micropoise for Barua (*2*) and Kestin (*10*) to values greater than 10 micropoises for the earlier measurements of the rolling-ball viscometer (*16*) and the data of Bicher (*3*). The latter data exhibit a strong bias, and they are predominately higher than the more recent measurements.

Values for the viscosity of methane are reported in Table II for even values of pressure for a number of temperatures lying between 40° and 400° F. These values are based, for the most part, upon current measurements, and they are in good agreement with measurements obtained

Table III. Coefficients for Polynomial Expressions

Number of Points		Coefficients[b]				Standard Deviation[c]	Average Deviation[d]	Source of Data
Used	Rejected[a]	*A*	*B*	*C*	*D*			
				Viscosity at Attenuation, η_o				
5	0	24.5037	0.15984	0.1012×10^{-4}	-0.6488×10^{-8}	0.007	0.000	Authors
26	0	104.264	−0.24552	0.6682×10^{-3}	-0.3521×10^{-6}	1.285	0.008	Authors (*1*, *3*, *8*, *10*, *11*, *16*)
				Residual Viscosity, $\eta - \eta_o$				
103	–[e]	3.1250	0.65202	−0.02202	0.00112	1.082	0.288	Authors
103	13	3.0122	0.70758	−0.02896	0.00136	0.703	0.320	Authors
209	–[e]	3.5281	0.58362	−0.01794	0.00103	1.882	0.256	Authors (*1*, *2*, *8*, *10*)
209	20	3.3461	0.64463	−0.02392	0.00121	1.063	0.264	Authors (*1*, *2*, *8*, *10*)
325	–[e]	4.3023	0.6714	−0.04604	0.00227	6.449	0.483	Authors (*1*, *2*, *3*, *8*, *10*, *11*, *16*)
325	43	4.3852	0.3222	−0.00572	0.00037	2.894	0.479	Authors (*1*, *2*, *3*, *8*, *10*, *11*, *16*)

[a] Statistically rejected when deviation exceeds $x(\sigma)$. $x = 2$.

[b] Coefficients expressed in micropoise.

[c] Standard deviation expressed in micropoise and defined as:

$$\sigma = [\{ \sum_{1}^{N} [(\eta_o)_e - (\eta_o)_c]^2\}/(N-4)]^{1/2} \text{ or } [\{ \sum_{1}^{N} [(\eta - \eta_o)_e - (\eta - \eta_o)_c]^2\}/(N-4)]^{1/2}.$$

[d] Average deviation expressed in per cent and defined as:

$$s = [\{ \sum_{1}^{N} | [(\eta_o)_e - (\eta_o)_c]/(\eta_o)_e | \}/N]100 \text{ or } [\{ \sum_{1}^{N} | [(\eta - \eta_o)_e - (\eta - \eta_o)_c]/(\eta - \eta_o)_e | \}/N]100.$$

[e] No rejection factor, *x*, used.

by Kestin (*10*) with an oscillating-disk viscometer and those reported by Barua (*2*). The smooth values of the viscosity recorded in Table II are based upon graphical smoothing operations on large-scale plots similar to the information presented in Figures 1 through 5.

Utilizing the data from several investigators (*1, 3, 8, 10, 11, 16*), a polynomial expression of the following form was employed to establish the effect of temperature upon the viscosity at attenuation:

$$\eta_o = A + BT + CT^2 + DT^3 \qquad (1)$$

The small change in viscosity from atmospheric to attenuation was determined from the rate of change of viscosity with pressure at atmospheric conditions. Utilizing all of the data involving 26 points, a standard deviation of 1.28 micropoises was found, and there were no points which yielded local deviations from the curve of more than twice the standard deviation for the whole set. The coefficients are set forth in a part of Table III. If only the present data are employed, the standard deviation is 0.007 micropoise, and the curvature is higher. In this instance also, no points were rejected.

Following the same techniques involving the viscosity excess as a single-valued, nontemperature-dependent function of specific weight, a second expression involving four coefficients was employed:

$$\eta - \eta_o = a\sigma + b\sigma^2 + c\sigma^3 + d\sigma^4 \qquad (2)$$

Utilizing the current experimental data involving 103 points and no rejections, a standard deviation of 1.08 micropoises was found which was comparable to that arrived at by purely graphical operations. If all points showing local deviations from the calculated values greater than twice the standard deviation are rejected, 13 points are rejected, and the standard deviation is decreased to 0.70. The corresponding coefficients, the number of points rejected, and the total considered are set forth in a part of Table III. If the current measurements together with those of Baron (*1*), Barua (*2*), Comings (*8*), and Kestin (*10*) are employed, making a total of 209 experimental points with the same rejection criteria as was used before, a standard deviation of 1.06 micropoises is obtained and 20 points are rejected.

If, on the other hand, substantially all the data are included, making a total of 325 experimental points with the same rejection criteria, the deviation is 2.89 micropoises and 43 points are rejected.

After critical consideration of the data, the coefficients designated in the following equation are recommended as being the most representative of the behavior of the viscosity of methane as evaluated from selected (*1, 2, 8, 10*) experimental data, and they are expressed in micropoises:

$$\begin{aligned}\eta &= \eta_o + (\eta - \eta_o)\\ &= [A + BT + CT^2 + DT^3] + [a\sigma + b\sigma^2 + c\sigma^3 + d\sigma^4]\\ &= [24.504 + 0.1598T + 0.1012 \times 10^{-4}\,T^2 - 0.6488 \times 10^{-8}\,T^3]\\ &\qquad + [3.346\sigma + 0.6446\sigma^2 - 0.02392\sigma^3 + 0.000121\sigma^4] \qquad (3)\end{aligned}$$

As a matter of interest, a comparison was made between the data reported in a part of Table II and values computed by Equation 3 for the same states. The results yielded a standard deviation of 1.2 micropoises and an average deviation of −0.8 micropoise for the 68 states used in the comparison. It should be recognized that these expressions are empirical and have been included only to permit analytical representation of the results often desired in machine computations. They have not been included as a new method of correlation but rather for utilitarian purposes.

ACKNOWLEDGMENT

This work was supported by a grant from the Petroleum Research Fund of the American Chemical Society and a grant from the National Science Foundation. Lorine Faris carried out all of the graphical operations involved in the preparation of Table II, while June Gray prepared the figures, and Grace Fitzsimons assisted in the preparation of the manuscript.

NOMENCLATURE

A, B, C, D = coefficients, micropoise
a, b, c, d
N = number of points
s = average deviation, fraction
T = thermodynamic temperature, °R.
x = coefficient of standard deviation
η = viscosity, micropoise
Σ = summation operator
σ = specific weight, lb./cu. ft.
σ = standard deviation or standard error of estimate, micropoise

Subscripts

c = calculated
e = experimental
o = attenuation
s = smooth

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Received for review August 24, 1964. Accepted December 8, 1964. This paper was accepted as a contribution to this journal by R.L. Pigford, Editor of *Ind. Eng. Chem. Fundamentals*.