Liquid Viscosities Above the Normal Boiling Point for Methane, Ethane, Propane, and *n*-Butane

G. W. SWIFT, JOHN LOHRENZ, and FRED KURATA
University of Kansas, Lawrence, Kansas

Viscosities, obtained with a falling-cylinder viscometer, are presented for liquid methane, ethane, and propane from their normal boiling points to their critical points and for *n*-butane from its normal boiling point to 100°C. The data of this study are compared with those of other investigators.

The experimental viscosities of this study are correlated within ± 5% over the reduced-temperature range from 0.65 to 0.95 by means of a modified Smith-Brown correlation. The Grunberg-Nissan equation for estimating the critical viscosity was tested with the experimentally determined critical viscosities of this study and was found satisfactory.

The importance of accurate viscosity data to the chemical engineer cannot be overemphasized. A knowledge of viscosity and its variation with temperature and pressure is required for the solution of many of the problems that confront him, for example heat transfer, mass transfer, and fluid flow. A study of the literature on viscosity will show that no systematic approach has been formulated for the collection of these data.

One reason for this lack appears to be caused by the limitations of the instruments used to measure viscosity. Instruments which give good results for gas viscosity, for example the Rankine viscometer, are often unsuited for liquid-viscosity measurement. Instruments which employ mercury drives are restricted to temperatures above the freezing point of mercury. The rolling ball viscometer is severely handicapped in regions where turbulent flow exists.

The problem of evaluating and correlating gas and liquid viscosities of a single substance over the range of temperature and pressure of interest is compounded when the data are not internally consistent. Thus it would be desirable to obtain all the pertinent data with one viscometer.

In the present research the materials investigated were methane, ethane, propane, and *n*-butane, and the falling-cylinder viscometer apparatus was developed to meet the needs of this research because it has the following advantages:

1. The design and construction of the falling-cylinder viscometer are simple.
2. It can be used at extremes of temperature and pressure.
3. The motion of the cylinder can be controlled to eliminate the undesirable components, for example spin and fishtailing.
4. Calibration is relatively simple.
5. All ranges of viscosity can be determined by using a series of bodies with different dimensions.

Since it has been shown that the falling-cylinder viscometer can measure fluid viscosities accurately, this instrument offers a method of determining internally consistent data for substances (in the gas or liquid phase) over wide ranges of temperature, pressure, and viscosity. This equipment can also be used to measure volumetric behavior concurrently with viscosity measurements.

EXPERIMENTAL APPARATUS

An article by Swift, Christy, Heckes, and Kurata (*21*) describes the basic experimental apparatus used in this investigation. Recent improvements in temperature control, viscometer falling-body design, and timing are discussed in detail by Swift (*20*).

Temperature in the viscometer bath was controlleed to within ± 0.01 °C. and was measured with a platinum resistance thermometer. The average uncertainty of temperature measurement was estimated to be ± 0.01°C. Experimental fall times were measured to four significant figures with a digital time-interval meter. A mean fall time was computed from ten consecutive experimental fall times at a given temperature and pressure. Percentage error for mean fall time, computed statistically for 98% probability, was about 0.1% on the average. Pressure was measured with a 0 to 2,000 lb./sq. in. Bourdon gauge with an uncertainty of ± 1 lb./sq. in.

EXPERIMENTAL RESULTS

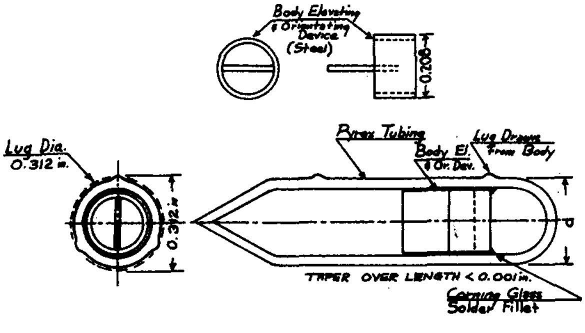
Values of the viscosities of the different substances used for calibration

TABLE 1. PERCENTAGE OF ERRORS FOR THE VISCOMETER CALIBRATION DATA

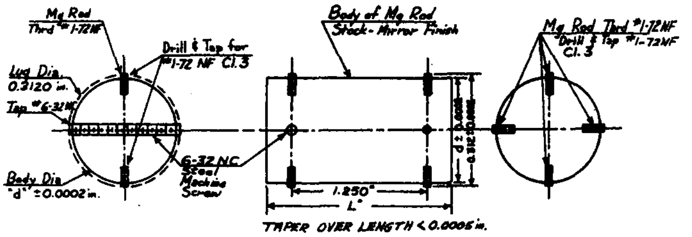
Float number	Error in β_o, laminar region*, %	Maximum error in β_o, turbulent region, %	Average error in β_o, turbulent region, %
GCL-301	0.27	3.85	1.48
GCLO-304	0.76	1.72	0.74
MgSLO-303	0.49	3.20	1.20
MgSLO-305	0.21	2.00	1.08
MgSLO-307	0.63	2.39	1.09
MgSLO-309	0.93		

* Computed for 98% probability with t statistic used.

G. W. Swift is now with the Continental Oil Company, Ponca City, Oklahoma.



GLASS FALLING BODY



MAGNESIUM FALLING BODY

Fig. 1. Schematic drawing of falling bodies.

of the viscometer were taken from Rossini (*14*); Comings, Mayland, and Egly (*3*); and Michels and Gibson (*12*). Liquid densities, vapor pressures, and critical properties were taken from Rossini (*14*); Matthews and Hurd (*11*); Barkelew, Valentine, and Hurd (*1*); Hanson (*8*); Deschner and Brown (*4*); Kay (*9*); and Eilerts, *et al.* (*5*).

Six viscometer falling bodies were used in this investigation. Two of these were fabricated from glass, the others from magnesium. The glass bodies were cylindrical with streamlined ends; the magnesium bodies were true cylinders. All the bodies were equipped with projections at either end to stabilize the motion of the bodies in the viscometer tube. Figure 1 shows sketches of the two types of falling cylinders used. Each body was identified by the following code system:

G = material of construction, glass
Mg = material of construction, magnesium
C = closed or hollow construction
S = solid construction
L = lugs or projections on the body
O = oriented

The three-digit number following the code group represents the diameter of the body in thousandths of an inch. (The internal diameter of the viscometer tube was 0.315 in.)

The viscometer was calibrated to account for the effects of temperature and turbulence. A linear coefficient of temperature for the viscometer constant was determined for each falling body. The effect of pressure on viscometer calibration was checked for *MgSLO*-309 and found to change the calibration constant by 2 to 3% at 1,000 lb./sq. in. abs. It was impossible to separate the effect of pressure from the turbulence effect for the other falling bodies; thus no correction for pressure effect on the calibration constant was made, since approximate methods for determining the pressure effect might compound an error of 2 to 3%, rather than correct it. The complete calibration procedure is discussed by Swift (*20*).

The accuracy of the calibration plots is given by the data of Table 1. Even in the region of turbulent flow the errors are quite low.

Phillips pure grade (99 mole % minimum) methane, propane, and *n*-butane and Phillips research grade (99.9 mole % minimum) ethane were used. Analyses by mass spectrometer made on these materials are given in Table 2.

Liquid viscosities were determined for methane, ethane, and propane over their respective temperature ranges from normal boiling point to critical point and for *n*-butane from below its normal boiling point to 100°C.

The computations for viscosity were made by the viscometric equation:

$$\mu = \beta_{t,p}(\sigma - \rho)\theta \tag{1}$$

The original calibration plots of the type used by Sage and Lacey (*16*) were constructed on a scale such that four significant figures could be read for β_0 for all bodies except *MgSLO*-307, where it was possible to read only

TABLE 3. EXPERIMENTAL VISCOSITIES OF LIQUIDS

Temperature, °C.	Pressure, lb./sq.in.abs.	Viscosity, centipoise
	Methane	
-140	85	0.0742
	600	0.0762
-120	195	0.0531
	600	0.0544
-100	400	0.0376
	600	0.0396
-90	540	0.0301
	600	0.0303
-85	630	0.0262
-82.2	675	0.015
	Ethane	
-80	25	0.147
	600	0.149
-60	65	0.119
	600	0.121
-40	115	0.0959
-20	230	0.0755
	600	0.0786
0	370	0.0580
	595	0.0604
20	565	0.0418
	600	0.0428
25	625	0.0370
30	695	0.0327
32.3	716	0.0306
	Propane	
-30	50	0.173
-20	50	0.157
	600	0.159
0	100	0.124
20	150	0.105
	600	0.110
40	245	0.0819
	600	0.0881
60	330	0.0649
	600	0.0694
80	475	0.0481
	600	0.0511
90	545	0.0404
96.8	620	0.022
	n-Butane	
20	45	0.164
40	65	0.136
60	110	0.113
80	160	0.0950
100	250	0.0787

TABLE 2. PURITY ANALYSES FOR THE METHANE, ETHANE, PROPANE, AND *n*-BUTANE USED IN THIS INVESTIGATION

MOLE %

	H_2	N_2	CH_4	C_2H_6	C_3H_6	C_3H_8	$n\text{-}C_4H_{10}$
Methane	0.06	0.95	98.99				
Ethane	0.09			99.91			
Propane			0.08	0.62	0.11	99.19	
n-Butane		0.80				1.33	97.87

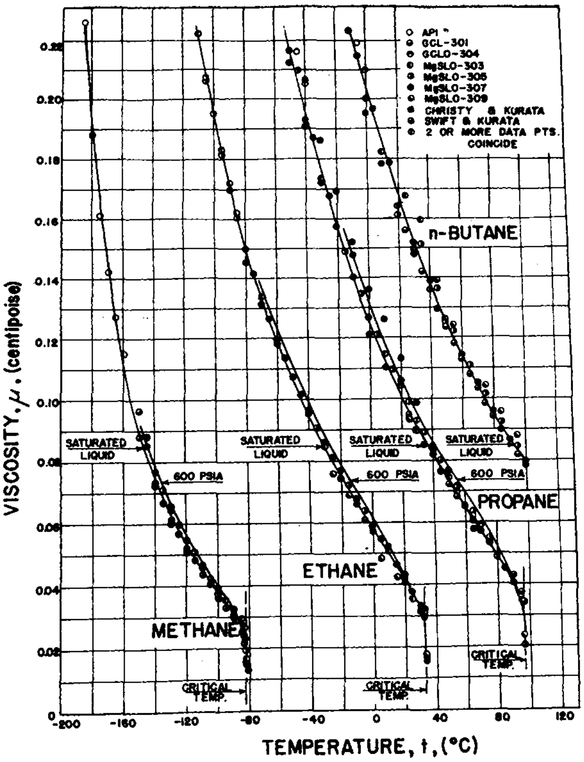


Fig. 2. Experimental viscosities of liquid methane, ethane, propane, and n-butane.

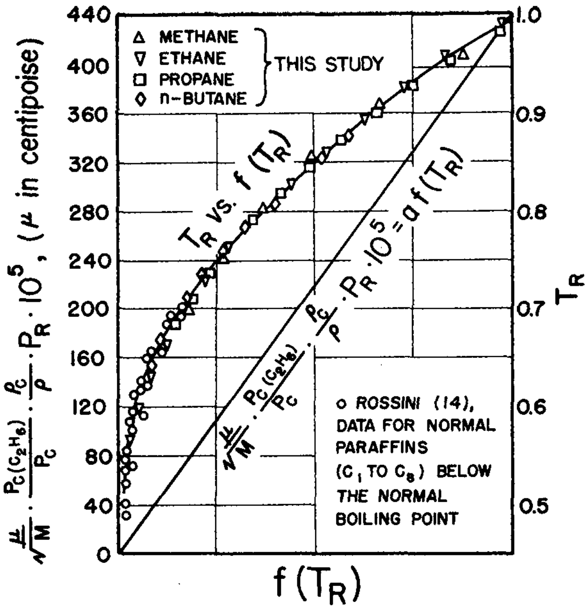


Fig. 3. Correlation for saturated-liquid normal paraffins.

three significant figures. The solution for viscosity in cases where turbulent flow existed was of a trial-and-error nature, since the viscosity had to be assumed before β_o could be determined. The solution converged rapidly however, and two, or at most three, trials were necessary to compute viscosity.

Some of the experimental data are tabulated in Table 3.[*] In the tabulated data the average value for viscosity for each temperature and pressure is reported. As this value was computed from experimental values determined by two or more falling bodies, bias from improper calibration of any one body is minimized. The precision of the experimental results, reported as average maximum error, was ± 4.0% for methane, ± 2.1% for ethane, ± 2.5% for propane, and ± 2.4% for n-butane.

Figure 2 gives a plot of viscosity as a function of temperature. The experimental data points are shown for each body on the saturated liquid curves. The data points which define the 600 lb./sq. in. abs. curves for methane, ethane, and propane were omitted to preserve the clarity of the plot.

The viscosity decreases quite rapidly with increasing temperature in the immediate vicinity of the critical point. Thus it is difficult to obtain accurate viscosity data in this region. This situation is aggravated by the sensitivity of the liquid phase to temperature and pressure in this region. In this investigation critical viscosities for methane and propane were obtained at the respective temperatures and pressures which gave the critical phenomena of opalescence. In the case of ethane the critical viscosity reported was interpolated from the data of a temperature traverse through the critical region.

COMPARISON OF EXPERIMENTAL DATA

An extensive survey of the literature was made for the purpose of comparing data. Table 4 lists data source, method, and approximate deviation of results of the different investigators.

The comparison of the experimental data strongly illustrates the need for a consistent set of viscosity data. The data of this study are consistent, and furthermore the agreement with the

TABLE 4. RESULTS OF LITERATURE SURVEY

Source	Compound	Method	Approximate deviation from this study
(2)	Propane	Rolling ball	3% higher
(6)	Methane	Oscillating disk	20 to 25% higher
	Ethane		From 17% lower at low temperatures to 20% higher at high temperatures
(10)	Propane	Capillary	4 to 5% higher
	n-Butane		4 to 5% higher
(13)	Methane	Capillary	10 to 15% higher
(14)	Ethane	Compilation	Less than 1% higher
	Propane		4% higher
	n-Butane		2% higher
(15)	Methane	Oscillating disk	20 to 25% higher
(16)	Propane	Rolling ball	2% higher
(17)	n-Butane	Rolling ball	± 2%
(18)	Propane	Rolling ball	4% higher
(19)	Propane	Capillary	Less than ± 1%
(22)	Methane	Falling cylinder	6% lower
	Propane		10 to 12% higher at intermediate temperatures; ± 2% at higher temperatures
(23)	Propane	Falling cylinder	High-pressure data only; not directly comparable

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[*] Tabular material has been deposited as document No. 6267 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $3.75 for photoprints or $2.00 for 35-mm. microfilm.

data of Rossini (*14*) and Starling, Eakin, and Ellington (*19*) is good. In view of the precision of the data of this study, agreement with the data of all investigators save Pavlovich and Timrot (*13*); Gerf and Galkov (*6*); Rudenko (*15*); and Swift, Christy, and Kurata (*22*) is reasonable. The disagreement with the data of Swift, Christy, and Kurata is believed to be caused by improper low-temperature calibration on the part of those investigators. No explanation can be offered for the lack of agreement of the other data.

CORRELATION

A study of the literature was made to determine whether any satisfactory correlations had been made for saturated liquid hydrocarbons above their normal boiling points. A correlation by Smith and Brown (*18*) seemed most suitable. They plotted

$$\frac{\mu}{\sqrt{M}} \cdot \frac{P_{c(x)}}{P_c} \cdot P_R \text{ vs. } T_R$$

The purpose of the term $P_{c(x)}/P_c$ was to adjust all ordinate values to the common pressure basis of reference substance x. Data for saturated *n*-pentane and *n*-hexane were correlated by Smith and Brown for reduced temperatures up to 0.93.

The data of the present study were plotted in like manner and were fairly well correlated up to reduced temperatures of 0.8. For higher reduced temperatures the data scattered, but the data for each homologue followed an internally consistent trend. This behavior indicated that some correlation parameter, which was in effect primarily in the high reduced-temperature region, was not being considered. The inclusion of ρ_c/ρ in the ordinate group was found to correct the data scattering in the high reduced-temperature region.

The correlation presented graphically in Figure 3 is based upon the following equation:

$$\frac{\mu}{\sqrt{M}} \cdot \frac{P_{c(x)}}{P_c} \cdot \frac{\rho_c}{\rho} \cdot P_R \cdot (10^5) = af(T_R) \tag{2}$$

For any T_R, $f(T_R)$ is represented by the curved line in Figure 3. To use the correlation, compute the reduced temperature and locate it on the right-hand ordinate scale. Draw a horizontal line through this value of T_R to intersect the T_R vs. $f(T_R)$ curve. The intersection on this curve defines the correct $f(T_R)$. Move vertically to the line representing Equation (2) and read the left-hand ordinate at the point of intersection. The saturated viscosity can then be computed, with $P_{c(x)}$, P_c, ρ , ρ, and M known.

The accuracy of the correlation is dependent upon the selection of critical constants. To obtain best results the values for T_c, P_c, and ρ_c given by Eilerts *et al.* (*5*) and used in this study are recommended.

The correlation is based on ethane as reference substance x. Smoothed data of this study and the compilation of Rossini (*14*) were used to construct Figure 3. Saturation pressures corresponding to actual temperatures were used.

The correlation predicts saturated liquid viscosities for normal paraffins from methane to *n*-octane within ± 5% over the reduced-temperature range from 0.65 to 0.95. The values computed from the Smith-Brown correlation for methane, ethane, propane, and *n*-butane at a T_R of 0.90 disagree with the experimental data of this study by as much as 30%.

A reduced temperature of 0.65 corresponds roughly to the normal boiling point for most paraffins and thus poses no restriction on the value of the correlation, since experimental viscosities for all paraffins are available at temperatures up to the normal boiling point (*14*). On the other hand the region of reduced temperature from 0.95 to 1.0 could be of considerable interest, and little experimental data are available in this region. Thus a method for extrapolating viscosity data in this region is required.

Grunberg and Nissan (*7*) proposed the following equation for the computation of critical viscosity:

$$\mu_c = K\left(\frac{\rho_c^{2/3}}{M^{1/6}}\right)T_c^{1/2} \tag{3}$$

For the purposes of this discussion K will be defined in terms of Equation (3), where ρ_c is in grams per cubic centimeter, T_c in Kelvin degrees, and μ_c in centipoise. K was computed for methane, ethane, and propane, with the experimental critical viscosities of this study (Table 3) used. The calculated values for K were $K_{\text{methane}} = 0.00575$, $K_{\text{ethane}} = 0.00552$, and $K_{\text{propane}} = 0.00580$. The average value for K, with equal weight given to each of the three compounds was: $K_{\text{avg}} = 0.00569$.

By means of K_{avg}, the critical viscosities for straight-chain paraffins from C_4 through C_8 were calculated. As Grunberg and Nissan predicted, the computed critical values for *n*-butane through *n*-octane were constant at 0.023 centipoise with the exception of *n*-heptane, which had a computed critical viscosity of 0.024 centipoise.

When one assumes that the calculated values for critical viscosities are reasonable, saturated liquid viscosities in the region of reduced temperature for T_R's from 0.95 to 1.00 can be mapped using values from Figure 3 up to $T_R = 0.95$ and then extrapolating to the calculated critical viscosity.

CONCLUSIONS

1. The experimental apparatus used in this investigation employed a falling cylinder as a relative means of determining gas and liquid viscosities. The apparatus was operated within the temperature range from −185° to 100°C. and at pressures up to 1,000 lb./sq. in. abs. The performance of the falling cylinder was superior to the falling- or rolling-ball type of viscometer. Temperature was controlled and measured to within ± 0.01°C., pressure was measured to within ± 1 lb./sq. in., and fall times as low as 0.01 sec. were measured with a precision of ± 0.1%.
2. Experimental viscosity data were presented for liquid methane, ethane, and propane from their respective normal boiling points to their critical points, and for *n*-butane from its normal boiling point to 100°C.
3. Experimental values were determined for the critical viscosities of methane and propane, and the critical viscosity of ethane was estimated by interpolation.
4. The experimental data were correlated within ± 5% by a modified version of the Smith-Brown correlation for saturated hydrocarbon liquids over the reduced temperature range from 0.65 to 0.95. Estimates of saturated liquid viscosities for other normal paraffins can be made from this correlation.
5. The Grunberg-Nissan equation for estimating critical viscosities was tested with the experimentally determined values of critical viscosity for methane, ethane, and propane. The results may be used to estimate viscosities in the reduced temperature range from 0.95 to 1.00.

ACKNOWLEDGMENT

The Phillips Petroleum Company Fellowship Fund provided for the purchase of a major portion of the equipment used in this study and furnished all the hydrocarbons that were used.

The mass spectrometer analyses were performed by the Research and Development Department of the Continental Oil Company.

NOTATION

a = slope of Equation (2)
$f(T_R)$ = function of the reduced temperature in Equation (2)

K = universal constant in Equation (3)
M = molecular weight
P = pressure, lb./sq. in. abs.
P_c = critical pressure, lb./sq. in. abs.
$P_{c(x)}$ = critical pressure of reference substance x, lb./sq. in. abs.
P_R = reduced pressure, dimensionless
T_c = critical temperature, °K.
T_R = reduced temperature, dimensionless
t = temperature, °C.

Greek Letters

$\beta_{t,p}$ = viscometer constant at temperature and pressure, sq. cm./sec.^{2}
β_0 = viscometer constant corrected to 0°C. and 0 pressure, sq. cm./sec.^{2}
θ = fall time interval, sec.
μ = absolute viscosity, poise
ρ = density of fluid, g./cc.
ρ_c = critical density of fluid, g./cc.
σ = density of the falling body, g./cc.

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Suspension of Slurries by Mechanical Mixers

JOEL WEISMAN and L. E. EFFERDING
Westinghouse Electric Corporation, Pittsburgh, Pennsylvania

The production of essentially homogeneous slurries involves both initial solids suspension and expansion of the particle bed to fill the container. When geometry and solids concentration are held constant, both phenomena are found to be controlled by similar dimensionless groupings of power per unit volume, density, and relative velocity between the fluid and particle. The dimensionless group applicable to bed expansion is shown to be consistent with hydrodynamic theory. Design equations for use with the paddle type of impeller are presented.

Slurries have recently been used in an increasing number of industrial situations. An application of major interest is the proposed use of an aqueous thoria-urania slurry as a nuclear reactor fuel. Solving the problems associated with the use of this fuel in a large-sized power plant has been the subject of an extensive research and development program (*7, 8*).

Maintenance of an essentially homogeneous suspension is one of the prime requisites for successful operation of a slurry-fueled nuclear power plant. Therefore as part of the development program the problems of slurry suspension were investigated in several types of equipment. The mixing studies reported in this paper were one aspect of this investigation. The specific objectives of these mixing experiments were to determine for the turbulent region the factors controlling the production of essentially homogeneous suspensions of solid particles by mechanical mixers and to obtain the information necessary for the design of large mixers suitable for use in plant-sized slurry storage tanks.

PREVIOUS STUDIES ON SLURRY AGITATION

Hixson and co-workers (*3* to *6*) in an extensive study of the agitation of slurries of soluble salts determined mass transfer coefficients as a function of mixing Reynolds number and system geometry.

White, Summerford, *et al.* (*14, 15*) and Raghavendra and Mukherji (*11*) studied the distribution of sand in unbaffled tanks using paddle agitators. White *et al.* found that with coarsely sized material the fines were suspended but the large particles remained at the tank bottom. Later studies with more closely sized material of various sizes (0.14 to 0.42 mm.) showed that it was not possible to achieve complete suspension of all the sand particles in

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