Viscosity Correlations for Nonpolar Dense Fluids

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The need for methods to accurately predict the behavior of fluids at high density is well known. Many of the methods which have been developed have been either purely theoretical or purely empirical; in this investigation the two approaches were combined. Empirical modifications of theoretical molecular theory relationships have been fitted to experimental data with very reasonable standard deviations. To achieve even better representations use has been made of semitheoretical relationships and interpretations of observed behavior to develop a relationship which fits the viscosity behavior of eight nonpolar materials over a wide range of conditions for the liquid, gas, and supercritical or dense fluid conditions. It is believed that the greatest potential for the ultimate solution of the problem of development of methods for accurate prediction of fluid behavior lies in refinement of the general molecular theory of fluids developed by Kirkwood (*11, 12*), Born and Green (*2, 3*), and others. However progress in this direction has been slow, for although the general theory has been formulated on a rigorous basis, mathematical difficulties have prevented reduction of the formal theory to tractable expressions for the thermodynamic and transport properties, except in the dilute gas limit or when very simple molecular interactions can be assumed. Neither of these reductions can be used for real fluids, except for very restricted density ranges. For fluids in which realistic molecular interactions must be considered, it has been necessary to make extensive assumptions to simplify the mathematical problems. The introduction of specific assumptions has led to a number of what may be termed "approximate" theories. These theories have been derived only for simple fluids, that is fluids for which the potential field about a molecule is spherically symmetric. They must be tested and verified through detailed comparisons of predicted and experimental results for simple fluids before similar theories for complex fluids can be formulated satisfactorily.

It is evident that much work remains to be done before a generalized approximate theory will be possible for real fluids for wide ranges of the state variables. Nevertheless it is felt that some important new theoretical considerations, not familiar to most chemical engineers, should be reviewed to show that the theories for simple fluids can be used as a basis for the development of semiempirical expressions for the properties of complex fluids. Expressions for the viscosity coefficient were derived in this manner in the course of this investigation. Similar approaches should be applicable to develop analytical expressions for other fluid properties.

MOMENTUM TRANSPORT IN DENSE FLUIDS

The modern theories of the general fluid (*3, 12*) indicate that the coefficient of viscosity should be expressed as the sum of two terms:

$$\mu = \mu_K + \mu_\Phi \tag{1}$$

The terms μ_K and μ_Φ are usually referred to as the kinetic and intermolecular force contributions to viscosity, respectively. The first term arises from consideration of the transfer of momentum due to the free motion of the molecules between collisions. This is the only type of momentum transfer considered in simple kinetic theory, that is at low density. The second term arises from consideration of the transfer of momentum due to the action of intermolecular forces. Consideration of these forces is most important at high density.

The kinetic contribution to viscosity is a function of temperature and density. In the dilute gas limit, where the only contribution to viscosity is by the thermal motion of the molecules, μ_K is a function of temperature only. Thus the condition

$$\lim_{\rho \to o} \mu_K(T, \rho) = \mu_o(T) \tag{2}$$

where μ_o is the dilute gas viscosity, must be satisfied. Accurate expressions for μ_K for high densities have not been developed. At higher densities more molecules would be expected to cross any given plane in the fluid per unit time, which would cause μ_K to be increased. Also shielding of molecules would be expected owing to the increased molecular density which would cause μ_K to be decreased. These effects are mentioned merely to provide an indication of the gross effect of increased density on μ_K.

Enskog derived an approximate expression for μ_K for dense gases by application of corrections to the point-particle dilute gas kinetic theory formulated by Boltzmann (*10*). Enskog corrected for the finite volume of the molecules by consideration of rigid spheres of diameter σ. He corrected for the increased frequency of molecular collision by multiplication of the point-particle collision frequency by the factor Y, which for a low-density fluid can be represented by a power series in density. Enskog's expression for μ_K is

$$\mu_K = \left[\mu_o \frac{1}{Y} + 0.4\, b\rho \right] \tag{3}$$

where $b\rho = \frac{2}{3}\pi n\sigma^3$. Recently Rice et al. (*19*) have derived an identical expression for μ_K from more rigorous arguments. These investigators have shown that the factor Y is proportional to the equilibrium radial distribution function and could therefore be determined even for liquid densities. In yet more recent work Rice and coworkers (*1, 18*) have derived an expression for μ_K for the case of rigid sphere molecules with an attractive intermolecular potential. This expression, which is rather lengthy, is essentially the Enskog expression multiplied by a factor which arises from consideration of the attractive part of the intermolecular potential function.

The intermolecular force contribution to viscosity is a function of temperature and density which must become negligible in the dilute gas limit. Thus the condition

$$\lim_{\rho \to o} \mu_\Phi(T, \rho) = 0 \tag{4}$$

must be satisfied. For the case of a dense gas of rigid sphere molecules Enskog derived the expression

$$\mu_\Phi = 0.4\,\mu_o\,b\rho Y\left[\frac{1}{Y} + 0.4\,b\rho\right] + 0.6014\,\mu_o b^2\rho^2 Y$$

Rice, et al. (*19*) also derived this expression for μ_Φ from the more rigorous theory. Thus, according to these investigators, the viscosity of a dense fluid of rigid spheres is

$$\mu = \mu_o\left[\frac{1}{Y} + 0.8b\rho + 0.7614\,b^2\rho^2 Y\right] \qquad (5)$$

This equation can be used semiempirically to describe the viscosity behavior of real fluids for restricted ranges of density by fitting it to experimental values after expressing Y by use of a valid equation of state.

For fluids at high density, molecular attractions have a much greater influence on momentum transfer than do repulsions. In fact repulsions have been neglected by Kirkwood, et al. (*13*) and by Born and Green (*3*) in the formulation of approximate expressions for μ_Φ. The simpler but probably less exact expression is that of Born and Green:

$$\mu_{\Phi A} = \frac{2\pi}{105}\left[42\,\pi\,m\,\gamma\,r_1^{-6}\right]^{1/2} n^2\,r_1^4 \exp\left[-\frac{\phi(r_1)}{kT}\right] \qquad (6)$$

The factor γr_1^{-6} is the negative of the attractive part of the intermolecular potential function ϕ, and r_1 corresponds roughly to the average distance between neighboring molecules. To calculate $\mu_{\Phi A}$ from this expression requires a relationship for r_1 in terms of the fluid density. Only under certain conditions, such as at the melting point, does an explicit relationship exist.

To date expressions have not been developed for μ_Φ for as sufficiently realistic molecular interactions as is desirable. The recent efforts of Rice and co-workers however show great promise. These investigators have derived general expressions for μ_Φ for rigid sphere molecules with an attractive potential (*1, 18*) and have carried out limted calculations for the case of square-well attraction.

EXPRESSIONS FOR VISCOSITY DEDUCED FROM THEORY

The theoretical expressions for viscosity have been derived for hypothetical fluids, that is those in which there are only simple molecular interactions. These expressions generally cannot be used for accurate predictions of the viscosity of real fluids. However it is possible to use the theoretical relationships as a basis for derivation of semiempirical expressions for viscosity. For example the Born and Green expression for $\mu_{\Phi A}$ as a function of temperature, the intermolecular potential function ϕ, and the intermolecular distance r_1 can be reduced to a form which is amenable to empirical analyses if the repulsive part of ϕ is neglected and if r_1 is assumed to be inversely proportional to the cube root of the molecule number density. If the assumed relationship between r_1 and n is taken to be $r_1 = (wn)^{-1/3}$ and the equality $n = \rho N/M$ is applied, the expression for $\mu_{\Phi A}$ becomes

$$\mu_{\Phi A} = \frac{2\pi(42\pi)^{1/2}\,N^{7/6}\,\gamma^{1/2}\,\rho^{5/3}}{150\,w^{1/3}\,M^{7/6}} \exp\left[\frac{w^2\,N^2\,\gamma\,\rho^2}{M^2\,k\,T}\right] \qquad (7)$$

At liquid densities, where μ_Φ predominates over μ_K, viscosity values of the correct order of magnitude can be calculated from this expression by setting $\mu = \mu_{\Phi A}$. The factor w can be taken as $1/\sqrt{2}$ since it is equal to $1/\sqrt{2}$ for a face centered cubic lattice molecular structure and is of this order for high-density liquid structures. The factor γ can be taken as the coefficient of $-r^{-6}$ in an intermolecular potential function which accurately describes low-density behavior. Obviously this type of calculation is less accurate for more complex-molecule fluids and certainly cannot be used for densities at which μ_K is of the order of μ_Φ. In this investigation, the temperature and density dependence of $\mu_{\Phi A}$ predicted by the Born and Green relationship was retained in μ_Φ, but the factors involving w and γ were treated as empirical parameters.

The simplest equation for dense fluid viscosity which can be derived from the preceding considerations is

$$\mu = \mu_o + K_1\rho^{5/3} \exp\left[\frac{K_2\,\rho^2}{T}\right] \qquad (8)$$

where K_1 and K_2 are constants, specific for each material. This form results if the kinetic contribution to viscosity is assumed to be independent of density and the intermolecular force contribution is assumed to be due to attractions alone.

A second equation for dense fluid viscosity can be derived by assuming that the combination of the kinetic contribution with the repulsion part of the intermolecular force contribution can be represented by the Enskog relationship given in Equation (5). For low densities the factor Y can be expressed for rigid spheres by

$$Y = 1 + 0.625\,b\rho + 0.2869\,b^2\rho^2 + 0.115\,b^3\rho^3 \qquad (9)$$

Substitution of this expression for Y into Equation (5) yields the relationship

$$\mu_K + \mu_{\Phi R} = \mu_o \sum_{j=0}^{4} a_j(b\rho)^j \qquad (10)$$

in which the constants a_j have the values 1.0, 0.175, 0.8651, 0.475, and 0.26, respectively. If the attraction part of the intermolecular force contribution is again assumed to be the Born and Green approximate form, the resulting expression for viscosity is

$$\mu = \mu_o \sum_{j=0}^{4} a_j(b\rho)^j + K_3\,\rho^{5/3} \exp\left[\frac{K_4\rho^2}{T}\right] \qquad (11)$$

An iterative least-square method (*22*) was used to obtain estimates of the parameters in Equations (8) and (11) from a large mass of internally consistent experimental viscosity data for ethane (*9*), propane (*23*), and *n*-butane (*7*) obtained at the Institute of Gas Technology. The standard deviations of the parameters and their correlation coefficients were also computed. Sage and Lacey's (*20*) density data and Titani's (*25*) atmospheric pressure viscosity data were used in these calculations. The molecular covolume b was taken as the van der Waals covolume $1/3\ \rho_c^{-1}$. Data which deviated by more than three times

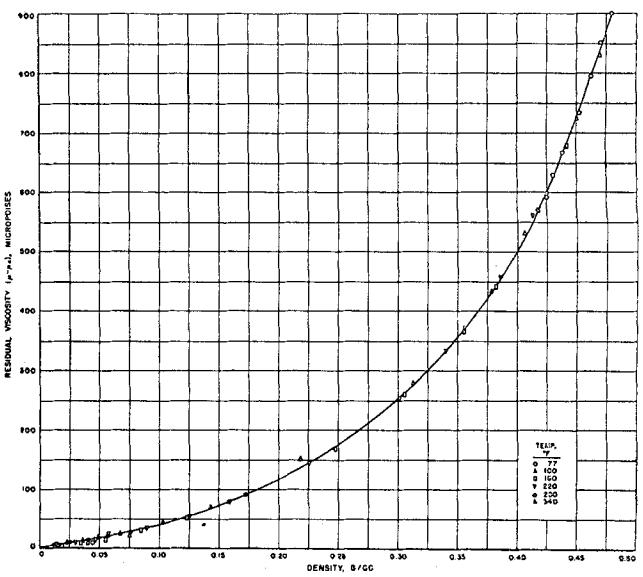

Fig. 1. Residual ethane viscosity vs. density-linear coordinates.

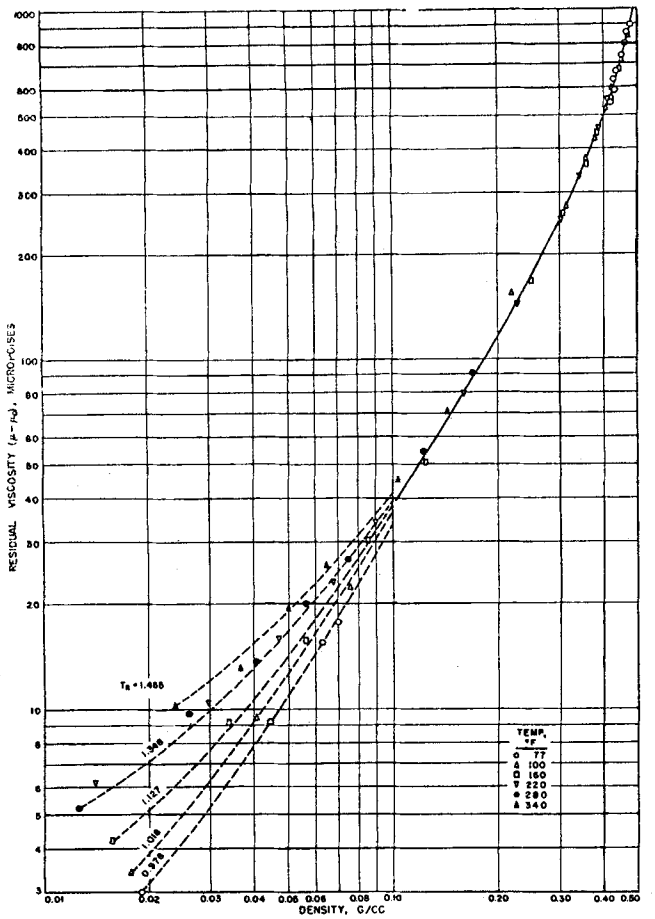

Fig. 2. Residual ethane viscosity vs. density-logarithmic coordinates.

the calculated standard deviation were omitted in the final calculations.

The complete results are too extensive to reproduce here. The standard deviations for the data are 2.47, 3.55, and 3.62% for ethane, propane, and *n*-butane, respectively, for Equation (8), and 1.89, 3.10, and 3.46% for Equation (11). Although these semitheoretical expressions represent behavior quite well, the standard deviations are greater than the uncertainty of the data, which is approximately ½%. To obtain a better description of the observed behavior further empirical studies were carried out.

EXPRESSIONS FROM OBSERVED BEHAVIOR

Many expressions have been derived for dense fluid viscosity from analyses of observed behavior. The forms of the expressions are greatly dependent on the compositions of the fluids studied and the range of the available experimental data. Three expressions with apparent potential were derived in this work from analyses of experimental viscosity data for ethane, propane, and *n*-butane and the analysis in the preceding section. The first expression, which resembles a known theoretical form was obtained from analysis of the dependence of the quantity $(\mu - \mu_o)$, known as *residual viscosity*, as a function of density and temperature. The second, which is entirely empirical, was derived through an analysis of the behavior of isotherms of viscosity as a function of density. The third was obtained by a modification of the second expression. The dependence of residual viscosity on density has recently been utilized extensively for viscosity data correlations (7, 9, 23, 24). For many fluids, when $(\mu - \mu_o)$ is plotted vs. density, one continuous curve results, Figure 1. Eakin and Ellington (8) represented the viscosity of light hydrocarbons relatively accurately by treatment of $(\mu - \mu_o)$ as a function of density only for densities between one half and twice the critical density. For densities less than about one half the critical density there is separation of the data into distinct isotherms, when the residual viscosity-density plot is on logarithmic coordinates, Figure 2. In the present analysis attempts were made to account for the observed temperature dependence.

The starting point for this analysis was the residual viscosity-density plot presented in Figure 2. It can be determined that the slope of the single curve for densities greater than 0.10 g./cc. is approximately five-thirds. Thus the residual viscosity of ethane is approximately proportional to density to the five-thirds power for a considerable range of density. A simple method of accounting for the low-density separation is suggested by the behavior predicted by the Enskog series. Because this analysis is essentially empirical a truncated series of only two terms with one empirical parameter was used. Finally it can be determined from Figure 2 that for densities greater than approximately 0.30 g./cc. the residual viscosity of ethane increases very rapidly with density. To describe the behavior for the full range of density the expression

$$\mu = \mu_o (1 + K_5\rho) + K_6\rho^{5/3} F(T, \rho, K_7) \qquad (12)$$

would seem to have possibility. The following forms for $F(T, \rho, K_7)$ were investigated:

$$F = \exp\left[\frac{K_7\rho^2}{T}\right] \qquad (13)$$

$$F = \exp\left[K_7\rho^2\right] \qquad (14)$$

$$F = T^{1/2} \exp\left[\frac{K_7\rho^2}{T}\right] \qquad (15)$$

The first form is essentially that investigated previously [Equation (8)]. From graphical studies it was determined that the second two forms should describe ethane viscosity behavior with about the same accuracy. However because the expression of Davis et al. (6) for μ_Φ for a fluid rigid spheres with a square-well attraction contains

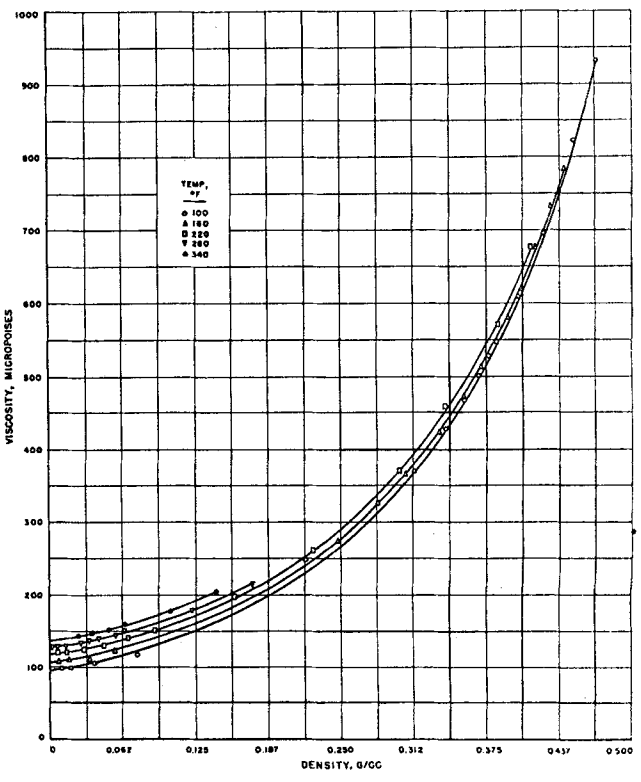

Fig. 3. Experimental ethane viscosity vs. density.

$T^{1/2}$ as a factor, the third form for $F(T, \rho, K_7)$ was investigated more carefully.

Estimates of parameters K_5, K_6, and K_7 were calculated with the least-square method mentioned previously (*22*). The calculated standard deviations of the ethane, propane, and *n*-butane data are 0.93, 1.92, and 2.56%, respectively. These are smaller than for Equations (8) and (11) and are very near the values obtained by Eakin and Ellington (*8*). It is evident however that the expression is not adequate for describing *n*-butane viscosity behavior.

Because further study of residual viscosity seemed of little value, a wholly new approach based on the behavior of isotherms of viscosity as a function of density was then initiated. For many fluids the behavior of viscosity as a function of density is similar to that of ethane, Figure 3. An equation of the form

$$\mu = \mu_o \left[1 + \sum_{j=1}^{n} a_j (T)\, \rho^j \right] \qquad (16)$$

would describe this behavior. Although the functions $a_j(T)$ could, in principle, be determined empirically, the number of data which would be required to do so would be prohibitive. However if it were assumed that the bracketed factor in Equation (16) can be replaced by an exponential function, the resultant expression can be written in the form

$$\mu = \mu_o \exp [G(T, \rho)] \qquad (17)$$

It might not be apparent that the complexity of the problem is reduced by the introduction of this expression because the determination of the most appropriate form for $G(T, \rho)$ could prove difficult. However a reasonable form was obtained by a relatively simple analysis.

If it is assumed that $G(T, \rho)$ can be expressed as the product $G_1(T)G_2(\rho)$, Equation (17) becomes

$$\mu = \mu_o \exp [G_1(T)G_2(\rho)] \qquad (18)$$

Upon application of the approximation $\exp [G] = 1 + G$ an approximation of Equation (18) can be written as

$$(\mu - \mu_o) = \mu_o G_1(T)G(\rho) \qquad (19)$$

Because $(\mu - \mu_o)$ is nearly independent of temperature, it follows that the product $\mu_o G_1(T)$ is a slowly varying function of temperature. Furthermore, because $(\mu - \mu_o)$ is roughly proportional to density to the five-thirds power, it follows that $G_2(\rho)$ is an exponential function of density. Expressing Equation (18) in logarithmic form one obtains

$$\ln \mu = \ln \mu_o + G_1(T)G_2(\rho) \qquad (20)$$

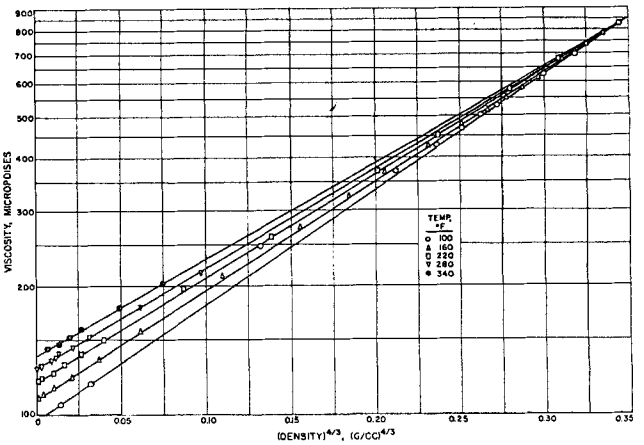

Fig. 4. Experimental ethane viscosity vs. density to the four-thirds power-semilogarithmic coordinates.

and a plot of ln μ vs. density to the proper power would yield a family of straight lines with slopes $G_1(T)$ and intercepts ln μ_o. These results were obtained for ethane when ln μ was plotted vs. $\rho^{4/3}$, Figure 4. For the temperature range of the ethane data it was determined from Figure 4 that $G_2(T)$ can be represented by either a linear function of temperature or a linear function of reciprocal temperature. Equation (18) therefore becomes

$$\mu = \mu_o \exp [(K_8 + K_9 T^{-1})\rho^{4/3}] \qquad (21)$$

To first order in $\rho^{4/3}$ this expression resembles one developed by Predvoditelev (*17*). The results of the least-square analysis for Equation (21) are summarized in Table 1. Besides the experimental data for ethane, propane, and *n*-butane selected data for methane (*5*), isobutane (*21*), ethylene (*5*), nitrogen (*16*), and carbon dioxide (*15*) were used in these calculations. Titani's (*25*) atmospheric pressure data were used to determine μ_o values for isobutane and ethylene; the values recommended by Licht and Stechert (*14*) were used for methane, nitrogen, and carbon dioxide.

A point-by-point analysis of the deviations obtained from Equation (21) suggested that Equation (17) might be written better in the form

$$\mu = \mu_o \exp [X(T)\rho^{Y(T)}] \qquad (22)$$

Values for $X(T)$ and $Y(T)$ were calculated for the isotherms of the ethane, propane, and *n*-butane data by the

TABLE 1. LEAST-SQUARE RESULTS FOR EQUATION (21)

	Ethane	Propane	*n*-Butane	Methane	Isobutane	Ethylene	Nitrogen	Carbon dioxide
K_8, (g./cc.)$^{-4/3}$	3.1886	3.3987	3.1805	5.5734	2.2445	3.0971	1.0129	0.9457
K_9, °R. (g./cc.)$^{-4/3}$	1668.6	1604.5	1764.0	179.1	2328.9	1785.1	623.0	624.3
σ data, %	1.01	1.36	2.08	2.24	1.96	3.08	1.78	2.05

TABLE 2. LEAST-SQUARE RESULTS FOR EQUATION (22)*

	Ethane	Propane	*n*-Butane	Methane	Isobutane	Ethylene	Nitrogen
K_{10}, (g./cc.)$^{-Y}$	2.8430	1.7755	3.0275	1.5904	—3.9449	0.5345	1.5794
K_{11}, °R. (g./cc.)$^{-Y}$	1797.6	2743.3	2172.4	2027.2	5448.0	2427.3	446.8
K_{12}, dimensionless	1.2717	0.7966	0.9226	0.8207	0.2878	1.0571	2.2047
K_{13}, (g./cc.)^{Y}	0.0066	0.0943	0.0830	0.0799	0.1509	0.0233	—0.3099
σ data, %	0.87	1.19	0.97	1.57	1.06	1.76	0.72

* $Y = K_{12} + K_{13}(K_{10} + K_{11}T^{-1})$.

least-square method. From plots of $X(T)$ and $Y(T)$ vs. temperature and reciprocal temperature it was determined that both $X(T)$ and $Y(T)$ can be represented as linear in T or T^{-1} and therefore that $Y(T)$ can be represented as a linear function of $X(T)$. The expression for dense fluid viscosity which results from these considerations is given by Equation (22) with the additional relationships

$$X(T) = K_{10} + K_{11}\,T^{-1} \tag{23}$$

and

$$Y(T) = K_{12} + K_{13}\,X(T) \tag{24}$$

The least-squares method was then used to calculate K_{10} through K_{13} simultaneously for each of the fluids used in the study of Equation (21), except carbon dioxide, for which the iterative method did not converge. The results are given in Table 2. No further modifications of Equation (17) were made because the calculated standard deviations approach the uncertainty of the data for most of the fluids.

Further analyses are in progress. These are directed toward generalized descriptions of pure material and mixture behavior. In the first attempt to describe pure material behavior with universal parameters the viscosity of methane, ethane, propane, and *n*-butane was treated as dependent upon molecular weight. It was found that the form

$$\mu = \mu_o \exp\left[X(T, M)\,\rho^{Y(T,M)}\right] \tag{25}$$

where

$$X(T, M) = K_{14} + K_{15}\,T^{-1} + K_{16}\,(M)^{K_{17}}$$

and

$$Y(T, M) = K_{18} + K_{19}\,X(T, M)$$

is capable of describing the viscosity of this series within 1.7%. A single set of parameters, K_{14} through K_{19}, was calculated by fitting the four sets of data simultaneously. Experimental data for methane-*n*-butane mixtures which are presently being obtained have also been described by Equation (25). A single set of the parameters describes the data for methane, *n*-butane, and five mixtures within 2.5%. These calculations have suggested improved relations, which will be studied. In the interim however the authors recommended that Equation (25) be used by others investigating the utility of this type of relationship.

ACKNOWLEDGMENT

This work is part of a continuing investigation under The Institute of Gas Technology's Basic Research Program and was supported in part by funds from The Institute of Gas Technology's Members and Contributors and in part by the American Petroleum Institute under Project 65.

The authors wish to thank Messrs. J. P. Dolan, A. L. Lee, and R. D. Shaw, and Drs. B. E. Eakin, D. M. Magasanik, and S. A. Weil for their help in various aspects of this work.

NOTATION

a_j = constants in Enskog series
$a_j(T)$ = function of temperature
b = molecular covolume
$F(\,)$ = function
$G(\,)$ = empirical function
j = summation subscript
K_m = empirical constant, $m = 1, \ldots 19$
k = Boltzmann's constant
M = molecular weight
N = Avogadro number
n = molecular number density
r = intermolecular distance
T = absolute temperature
w = constant
$X(\,)$ = empirical function
Y = probability of collision factor
$Y(\,)$ = empirical function

Greek Letters

γ = constant
μ = coefficient of viscosity
μ_o = dilute gas viscosity
μ_K = viscosity contribution due to motion of molecules between collisions
μ_Φ = viscosity contribution due to action of intermolecular forces
π = the constant
ρ = mass density
σ = diameter of rigid sphere molecule parameter in Lennard-Jones potential function
σ_i = standard deviation for quantity i
$\phi(r)$ = potential function
ϕ_A = attractive part of potential function
Σ = summation sign

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Manuscript received January 28, 1963; revision received June 27, 1963; paper accepted June 27, 1963. Paper presented at A.I.Ch.E. New Orleans meeting.