## LITERATURE CITED

1. Edwards, Charles L., Ph.D. thesis, University of Wisconsin, Madison, Wisconsin (1958).
2. Gilliland E. R., L. A. Gould, and I. H. Rinard, "A Series Method for the Analysis of Plug Flow Process Dynamics, Part I," Mass. Inst. Technol., Cambridge, Massachusetts (1961).
3. Hempel, Arvid, *Trans. Am. Soc. Mech. Engrs.*, 82, 244-251 (1961).
4. Koppel, Lowell B., *Ind. Eng. Chem. Fund.*, 1, No. 2, pp. 131-134 (1962).
5. Mozley, J. M., *Ind. Eng. Chem.*, 48, 1035-1041 (1956).
6. Stermole, F. J., Ph.D. thesis, Iowa State University, Ames, Iowa (1963).
7. ———, and M. A. Larson, *Ind. Eng. Chem. Fund.*, 2, 62-67 (1963).

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# Viscosity Correlation for Light Hydrocarbon Systems

**A. L. LEE, K. E. STARLING, J. P. DOLAN, and R. T. ELLINGTON**

**Institute of Gas Technology, Chicago, Illinois**

The needs of modern fluid processing and transmission and reservoir engineering for better information on fluid properties are well known. The authors and their associates have engaged in a series of studies to help meet these needs regarding data and prediction of hydrocarbon viscosities. These have included obtaining data on pure materials (*1, 2, 3, 4*) and mixtures (*5*) and efforts to use developments in modern molecular theory of fluids to obtain relationships for representing viscosity behavior (*6, 7*).

A semiempirical equation was quantitatively derived which represented the data on methane, ethane, propane, and *n*-butane including the continuity of states exhibited by the data. This paper reports the results of initial efforts to represent the viscosity behavior of binary light hydrocarbon mixtures.

## EXPERIMENTAL

All the data cited above were obtained with the same absolute capillary tube viscometer. The data obtained with it have proved to be internally consistent and to agree well with those of other investigations. The instrument and its operation have been described in detail elsewhere (*5, 8*); its operating range is from ambient temprature to 400°F. and atmospheric pressure to 8,000 lb./sq. in. abs.

The primary data analyzed in this investigation are the methane data of Comings et al. (*9*), the ethane, propane, and *n*-butane data of Institute of Gas Technology (*1, 2, 4*), and the methane-*n*-butane binary mixture data of Dolan, Ellington, and Lee (*5*).

## THEORY AND PREVIOUS WORK

The viscosity fields of ethane, propane, and *n*-butane were determined experimentally with sufficient detail that extensive correlative efforts were justified. The primary objective of these efforts was to achieve predictability of values of the same order of accuracy as the data (average error felt to be less than 0.5%) and to achieve the continuity of states exhibited by the data for the single-phase regions.

The modern theories of the general fluid indicate that the coefficient of viscosity should be expressed as the sum of two terms (*6, 7*)

$$\mu = \mu_K + \mu_\phi \qquad (1)$$

The terms $\mu_K$ and $\mu_\phi$ 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.

Both the kinetic and intermolecular force contribution to viscosity are a function of temperature $T$ and density $\rho$. In the dilute gas limit, where the only contribution to viscosity is by the thermal motion of the molecules, $\mu_K$ is a function of temperature only, and $\mu_\phi$ vanishes. Thus the following conditions must be satisfied:

$$\lim_{\rho \to 0} \mu_K (T, \rho) = \mu_o (T) \qquad (2)$$

$$\lim_{\rho \to 0} \mu_\phi (T, \rho) = 0 \qquad (3)$$

Accurate expressions for $\mu_K$ and $\mu_\phi$ for high density have not been developed. However because $\mu_K$ does not differ greatly from $\mu_o$ even for moderate densities, it usually may be replaced by $\mu_o$ in Equation (1) for semiempirical analysis.

Starling and Ellington (*7*) developed several semiempirical equations, based in varying degrees on the theory of viscosity due to Born and Green (*10*). The correlation presented here is derived from their final equation. The following expression for viscosity

$$\mu = \mu_o + K_1 \rho^{5/3} \exp \left[ \frac{K_2}{T} \rho^2 \right] \qquad (4)$$

which Starling and Ellington derived directly from the Born and Green theory is presented here. For theoretical

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K. E. Starling is with Humble Oil Company, Houston, Texas. R. T. Ellington is with Sinclair Research, Inc., Tulsa, Oklahoma.

calculations the constants $K_1$ and $K_2$ may be calculated from the intermolecular potential parameters of the fliud under consideration. Since the Born and Green theory of viscosity is not exact, these constants can also be treated as empirical parameters in semiempirical studies. Expansion of the exponential function in Equation (4) yields

$$\mu = \mu_o \left[ 1 + \left( \frac{K_1}{\mu_o} \right) \rho^{5/3} + \left( \frac{K_1 K_2}{\mu_o T} \right) \rho^{11/3} + \frac{K_1 K_2^2}{2\mu_o T} \rho^{17/3} + \ldots \right] \tag{5}$$

For the data studied by Starling and Ellington, $K_2/T$ is of the same order as $K_1/\mu_o$, so that Equation (5) may be approximated by

$$\mu = \mu_o \exp \left[ \frac{K_1}{\mu_o} \rho^{5/3} \right] \tag{6}$$

Obviously, for sufficiently low densities, Equation (6) approximated Equation (5) regardless of the value of $K_2/T$; therefore Equation (6) may be taken as a limiting form of Equation (4).

Equation (6) is the final semiempirical expression reported by Starling and Ellington except that the empirical parameters determined from the experimental data were used in place of $K_1/\mu_o$ and the exponent 5/3. Their final equation is

$$\mu = \mu_o \exp \left[ X(T) \, \rho^{Y(T)} \right] \tag{7}$$

where

$$X(T) = C_1 + C_2/T \tag{8}$$

$$Y(T) = C_3 + C_4 X(T) \tag{9}$$

Further analysis of the results reported by Starling and Ellington indicate that $X(T)$ is generally somewhat smaller than $K_1/\mu_o$ and $Y(T)$ is generally between 4/3 and 5/3. Although Equation (7) is to be treated simply as an empirical equation, its form is not wholly without theoretical significance.

With parameters calculated by the method of least squares, Equation (7) represents the viscosity behavior of ethane, propane, and *n*-butane, with calculated Standard deviations* for the experimental data of 0.87, 1.19, and 0.97%, respectively. It also represents other data sets with the following standard deviations: methane, 2.24%; *i*-butane, 1.96%; ethylene, 3.08%; nitrogen, 1.78%; and carbon dioxide, 2.05%. Plots of the values of $X(T)$ and $Y(T)$ vs. molecular weight indicated the possibility of a rather simple mixing rule for using the equation to represent mixtures.

The results achieved with Equation (7) naturally led to an effort to fit it to mixtures. Little progress could be made in this direction because of the paucity of detailed data on mixtures in the literature and the possibility that those which existed were not internally consistent with the pure component data. Because of this, extensive experimental data were obtained by Dolan, Ellington, and Lee. Methane-*n*-butane mixtures with nominal methane contents of 25, 50, 70, and 90 mole % (5) were studied. It was found that the residual viscosity-density plot would rectify the data for reach mixture in the same way as for a pure component, but that the curves for different mixtures intersected and exhibited no specific composition trends. A new type of plot was developed in which the composition trend was displayed regularly; this was obtained by plotting residual viscosity vs. density in grams-mole per cubic centimeters.

TABLE 1. EQUATION (11) PARAMETERS

| Constant | Value |
|---|---|
| $A_1$ | 7.77 |
| $A_2$ | 0.0063 |
| $A_3$ | 122.4 |
| $A_4$ | 12.9 |
| $A_5$ | 2.57 |
| $A_6$ | 1914.5 |
| $A_7$ | 0.0095 |
| $A_8$ | 1.11 |
| $A_9$ | 0.04 |

## CORRELATION FOR MIXTURES

The availability of the mixture data and the regular behavior exhibited in the residual viscosity-molar density plots led to further efforts to apply Equation (7). Equation (7) was fitted to the data for each mixture and the values $X(T)$ and $Y(T)$ plotted vs. mixture molecular weight. On the basis of these plots $X(T)$ was modified to include a molecular weight term which was calculated by use of a simple linear mixing rule; that is

$$X(T) = C_1 + \frac{C_2}{T} + C_6 M^{C_7} \tag{10}$$

With this modification Equation (7) was fitted to the pure component data on methane through *n*-butane simultaneously with a standard deviation of 1.7%.

Examination of Equation (7) shows that a plot of logarithm of viscosity vs. density to the proper power should rectify the data for each isotherm on a given test fluid into a straight line. The zero-density intercepts of these lines represent dilute-gas $\mu_o$ values. They should, and do, obey Sutherland's equation.* With these facts of behavior in mind it was felt that Equation (7) could be further generalized by inserting Sutherland's equation for $\mu_o$. Previous work by B. E. Eakin showed that a simple mixing rule could be applied to the pure component Sutherland constants to obtain the Sutherland constants for mixtures. In further work by the authors it was found that the Sutherland constants could be represented as functions of molecular weight and that a simple mixing rule could be applied to the terms of Equation (7). The equation was then rewritten in the form

$$\mu = K(T, M) \exp X(T, M) \, \rho^{Y(T, M)} \tag{11}$$

where

$$K(T, M) = \frac{(A_1 + A_2 M^q) \, T^{1.5}}{A_3 + A_4 M^r + T} \tag{12}$$

$$X(T, M) = A_5 + \frac{A_6}{T} + A_7 M^p \tag{13}$$

$$Y(T, M) = A_8 + A_9 X(T, M) \tag{14}$$

$$P, q, r = 1.0 \text{ in this analysis} \tag{15}$$

This equation was fitted to the data on methane, ethane, propane, and *n*-butane simultaneously with a standard deviation of 1.34%. It was fitted to these data plus the data on the four methane-*n*-butane mixtures simultaneously with a standard deviation of 1.89%. The density values reported by Sage and Lacey (*11*) were used in these calculations.

The nine constants which were determined from the experimental data on methane, ethane, propane, *n*-butane, and four methane-*n*-butane mixtures simultaneously are presented in Table 1.

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* Formula for calculation of standard deviation;

$$\sigma = \left[ \frac{1}{n - m} \sum_{i-1}^{n} \left( \frac{\mu_E (T_i, \rho_i) - \mu_c (T_i, \rho_i)}{\mu_E (T_i, \rho_i)} \right)^2 \right]^{1/2}$$

* Sutherland's equation: $\mu_o = \dfrac{BT^{1.5}}{T + S}$.

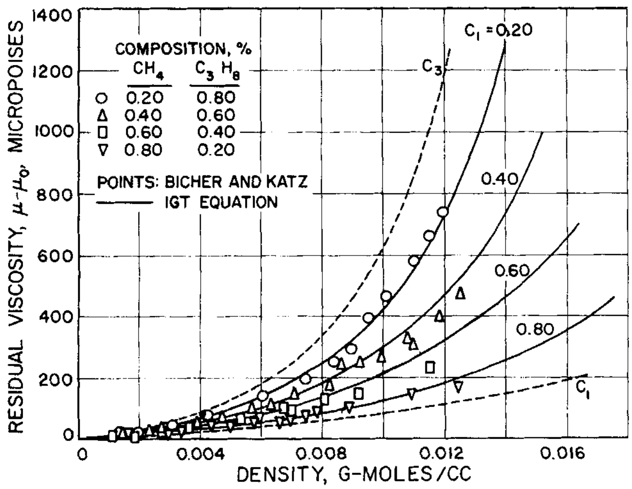

Fig. 1. Viscosity of methane-propane mixtures, comparison of experimental data by Bicher and Katz with values predicted by authors' equation.

In order to determine whether Equation (11) might have general applicability, viscosity values for 20 mole % methane, 40% methane, 60% methane, and 80% methane in a methane-propane mixture were calculated by use of these nine constants. The results were compared with the data reported by Bicher and Katz (*12*) and are shown in Figure 1. As can be seen from this figure the deviation ranged from 0 to as high as 20%.

This deviation was not regarded as serious however because some of the values obtained by Bicher and Katz for the viscosity of pure materials with the rolling ball viscometer differed as much as 20% from those of other investigators (*13*).

Recently Giddings (*14*) reported data on methane-propane mixtures, which were obtained by use of a capillary tube viscometer. These data are compared with values calculated for regular composition intervals by use of the authors' equation in Figure 2, which gives overall representation of methane-propane mixtures as residual viscosity vs. molar density. The viscosity values predicted by the authors' equation are for 20, 40, 60, and 80 mole % methane and are shown as solid lines. The viscosity values reported by Giddings are for 22.07, 38.78, 61.39, and 70.10 mole % methane and are shown as points. In comparing two methane-propane mixtures on a residual plot the mixture richer in propane should have a higher viscosity for the same density. Therefore the 79.10% methane curve should be closer to the pure propane curve than the 80% methane curve, which is the case. The plot shows that there is very close correspondence between the trends of the experimental and calculated values for all compositions, except that the values for the 22.07% methane mixture fall in the wrong position relative to the 20% methane data.

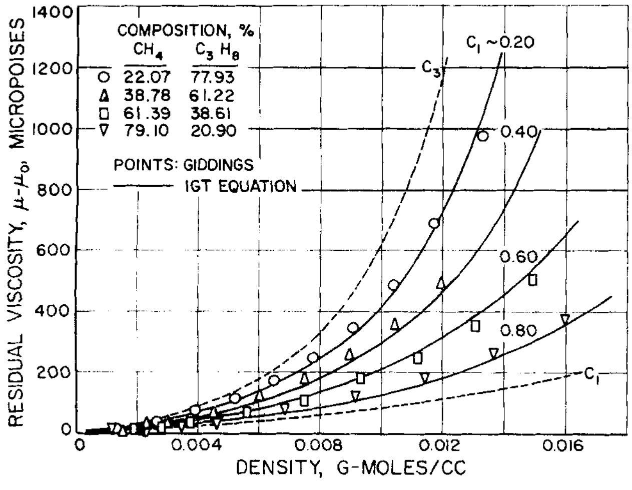

Fig. 2 Viscosity of methane-propane mixtures, comparison of experimental data by Giddings with values predicted by authors' equation.

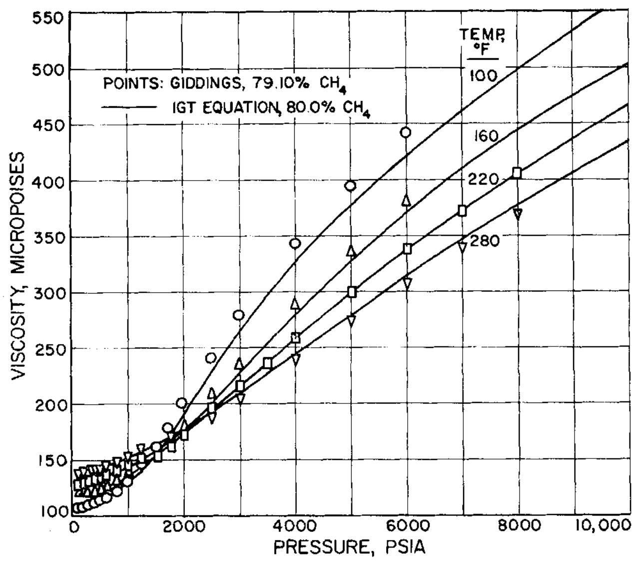

Fig. 3. Comparison of predicted and experimental viscosities for a 80 mole % methane—20 mole % propane mixture.

To show how well the behavior of a given mixture was predicted the values for the 80% methane mixture are plotted in Figure 3. From this it can be seen that the fit is good for all temperatures and pressures except for 100°F. at high pressures, where the deviation is about 4%. It was found that the viscosity values obtained by use of Equation (11) are closer to the experimental data for the low-density region than for the high-density region in all cases. This occurs because the nine constants in Equation (11) were determined from experimental data in which the major portion were in the low-density region.

The test on other data systems were sufficiently encouraging that it was felt that detailed analysis of the methane-*n*-butane system was in order. The results of these tests are presented in a residual plot in Figure 4 and as viscosity vs. pressure with temperature as parameter for some of the pure components and mixtures in Figures 5 and 6. As

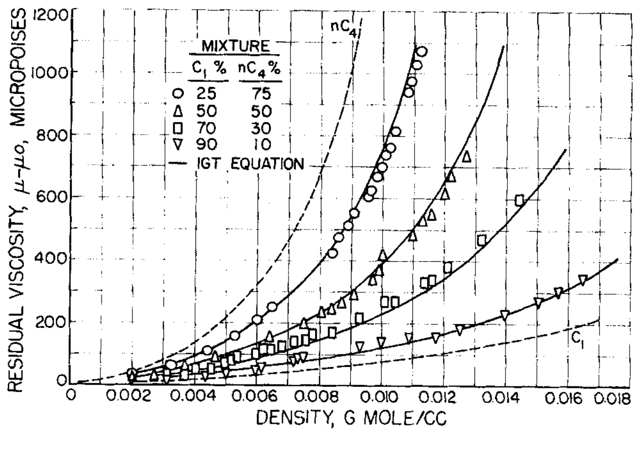

Fig. 4. Viscosity of methane-*n*-butane mixtures, comparison of experimental data by IGT with values predicted by authors' equation.

can be seen from these figures the agreement is good in the high-temperature region, that is the low-density region, and the deviation increases as the density of the system increases.

It should be noted that the residual viscosity plots have been presented in terms of molar density (Figures 1, 2, 3, and 4), while mass densities are used in Equation (11). Use of mass density in the residual viscosity plots results in intersection of the curves in the low-density region; use of molar density gives a much clearer presentation. Mass densities were used in the analytical work in anticipation of the need for this basis for very complex naturally occurring systems. Parallel work on the use of molar density values is being carried out for its instructional value.

## SUMMARY

It has been found that Equation (11) with the recommended constants can be used to represent the behavior of methane, ethane, propane, and *n*-butane with a standard deviation of 1.3% for the range of experimental data presently available. By use of a linear molecular weight mixing rule the equation is satisfactory for representing the data for methane-propane and methane-*n*-butane mixtures.

The authors feel that Equation (11) will also represent the behavior of other binary mixtures of these components within 5%, provided accurate density values are known.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = empirical constant
$B$ = Sutherland constant
$C$ = empirical constant
$K$ = empirical constant
$m$ = number of parameters occurring in the empirical equation
$M$ = molecular weight
$n$ = number of experimental data points
$P$ = weighting constant
$Q$ = weighting constant
$R$ = weighting constant
$S$ = Sutherland constant
$T$ = absolute temperature, °R.
$\mu$ = viscosity, $\mu$
$\rho$ = density, g./cc.
$\sigma$ = standard deviation

### Subscripts

$c$ = calculated
$E$ = experimental
$i$ = index for component
$K$ = kinetic
$o$ = dilute gas phase
$\phi$ = intermolecular force

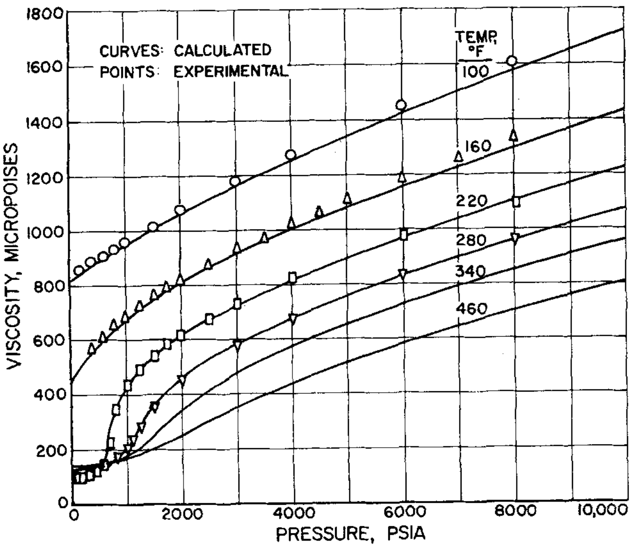

Fig. 5. Comparison of viscosity values for propane with authors' equation.

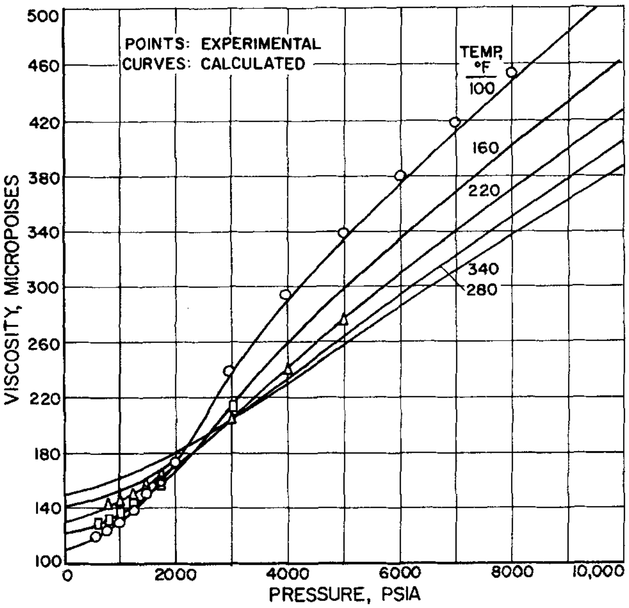

Fig. 6. Comparison of viscosity values for a 90 mole % methane—10 mole % *n*-butane mixture with authors' equation.

## LITERATURE CITED

1. Dolan, J. P., K. E. Starling, A. L. Lee, B. E. Eakin, and R. T. Ellington, *J. Chem. and Eng. Data,* **8**, 369-399 (1963).
2. Eakin, B. E., K. E. Starling, J. P. Dolan, and R. T. Ellington, *ibid.*, **7**, 33-36 (1962).
3. ———, "Progress in International Research on Thermodynamic and Transport Properties," pp. 530-40, Academic Press, New York (1962).
4. Starling, K. E., B. E. Eakin, and R. T. Ellington, *A.I.Ch.E. Journal,* **6**, 438-42 (September, 1960).
5. Dolan, J. P., R. T. Ellington and A. L. Lee, *J. Chem. and Eng. Data,* to be published.
6. Starling, K. E., Ph.D. dissertation, Illinois Institute of Technology, Chicago, Illinois (1962).
7. ———, and R. T. Ellington, *A.I.Ch.E. Journal,* **10**, 11-15 (1964).
8. Eakin, B. E., and R. T. Ellington, *Petrol. Trans. (AIME),* **216**, 85-91 (1959).
9. Comings, E. W., and B. J. Mayland, *Chem. and Met. Eng.,* **52**, 115-16 (1945).
10. Born, M., and H. S. Green, *Proc. Roy. Soc.,* **A190**, 455-74 (1947).
11. Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of The Lighter Paraffin Hydrocarbons and Nitrogen," American Petroleum Institute, New York (1950).
12. Bicher, L. B., and D. L. Katz, *Ind. Eng. Chem.,* **35**, 754-61 (1943).
13. Carr N. L., *Institute of Gas Technology Research Bulletin No. 23* (June, 1953).
14. Giddings, J. G., Ph.D. dissertation, Rice University, Houston, Texas (1963).

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