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Predicting the Viscosity of Pure Light Hydrocarbons

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ABSTRACT

The following equation, which describes the viscosity of methane, ethane, propane and n-butane in the vapor, liquid and dense-fluid regions for densities up to 2.4 times the critical density, is presented.

$$\mu = \mu_{g,a} + A(e^{7.237\rho} - e^{-45.9\rho^2})$$

where $A = 32.80 - 0.1637(M)$, micropoises,

$\mu_{g,a}$ = gas viscosity at atmospheric pressure and the fluid temperature, micropoises,

ρ = density of the fluid, gm/cc, and

M = molecular weight

The atmospheric-pressure viscosity can be represented satisfactorily by Sutherland's equation for which values of the necessary constants are given. The equation represents the data on these materials over the entire region with a standard deviation of 1.6 per cent for 288 points. Except in the immediate vicinity of the critical density, the largest difference between predicted and observed viscosity was 4.3 per cent. To facilitate calculations, the equation is presented as a single curve of $\mu - \mu_{g,a}$ evaluated for a gas of zero molecular weight. By modification of the co-ordinates, the curve becomes a straight line. The factor for converting the curve value of $\mu - \mu_{g,a}$ to that for the actual gas is a linear function of molecular weight, and is also plotted.

INTRODUCTION

The pressures at which fluids are produced, transferred and processed have increased steadily in the petroleum and chemical industries. This has resulted in increased interest in the effect of pressure on the thermodynamic and transport properties of fluids. The relationships derived from simple kinetic theory often may be applied in estimating gas properties for low and moderate pressures. These have the advantage of simplicity, a fact which has frequently led to use beyond the range of proper applicability. At high pressures and low temperatures, these relationships may be greatly in error, and other means of calculation are needed for the dense gas and liquid regions.

The thermodynamic properties of fluids have been studied extensively, both theoretically and experimentally. The volumetric behavior of a large number of fluids has been measured experimentally to high pressures for wide ranges of temperature. It is more difficult, however, to obtain accurate experimental values for transport properties, and detailed data have been obtained for very few fluids for extensive ranges of temperature and pressure. This situation has greatly handicapped correlation efforts.

Because of the limited data available on transport properties and the complex relationships which exist between the transport and thermodynamic properties, generally one of three methods has been applied to represent these properties for pure fluids.

1. Tabulations of each transport property at selected pressure and temperature intervals.

2. Equations for each transport property of each fluid which relate these properties to PVT behavior.

3. Generalized co-ordinate chart for each transport property, frequently with serious restrictions as to accuracy.

The methods are listed in order of decreasing accuracy. The first and second methods are limited to pure components and certain commonly occurring mixtures such as air for conditions other than atmospheric pressure. Equations have been developed from kinetic theory which quite accurately represent the temperature dependence of viscosity of gases²¹ and liquids²⁴ at low pressures. Special equations have been developed to calculate the effects of pressure and temperature on viscosity of steam^{17,19} and nitrogen,¹⁷ but these equations are empirical and different for each fluid. No single equation is presently available for accurate prediction of viscosity in both the liquid and gas phases, for any fluid.

The third method is based on van der Waals' theory³⁶ of corresponding states. Uyehara and Watson³⁵ presented a plot of T_r vs μ_r with lines of constant p_r , which is generally accurate within 10 per cent, but in the critical region errors may be as large as 30 per cent. Carr⁷ and Comings, Mayland and Egly⁹ used p_r , T_r and $\mu/\mu_{g,a}$ as parameters and developed generalized correlations for gases, and Carr extended his to include mixtures. For natural gases Carr's chart is generally accurate within ± 3 per cent, but is less accurate for heavier hydrocarbons or other gases.

The purpose of this study was to examine the viscosity-pressure-temperature data on the light hydrocarbons in their liquid, gas and dense-fluid regions, and to develop an equation which relates viscosity to the state properties. The form of the equation should be such that it will approach the kinetic-theory relationships for temperature dependence of viscosity for gases at low pressures, and for liquids at high densities.

BACKGROUND

Most efforts at development of general relationships for prediction of fluid viscosities are based on equating the expression for momentum transfer per unit area, or shear force, developed by use of a molecular model to the defining equation for a continuous Newtonian fluid. The devel-

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²¹References given at end of paper.

opment based on the simple kinetic-theory model yields the expression for gases,

$$\mu = 2.715 \times 10^{-12} \sqrt{MT}/\sigma^2 \quad (1)$$

For real gases, the viscosity increases more rapidly with increasing temperature. The Sutherland²¹ model for simple repulsive force yields

$$\mu = BT^{3/2}/(T + S), \quad (2)$$

which has been found to fit a great deal of the data for gases at atmospheric pressure.²¹

TEMPERATURE DEPENDENCE OF LIQUID VISCOSITY

The viscosity of a liquid is due primarily to drag caused by attractive forces between molecules in adjacent fluid layers. Since the influence of intermolecular forces decreases with increasing distance between molecules, and the density of liquids decreases with increasing temperature, liquid viscosity should also decrease with increasing temperatures.

Over 70 empirical formulas have been proposed to represent the temperature dependence of liquid viscosity.²⁴ In 1866, Reynolds²⁵ proposed

$$\mu = A e^{B/T} \quad (3)$$

Eyring,¹⁶ Andrade² and Frenkel¹⁵ have derived similar expressions based on the kinetic theory of liquids, each arriving at different sets of parameters involved in the constants *A* and *B*. Eq. 3 has been found to represent the temperature behavior of some types of liquids (including some of the hydrocarbons), with a high degree of accuracy, and to give very poor results with other types.

PRESSURE DEPENDENCE OF VISCOSITY

According to Eq. 1, the viscosity of a gas is independent of pressure or density; this is generally true for gases at pressures below 100 psia. At higher pressures the viscosity increases with increasing density, as in Fig. 1, which shows the effect of both temperature and pressure on the viscosity of ethane. Enskog^{8,14} was the first to study the effect of density on viscosity, and his equations included two factors neglected in simple kinetic theory: (1) the transport of momentum on collision, and (2) a correction for the effect of the actual volume of the molecules on the probability of collisions.

The forms of equations for gas viscosity at high pressures fall into two groups:

$$\mu = \mu_{g,a}(f(\rho)) \quad (4)$$

or

$$\mu = \mu_{g,a} + g(\rho) \quad (5)$$

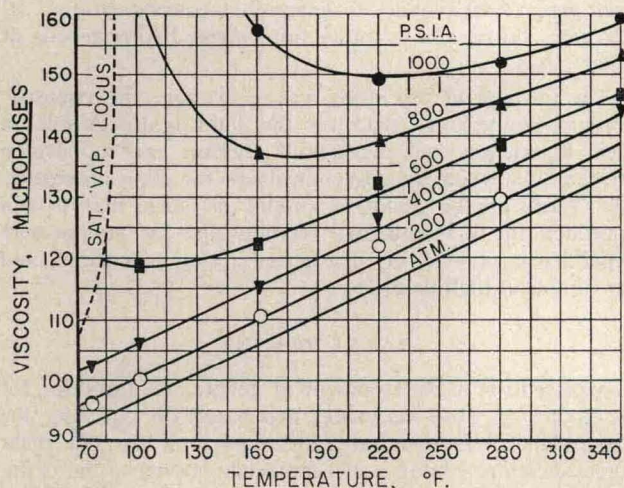


FIG. 1--EXPERIMENTAL ETHANE VISCOSITY VS TEMPERATURE AT LOW PRESSURE.

The theoretical equation of Enskog⁸ and the empirical equations of Jager²² and Dubief²³ are of the form of Eq. 4. The empirical equations of Vargaftik,²⁷ Jossi, Stiel and Thodos,¹⁸ and the new relationship presented here, are the form of Eq. 5.

The viscosity of all liquids except water increases with increasing pressure. After an initial small decrease with increasing pressure, the viscosity of water also increases with pressure. For liquefied gases, and the light hydrocarbons at pressures up to 10,000 psia, the viscosity increases almost linearly with pressure, as is shown for propane in Fig. 2. At pressures greater than 30,000 psia, Suge³⁰ and Bridgeman⁶ found that the viscosity increased almost exponentially with increasing pressure.

VISCOSITY AS THE SUM OF TWO FUNCTIONS

Recent theories of the liquid state imply that viscosity is the sum of two terms. Born and Green,⁴ Kirkwood²⁰ and Eischitz²³ have developed theoretical equations, based on molecular distribution functions, which can be written

$$\mu = G_f(T, \rho) + G_m(T, \rho) \quad (6)$$

where *G_f* = contribution due to drag-effect of intermolecular forces, and

G_m = contribution due to transport of momentum by molecular thermal motion.

These theories tend to imply also that *G_m* may depend on temperature alone. At least, when both *T* and ρ do not have large values, it can be assumed that

$$G_m(T, \rho) = G_o(T) \quad (7)$$

where *G_o*(*T*) = the low-pressure gas viscosity dependence on temperature.

Abas-Zade¹ applied this concept to prediction of thermal conductivity of fluids. Thodos and co-workers^{5,18,27} applied the concept for correlation of viscosity data. They plotted $\mu - \mu_{g,a}$ vs density for the monatomic and diatomic molecules, and demonstrated that a single smooth curve resulted for each material. Starling, Eakin and Ellington²⁰ made a similar plot for propane data (Fig. 3) and, again, a single smooth curve resulted.

On the basis of these results, it was determined that

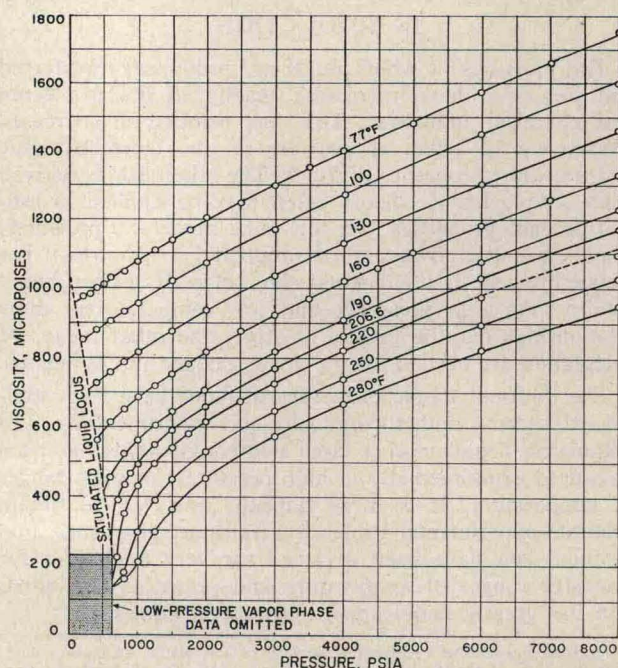


FIG. 2--EXPERIMENTAL PROPANE VISCOSITY VS PRESSURE.