Viscosity of Liquid Hydrocarbons and Their Mixtures

Hans Korsten
Mobil Technology Company, Paulsboro, NJ 08066

In the petroleum industry, the viscosity of mixtures containing thousands and millions of chemical species must be predicted over large temperature ranges. Traditional models are empirical based on bulk properties. If such models are applied to mixtures other than those for which they were developed, large errors may occur. New methods proposed calculate the viscosity of petroleum fractions over large temperature ranges, using a new mixing rule reflecting observed positive and negative mixing effects. The temperature range of equations for calculating pure component viscosity is extended to the entire liquid-phase range. If solid components are dissolved in the liquid, the viscosity increases sharply with further temperature reduction. This effect is captured in the new model by incorporating the freeze point distribution. For converting between absolute and kinematic viscosity, a new equation is proposed for the temperature effect on density.

Introduction

Viscosity is an important transport property required for hydrodynamic calculations in plant process units, such as pressure drop and flow regime prediction in pipes and reactors. Further is the viscosity, and especially its temperature dependence, a main characteristic determining the quality of lube oils. Thus, the reliable prediction of viscosity-temperature curves of mixtures as functions of composition is essential. Lube oils and other petroleum fractions consist of numerous hydrocarbon species. Because a general characterization of high boiling petroleum fractions was not available in the past, easy-to-measure bulk properties like density and average boiling point have been used to predict viscosity. This approach is empirical in nature, and the parameters obtained are based on a reference data set. For petroleum fractions of a different origin, viscosity predictions using traditional bulk property models are suspect.

In this article, two different routes for calculating viscosity curves of hydrocarbon mixtures are proposed. For traditional characterization using bulk properties, a procedure is proposed which requires at least two viscosities at two different temperatures together with the boiling point distribution in order to calculate the viscosity along a wider temperature range.

In the most advance approach, the whole fraction is analyzed in high detail and represented by characteristic components. For computer applications, these components can be represented by structure oriented lumping (Quann and Jaffe, 1992) or another group contribution method. A full analysis of all the numerous constituents of petroleum has not been achieved yet, and perhaps it will never be achieved. In general, the degree of compositional information decreases with increasing boiling range. Gas or light gasoline fractions can be completely analyzed. For heavier fractions, exact information about type and position of branches at paraffinic structures or paraffinic side chains on ring molecules is not available. In this case structure oriented pseudo components may be defined that lump together components of similar characteristics. For instance, pyrene with 3 paraffinic carbon atoms is a structure oriented pseudo component. How exactly these 3 paraffinic C-atoms are attached to the pyrene is beyond current analytical capabilities. However, the different structures within a lump can be considered to be small compared to the large number of different structures taken into account. With this type of lumping, a crude oil can be characterized by about 3,000–5,000 pseudo components.

Clearly, compositional modeling is the only viable technology in modern and future petroleum refining, because it captures the value of every molecule throughout the refining process (Katzer et al., 2000). The most important and most challenging application of high detailed lumping is its ability

---

Correspondence concerning this article should be addressed to H. Korsten at this current address: ExxonMobil Research and Engineering Company, 1545 Route 22 East, Annandale, NJ 08801.

to predict reactor performance as function of feedstock composition. Using complex reaction schemes, the product composition can be predicted; for an application to fluid catalytic cracking (FCC) see Christensen et al. (1999). However, known product composition would be worthless, if we couldn't predict all the important quality specifications like boiling range, viscosity at various temperatures, density vs. temperature, vapor pressure, phase behavior, and so on. For this type of application, structure oriented relationships and group contribution methods are very convenient for predicting pure component properties.

The models for representing viscosity as function of temperature are usually limited to certain temperature ranges. A new method for calculating the viscosity in the entire temperature range between the freezing point and the critical temperature is given in this article. This method can be combined with the group contribution method by van Velzen et al. (1972).

Many mixing rules for calculating the viscosity of simple mixtures have been proposed in the literature. The most widely used is that of Kendall and Monroe (1917). If the components within a mixture differ significantly in structure or size, the simple mixing rules do not calculate the actual mixture viscosity correctly. A new mixing rule is presented here which predicts positive and negative mixing effects, as they are observed in real systems. The interaction parameters of the model are calculated from pure-component critical data and from the slope of the viscosity curves.

Down to a certain temperature, the viscosity of pure components, defined mixtures and petroleum fractions follow the linear relationship (ln viscosity) = f(1/temperature). At and below the freezing temperature, the viscosity of a pure component increases towards infinity. In a mixture, such a component is dissolved in the liquid and increases the mixture viscosity above the value predicted by the linear relationship, but not toward infinity, because the component is in solution. It is shown in this article that the actual viscosity of mixtures can be calculated by combining the pseudo-liquid viscosity of the mixture with the freezing point distribution. The pseudo-liquid viscosity is obtained by extrapolating the linear relationship (ln viscosity) = f(1/temperature) towards low temperatures.

It is often necessary to convert from absolute viscosity to kinematic viscosity or vice versa. Thus, information about the density as a function of temperature is needed. During these investigations, it was found that the Rackett equation does not provide sufficient accuracy for viscosity interconversion, especially if applied to hydrocarbons containing more than eight carbon atoms. A new equation for calculating density as a function of temperature is proposed in this article showing good agreement with experimental data.

Viscosity of Pure Components

The kinetic gas theory represents a fundamental tool for predicting gas viscosity (Reid et al., 1987). The mobility in gases is primarily determined by the molecules in free flight, ideally without interactions, and so is viscosity. In the liquid phase, molecules travel only short distances, and interactions between colliding molecules play the most important role. These interactions are determined by the structure of the molecules and by the degree of disorder within the arrangement. Statistical mechanics represents a fundamental idea about the interactions of molecules in liquids. However, in order to be able to predict properties like viscosity, proper distribution, functions describing the intermolecular force field or the intermolecular potential energy function are needed. Those distribution functions, as, for instance, the Lennard-Jones potential function, require information about a characteristic collision diameter and a reference intermolecular potential of the molecule. This information is not available *a priori* and must be obtained by fitting experimental data. The uncertainties contained in the distribution function transform the theoretically fundamental statistical mechanical approach into a semi-empirical method, if used in practice. As pointed out by Monnery et al. (1995), viscosities calculated by statistical mechanics are usually inaccurate even for simple molecules.

The most widely used correlation for calculating the viscosity μ as function of temperature T is probably the Andrade equation (Reid et al., 1987)

$$\ln \mu = A + \frac{B}{T} \tag{1}$$

where A and B are parameters. Equation 1 can be used successfully for interpolating experimental viscosity data, as well as for extrapolation up to approximately the normal boiling point for light boiling components. The curve denoted as van Velzen et al. (1972) in Figure 1 gives an example. The representation of the viscosity data is excellent up to a temperature of about 450 K. Assuming that the dependence of viscosity on temperature is mainly determined by the value of the viscosity, Lewis and Squires (Reid et al., 1987) proposed a chart from which the viscosity at a temperature can be obtained from one single known viscosity. This is only a rough approximation and should not be applied, if the temperature of interest differs from the temperature associated with the reference viscosity by more than about 50 K (see Figure 1).

On the basis of reaction rate theory, the following model can be derived (Eyring, 1936)

$$\mu = \frac{N_A \cdot h}{V} \cdot \exp\left(- \frac{\Delta_\mu G}{R \cdot T} \right) \tag{2}$$

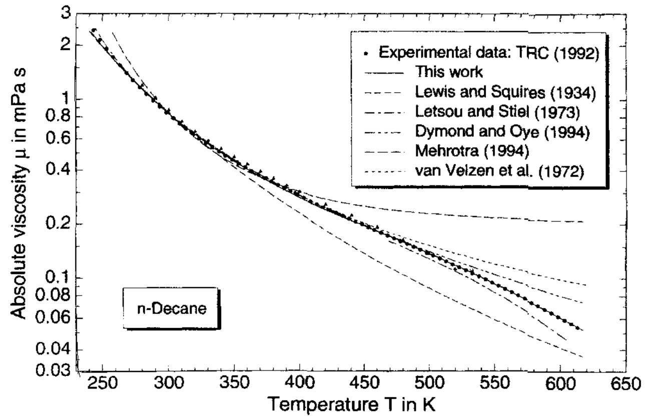

Figure 1. Methods for calculating viscosity.

in which N_A, h and R are Avogadro's, Planck's, and the gas constant, respectively, V represents the molar volume, and $\Delta_\mu G$ is the free energy of activation for flow. Comparison of Eqs. 1 and 2 reveals

$$A = \ln \frac{N_A \cdot h}{V} \tag{3a}$$

$$B = -\frac{\Delta_\mu G}{R} \tag{3b}$$

Since the molar volume is affected by temperature, the coefficient A is not constant. For instance, from the volumetric data of cyclopentane, $V(T = 253\text{ K}) = 89.5\text{ cm}^3/\text{mol}$ and $V(T = 393\text{ K}) = 110.8\text{ cm}^3/\text{mol}$, it follows that $A(T = 253\text{ K}) = -5.41$ and $A(T = 393\text{ K}) = -5.63$ in order to give the absolute viscosity in mPa·s. This difference is small compared with the deviation from the constant value $A = -4.03$ that best represents the experimental data in the given temperature range.

Several modifications of Eq. 1 have been proposed in order to improve the accuracy, especially over an extended temperature range, by introducing additional parameters. The Vogel equation (Reid et al., 1987) contains a third parameter C

$$\ln \mu = A + \frac{B}{T + C} \tag{4}$$

Dymond and Øye (1994) proposed a four-parameter equation in reduced form that requires the viscosity μ_0 at $T_0 = 298.15$ K in addition

$$\ln \frac{\mu}{\mu_0} = A + \frac{B}{T/T_0} + \frac{C}{(T/T_0)^2} + \frac{D}{(T/T_0)^3} \tag{5}$$

Compared with the Andrade equation, Eq. 1, the data representation can be improved by Eq. 5, as shown in Figure 1.

Hildebrand (1977) favors the free volume theory for calculating viscosity and states that a plot of inverse viscosity as function of volume V gives a straight line. Since this holds only in the low-temperature range and not near the freezing point, Hildebrand proposed a set of equations for the low- and the high-temperature range.

A new model

An analogy may be discerned between the effect of temperature on vapor pressure and on viscosity. The Clapeyron equation has the same mathematical form as the Andrade equation, and the Antoine equation is equivalent to the Vogel equation, for instance. Recently, a new model for predicting vapor pressure curves as a function of structural composition over wide temperature ranges has been proposed (Korsten, 2000). By introducing μ_α, the viscosity at the temperature T_α, one might apply that model to viscosity

$$\ln \frac{\mu}{\mu_\alpha} = B \cdot \left(\frac{1}{T^{1.30}} - \frac{1}{T_\alpha^{1.30}} \right) \tag{6}$$

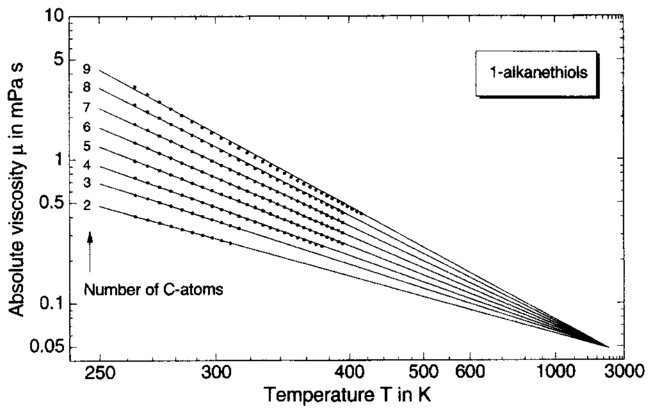

Figure 2. Viscosity by analogy to vapor pressure.

Figure 2 shows a comparison between experimental data and viscosities calculated by Eq. 6. In the range of temperature and molecule size shown in Figure 2, the results look promising. Unfortunately, the errors increase with increasing molecular weight, and Eq. 6 cannot predict the right shape of the viscosity curves at temperatures greater than about 0.7 times the critical temperature. Thus, the analogy between vapor pressure curves and viscosity vs. temperature curves doesn't hold at elevated temperatures.

The new model for depicting the viscosity as function of temperature utilizes a reference viscosity μ_R at the reference temperature T_R according to the general equation

$$\frac{\mu}{\mu_R} = F\left[-\gamma_R \cdot (T^n - T_R^n) \right] \tag{7}$$

where the temperature coefficient γ_R is a measure of the slope of the viscosity curve at the reference point

$$\gamma_R = \left[\frac{1}{\mu} \cdot \frac{\partial \mu}{\partial T} \right]_{T_R} \tag{8}$$

The exponent n in Eq. 7 is not constant with temperature, but has two characteristic values within the temperature ranges from the freezing point to the characteristic temperature T_0 (index I), and from T_0 to the critical temperature T_c (index II)

$$\mu_I = \mu_0 \exp\left[B_I \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \qquad T \le T_0 \tag{9a}$$

$$\mu_{II} = \mu_c \cdot \exp\left[B_{II} \cdot (T^2 - T_c^2) \right] \qquad T_0 \le T \le T_c \tag{9b}$$

where μ_c is the critical viscosity. According to experimental observations, the viscosity of liquids is a continuous function of temperature from the freeze point to the critical point. Consequently, the following two constraints have to be considered, reducing the number of parameters in Eqs. 9 by two

$$\mu_I(T = T_0) = \mu_{II}(T = T_0) = \mu_0 \tag{10a}$$

$$\left(\frac{d\mu_I}{dT} \right)_{T = T_0} = \left(\frac{d\mu_{II}}{dT} \right)_{T = T_0} \tag{10b}$$

Combining these constraints with Eqs. 9 and introducing reduced viscosities and temperatures (index r) let us finally write

$$\mu_{r,I} = \exp\left\{\frac{T_\mu}{2\cdot T_{r,0}\cdot T_c}\cdot\left[\left(\frac{1}{T_{r,0}}\right)^2 + 2\cdot\frac{T_{r,0}}{T_r} - 3\right]\right\} \qquad T_r \le T_{r,0} \tag{11a}$$

$$\mu_{r,II} = \exp\left\{\frac{T_\mu}{2\cdot T_{r,0}^3\cdot T_c}\cdot\left(1 - T_r^2\right)\right\} \qquad T_{r,0} \le T_r \le 1 \tag{11b}$$

where the "viscous temperature" T_μ equals B_I. $T_{r,0}$ is the characteristic reduced temperature at the inflection point, and it seems to have the universal value

$$T_{r,0} = \frac{T_0}{T_c} = 0.7189 \tag{12}$$

Figure 1 shows the viscosity curve of *n*-Decane between the freezing temperature and the critical point. The two-parameter model proposed in this article is the only one that accurately covers the entire temperature range. Up to the characteristic temperature T_0, the logarithmic plot of viscosity is a linear function of the inverse temperature. In this temperature range, deviations between the curves calculated by Eq. 11a and the group contribution method by van Velzen et al. (1972) that utilizes the Andrade equation as well, are due to slightly different parameters. Figure 3 shows experimental viscosity data of *n*-paraffins and their representation by Eqs. 11 in the temperature range from the freezing point to the critical point. The largest deviations occur for the heavy species at temperatures close to the freezing point, which are most likely caused by non-Newtonian behavior.

Kinematic viscosity

Often, it is not the absolute viscosity μ that is of interest, but the kinematic viscosity ν, as, for instance, in the Reynolds number *Re*. Thus, for interconversion, we need to know the liquid density as function of temperature. The equation by Rackett (1970) is probably the most widely used and reliable equation for predicting liquid volumes. A further advantage of the Rackett equation for application to complex systems is that it is predictive and requires only critical temperature T_c, critical pressure p_c and critical compressibility factor Z_c (or critical volume V_c)

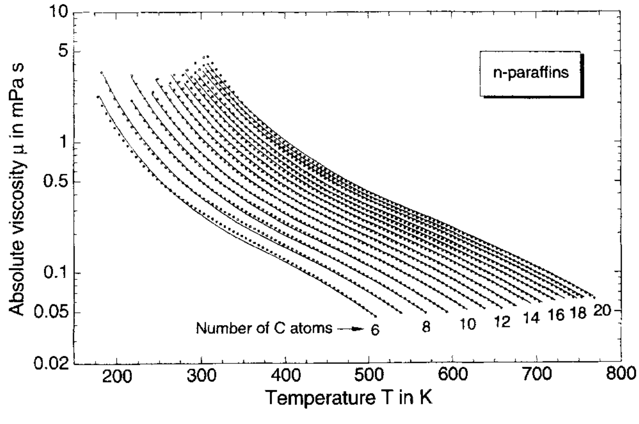

Figure 3. Viscosity between freezing and critical point.

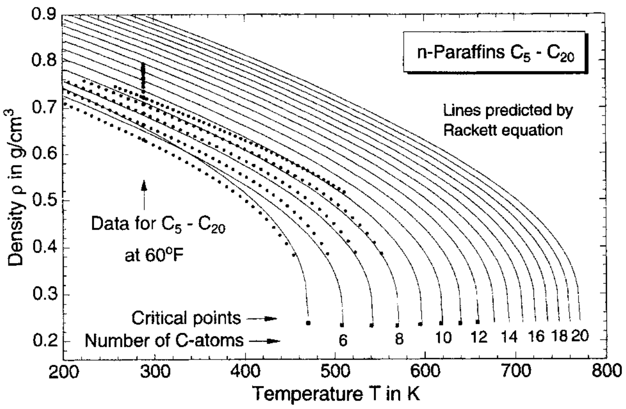

Figure 4. Density predicted by Rackett equation.

$$\frac{1}{\rho_s} = \left(\frac{R\cdot T_c}{p_c}\right)\cdot Z_c^{1+(1-T_r)^{2/7}} \tag{13}$$

where ρ_s is the density of the saturated liquid. Benzene and *n*-pentane are the heaviest hydrocarbons that were considered by Rackett. As shown in Figure 4, the method is not sufficiently accurate for predicting densities of heavier components. Equation 13 is very sensitive to the critical compressibility factor. Modified critical compressibility factors like the Rackett compressibility factor Z_{RA} proposed by Spencer and Danner (1972) can improve the situation shown in Figure 4. Since these modified critical data often deviate by a factor of 2 and more from the real values, and they cannot be predicted *a priori*, they are not desirable for application to complex systems. However, it is possible to view Z_{RA} as an adjustable parameter that can be determined from a known density vs. temperature data point.

Replacing viscosity μ by density ρ, Eqs. 8 and 9 are the basis for the development of the new equation for calculating liquid densities or volumes as function of temperature

$$\frac{\rho(T) - \rho_c}{\rho_0 - \rho_c} = \left(\frac{T_c - T}{T_c - T_0}\right)^n \tag{14}$$

where the exponent n has the value $n = 0.44$. Thus, the temperature dependency of density follows the same functionality as that of heat of vaporization, the only difference being that in the latter case n equals 0.38 (Watson, 1943). Equation 14 requires a reference density ρ_0 at the temperature T_0, and we may choose $T_0 = 60°\text{F}$ (16°C), the standard temperature for density measurements in the petroleum industry. Figure 5 shows a comparison of experimental densities with predicted values. The critical data required in Eq. 14 have been calcu-

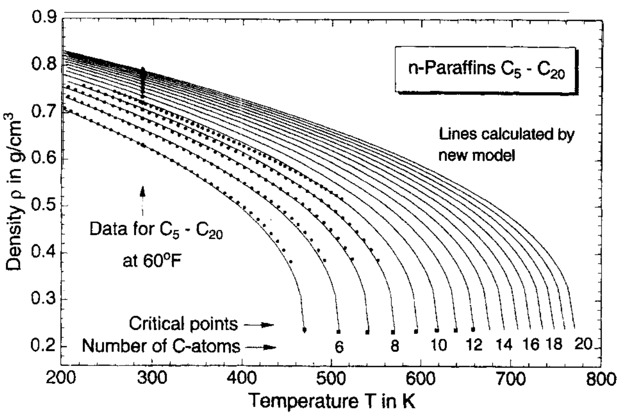

Figure 5. Density predicted by new model.

lated by the methods given by Korsten (1998), and the following simple structure relationship has been used for predicting the reference density of the n-paraffins at 60°F

$$\rho_0 = 0.8429 - \frac{15.27}{M} \tag{15}$$

The densities of other homologous series follow the same equation, in which the numerator of the last term differs from series to series.

Prediction of Viscosity

Often, viscosity data of a component are needed for which many experimental data at different temperatures are available. In order to get the viscosity at another temperature the Andrade equation (Eq. 1) or an extended modification like Eq. 5 may be used. The result will be reliable as long as temperatures are below the characteristic temperature T_0. Equations 11a and 11b are useful for calculating viscosity at any temperature between the freezing point and the critical temperature.

In typical petroleum streams there exist numerous species of different characteristic structure and size. Most are not available as pure substances, and, consequently, no experimental data are available. For applications like this, procedures are needed to predict the viscosity. There exist also less complicated applications, as, for instance, predicting the viscosity of a component containing 15 carbon atoms, but there are only data of 10- and 20-carbon species of the same homologous series available.

In order to predict the viscosity of any component at any temperature between the freezing point and the critical point by Eqs. 11, two characteristic properties, the viscous temperature T_μ and the critical viscosity μ_c are needed. In general, we can try to predict these values directly as functions of structure and size, or, alternatively, we might predict viscosities at different reference temperatures from which we then calculate T_μ and μ_c.

Viscosity at a reference temperature

Pachaiyappan et al. (1967) proposed the following equation for calculating the viscosity μ_{20} at 20°C as function of molecular weight

$$\mu_{20} = c \cdot M^n \tag{16}$$

The coefficients are characteristic for different homologous series, but, typically, the first one or two members of each series cannot be represented well by these characteristic values. The parameters of several homologous series are given by the authors. However, for application to complex hydrocarbon mixtures, the parameters of many additional types of components are needed.

It should be noted that molecular weight is not the characteristic measure determining the viscosity of a component. Important in this concern are size and shape. The combination of both may be called "effective molecular weight" M_{eff} defined as

$$M_{\text{eff}} = M + \Delta M \tag{17}$$

where ΔM depends on structural characteristics of each molecule. Using the viscosity vs. molecular weight curves of the n-paraffins as reference, the ΔM-values of other homologous series have been regressed to Eqs. 18. Based on this concept, we can calculate the viscosities μ_{40} and μ_{100} at 40°C and 100°C of any hydrocarbon in unit mPa·s by Eqs. 18

$$\ln \mu_{40} = -4.7874 + 0.370 \cdot M_{40,\text{eff}}^{0.5} \tag{18a}$$

$$\ln \mu_{100} = -19.741 + 11.4116 \cdot M_{100.\text{eff}}^{0.1} \tag{18b}$$

As shown in Figure 6, the viscosities of all the different species, except the first members of the homologous series, fall on one line for each constant temperature, confirming the validity of this approach. The structure and temperature-dependent molecular weight differences ΔM_i of some homologous series are given in Table 1. The viscosities of components other than those listed in Table 1 can be calculated by Eqs. 18, if experimental data of one member (not the first) of the same homologous series are available for determining ΔM.

It has been tried to calculate the critical viscosity on the basis of the kinetic gas theory. By modifying the Chapman-Enskog theory (see Reid et al., 1987), the critical viscosities

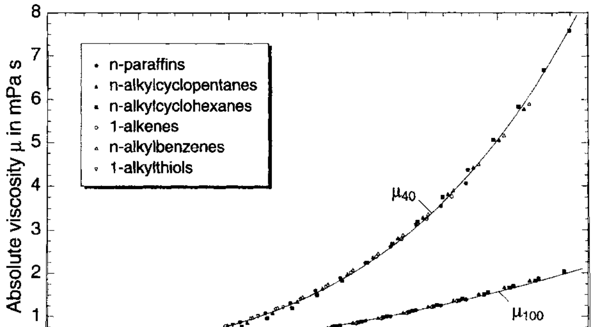

Figure 6. Viscosity at reference temperatures.

Table 1. Parameters for Predicting Viscosity

	ΔM_{40}	ΔM_{100}
n-Paraffins	0	0
n-Alkylcyclopentanes	+20	+23
n-Alkylcyclohexanes	+31	+28
n-Alkylbenzenes	+15	+18
1-Alkenes	−6	−3
1-Alkylthiols	+20	+23

of *n*-paraffins in mPa·s can be calculated by Eq. 19, if T_c and p_c are inserted in K and MPa, respectively

$$\mu_c = 0.2555 - 0.0305 \cdot \frac{\sqrt{M}}{T_c^{1/6}} \cdot \left(\frac{p_c}{Z_c}\right)^{2/3} \qquad (19)$$

Unfortunately, the development of a generalized relationship for calculating critical viscosities of components other than *n*-paraffins has not succeeded yet. From experimental observations, we know that the viscosities of *n*-paraffins at their normal boiling point are almost constant at $\mu_b = 0.197$ mPa·s. Other homologous series do not have characteristic constant values.

Viscosity as function of temperature

Polynomials like Eq. 5 have no physical background which makes it difficult to use them as a basis for developing a predictive equation. For this purpose, methods with a small number of parameters are preferred. Mehrotra (1994) presented the following correlation that contains only one parameter

$$\log_{10}(\mu + 0.8) = 100 \cdot (0.01 \cdot T)^b \qquad (20)$$

where T is the temperature in K, and μ has the unit mPa·s. Mehrotra presents equations for predicting the parameter b as a function of the Effective Carbon Number (ECN), which is defined as the number of carbon atoms of the *n*-paraffin that has the same normal boiling point as the component of interest. The curves presented by Mehrotra cover temperatures between 283°C and 373°C. As shown in Figure 1, large errors can be expected if the model is applied at elevated temperatures. A further problem of applying the ECN is that boiling point and viscosity do not have the same dependency on component structure. For instance, the normal boiling points of *n*-alkylbenzenes are slightly higher than those of *n*-alkylcyclohexanes of the same carbon number, whereas the viscosities of the latter are clearly higher.

Tham and Gubbins (1970) explained the temperature effect on viscosity by a harmonic oscillator theory. Geometrical data of the molecule are needed together with the acentric factor and an energy parameter. All these parameters need to be calculated from experimentally available viscosity data, because no procedure exists for predicting them.

Ely and Hanley (1981) calculated the viscosity by using a 32-parameter equation of state, a 20-parameter viscosity correlation of a reference fluid, and an 8-parameter shape factor equation by the principle of corresponding states. For each component of interest, the following values must be provided: molecular weight M, critical temperature T_c, critical pressure p_c, critical volume V_c, and acentric factor ω. Most of the data of Ely and Hanley are for paraffins, for which the average deviation is around 5%. Cyclohexane, ethylcyclohexane, and butylbenzene, as some examples for other homologous series, show errors of 49%, 31%, and 12%, respectively. The quality of the predictions can be improved by using the modified Ely and Hanley procedure as proposed by Hwang and Whiting (1987). In this modification, a so-called viscosity acentric factor is used instead of the acentric factor, and an association parameter is introduced for hydrogen-bonding fluids. The most restrictive shortcoming of this procedure is that the viscosity acentric factor differs strongly from the acentric factor and cannot be predicted *a priori.*

For temperatures above a reduced temperature $T_r = 0.7$, where the logarithmic viscosity is no longer a function of inverse temperature, Letsou and Stiel (1973) proposed a method that requires critical temperature, critical pressure, acentric factor, and molecular weight. The errors are usually high; applied to *n*-Decane, this method underpredicts the experimental data, as shown in Figure 1.

Van Velzen et al. (1972) developed a detailed group contribution method for calculating the parameter B and the temperature T_1 of the equation

$$\log_{10} \mu = B \cdot \left(\frac{1}{T} - \frac{1}{T_1}\right) \qquad (21)$$

Equation 21 is based on Eq. 1 introducing the reference temperature T_1 at which the viscosity has the value 1 mPa·s. The errors evaluated by van Velzen et al. and by Reid et al. (1987) are remarkably low, except for the first members of homologous series. How far the group contributions can be added to generate highly condensed polycyclic hydrocarbons is unknown because of the lack of experimental data. It can be expected that, similar to the one-ring homologous series, the first members of all the condensed compound series deviate from the general rule. If the prediction of the parameters in Eq. 21 succeeds, the results at temperatures lower than the characteristic temperature T_0 can be used as collocation points for calculating the viscosity of a liquid along the entire temperature range by Eqs. 11 (see Figure 1).

It has been pointed out by Kincaid et al. (1941) that there should exist a relationship between the viscous free energy $\Delta_\mu G$ in Eq. 2 and the energy of vaporization at the normal boiling point $\Delta_v U_b$. From experimental data, it is obvious that there exists a linear relationship between the two energies, but the relationship is different for different homologous series. It should be pointed out that $\Delta_\mu G$ represents the slope of the ln $\mu = f(1/T)$ curve, and, thus, small errors in $\Delta_\mu G$ cause huge errors in the predicted viscosity.

Viscosity of Mixtures

Three fundamentally different routes exists for calculating the viscosity of mixtures. In one approach the mixture is treated as a pure component, and its viscosity is calculated by using methods developed for pure species or by empirical correlations designed for certain mixtures. In this case, mixing effects are incorporated in the characteristic parameters of the equations. In a second approach, the viscosity of each single component of the mixture is calculated, and mixing rules are applied to obtain the actual value of the mixture. The third method contains mixing rules for the characterizing parameters of the viscosity equations. These mixture parameters then enter the same viscosity equation that is used for pure components.

One component procedure

The equation proposed by Glasø (1980) can be used to approximate the viscosity in mPa·s of gas-free crude oils as a function of temperature in K

$$\mu = 3.141 \times 10^{10} \cdot (1.8 \cdot T - 460)^{-3.444} \cdot [\log_{10}(\mathrm{API})]^{a} \quad (22a)$$

where the coefficient a is

$$a = 10.313 \cdot [\log_{10}(1.8 \cdot T - 460)] - 36.447 \quad (22b)$$

The only parameter required is the API gravity defined as

$$\mathrm{API} = \frac{141.5}{d_{60}} - 131.5 \quad (23)$$

where d_{60} is the ratio of the density of the oil at 60°F to the density of water at the same temperature. Equation 22 is useful as rough estimate for petroleum cuts, but should not be applied to pure components because specific gravity is an insufficient characterization parameter. As an example, Eq. 22 would imply that the viscosities of *n*-octadecane and *n*-propylcyclopentane are the same, since their specific gravities are almost identical. In fact, the viscosity of the former component is about one order of magnitude higher.

Singh et al. (1993) proposed the following equation for calculating the viscosity in Pa·s of heavy oil fractions as a function of temperature in K

$$\frac{\log_{10}\mu + C}{\log_{10}\mu_0 + C} = \left(\frac{T_0}{T}\right)^{n} \quad (24a)$$

where the parameter C has the value 3.0020, and the exponent n is given as a function of the known viscosity μ_0 at the reference temperature $T_0 = 303.15$ K

$$n = 0.0066940 \cdot \log_{10}\mu_0 + 3.5565 \quad (24b)$$

Abbott et al. (1971) proposed two empirical multiparameter equations for predicting the kinematic viscosities of petroleum fractions at 100°F (38°C) and 210°F (99°C) as functions of specific gravity and average boiling point. Many more empirical methods utilizing specific gravity and average boiling point have been published. In this article, these procedures are not considered further.

Mixing rules for viscosities

The most widely used mixing rule for calculating the viscosity of a mixture from pure component viscosities μ_i^0 weighted by their mole fractions x_i is that by Kendall and Monroe (1917)

$$\mu = \left[\sum_{i=1}^{N} x_i \cdot \left(\mu_i^0\right)^{1/3}\right]^3 \quad (25)$$

In the same article the authors show that other simple mixing rules like

$$\mu = \sum_{i=1}^{N} x_i \cdot \mu_i \quad (26a)$$

$$\ln \mu = \sum_{i=1}^{N} x_i \cdot \ln \mu_i \quad (26b)$$

$$\frac{1}{\mu} = \sum_{i=1}^{N} \frac{x_i}{\mu_i} \quad (26c)$$

lead to large errors, as does the use of volume or weight fractions instead of mole fractions. Assuming that the viscosity μ_T at a constant temperature T can be described as function of the number of carbon atoms n_C by

$$\ln \mu_T = A + B \cdot n_C \quad (27)$$

Ratcliff and Khan (1971) define an "ideal solution viscosity" that is equivalent to Eq. 26b. This ideal solution viscosity is the viscosity of a mixture containing similar components, as, for instance, paraffins of similar size.

New Mixing rule

In general, the viscosity of a mixture can be expressed by Eq. 28

$$\ln \mu = \ln \mu^0 + \Delta_M \ln \mu \quad (28)$$

where μ^0 is the ideal mixture viscosity as calculated by Eq. 26b, and $\Delta_M \ln \mu$ represents the mixing effect. Alternatively, the viscosity of the mixture may be calculated by using partial molar viscosities $\tilde{\mu}_i$

$$\ln \mu = \sum_{i=1}^{N} x_i \cdot \ln \tilde{\mu}_i \quad (29)$$

where the partial molar viscosity of a component in a mixture can be calculated from its pure component viscosity μ_i^0 and the derivative of the mixture viscosity as a function of composition at constant temperature T and pressure p

$$\ln \tilde{\mu}_i = \ln \mu_i^0 - \sum_{\substack{k=1 \\ k \neq i}}^{N} x_k \cdot \left(\frac{\partial \ln \mu}{\partial x_k}\right)_{T,p,x_{j \neq k}} \quad (30)$$

Finally, the mixture viscosity can be represented by Eq. 31

$$\ln \mu = \left\{\sum_{i=1}^{N} x_i \cdot \ln \mu_i^0\right\} - \left\{\sum_{i=1}^{N}\left[x_i \cdot \sum_{\substack{k=1 \\ k \neq i}}^{N} x_k \cdot \left(\frac{\partial \ln \mu}{\partial x_k}\right)_{T,p,x_{j \neq k}}\right]\right\} \quad (31)$$

in which the first expression is the ideal mixture viscosity ln μ^0, and the second one represents the mixing effects $\Delta_M \ln \mu$ (cf. Eq. 28). The partial derivatives in Eq. 30 are taken at constant T and p, that is, the mixing effect is a function of these two properties. In order to calculate the viscosity of a mixture as a function of temperature, we apply the viscosity mixing rule to the critical viscosity at the critical temperature and insert the result in Eqs. 11. For calculating the viscous temperature and the critical temperature of the mixture, the following mixing rules are used

$$T_\mu = \sum_{i=1}^{N} x_i \cdot T_{\mu,i} \qquad (32)$$

$$T_c = \sum_{i=1}^{N} x_i \cdot T_{c,i} \qquad (33)$$

From measured viscosities of binary mixtures, it has been found that the partial derivatives are determined by the viscous temperatures $T_{\mu,i}$ and the critical temperatures $T_{c,i}$ of the components

$$\Delta_M \ln \mu = \sum_{i=1}^{N-1} x_i \cdot \sum_{k=i+1}^{N} x_k \cdot \left| \frac{T_{\mu,k}}{T_{c,k}} - \frac{T_{\mu,i}}{T_{c,i}} \right|^{1/4} \cdot \frac{\dfrac{T_{\mu,k}}{T_{c,k}} - \dfrac{T_{\mu,i}}{T_{c,i}}}{\left| \dfrac{T_{\mu,k}}{T_{c,k}} - \dfrac{T_{\mu,i}}{T_{c,i}} \right|} \cdot \frac{T_{c,k} - T_{c,i}}{|T_{c,k} + T_{c,i}|} \qquad (34)$$

Thus, the mixing effect depends on the binary interactions in the mixture determined by the characteristic relative slope of the pure-component viscosity curves. Figure 7 shows a comparison between experimental mixture viscosities and those calculated by the new method and by Eqs. 25 and 26b. It should be noted that the mixing effect of the system benzene/n-hexadecane is positive, whereas the mixing effect in the system benzene/cyclohexane is negative. The latter effect happens if the pure-component viscosity curves cross each other between the freezing and critical temperatures.

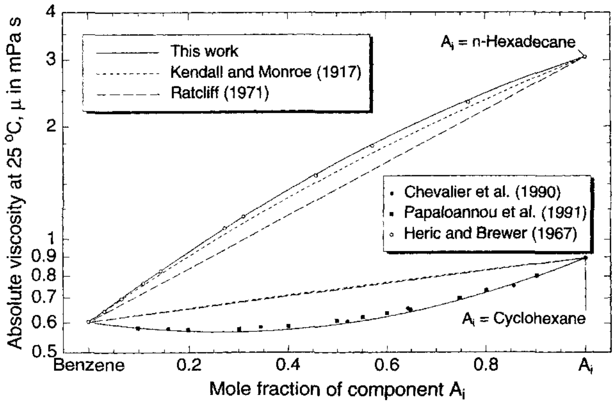

Figure 7. Viscosity of binary mixtures.

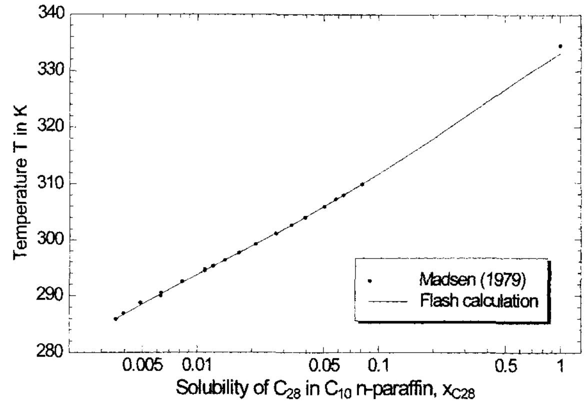

Figure 8. Solid solubility in a binary mixture.

Viscosity of mixtures at low temperature

If we follow the viscosity of a mixture in the direction of decreasing temperature, we observe that the relationship given in Eqs. 1 and 11a is valid down to a certain temperature. Below this temperature, the mixture viscosity increases far more than that predicted by these equations, because, with decreasing temperature, the freeze points of more and more species of the mixture are passed. If the temperature falls below the freezing temperature, the viscosity of a pure component would increase toward infinity, because it changed into a solid. Multicomponent mixtures like petroleum fractions contain numerous components, each one in small concentration. A component at temperatures below its pure component freezing point is in solution in the remaining liquid. If the sample is cooled further, clouds appear indicating the formation of solids. With decreasing concentration of the heavy, wax-forming components in the solvent oil, the temperature at which solids formation occurs can be substantially below its pure component freeze point, as shown in Figure 8. The viscosity of the whole mixture increases toward infinity if the temperature is below the lowest pure-component freezing point. The solubility effect on viscosity can be represented by the enhancement factor k_i

$$\tilde{\Phi}_i = \tilde{\Phi}_i^L \cdot k_i \qquad (35)$$

where $\tilde{\Phi}_i$ and $\tilde{\Phi}_i^L$ are the actual partial molar fluidity of the component in the mixture and the partial molar fluidity of the pseudo liquid, respectively. The latter is obtained by extrapolating the partial molar viscosity below the freezing point. Fluidity is defined as inverse viscosity

$$\Phi = \frac{1}{\mu} \qquad (36)$$

The enhancement factor k_i of a component equals one if the temperature is above its freezing temperature, and zero if the whole mixture is solid. Consequently, the enhancement factor is a function of the fraction of components in solution. Components in solution are those components that have a freeze point temperature above the temperature of the system. The viscosity of a liquid mixture can be expressed by Eq.

29. In terms of fluidity this is equivalent to

$$\Phi = \prod_{i=1}^{N} \tilde{\Phi}_i^{x_i} \tag{37}$$

After inserting Eq. 35, we obtain

$$\Phi(T) = \Phi_L(T) \cdot \Phi_S(T) \tag{38}$$

where Φ_L is the pseudo liquid fluidity, and Φ_S represents the solubility effect of the mixture

$$\Phi_S = \prod_{i=1}^{N} k_i^{x_i} \tag{39}$$

Supposing that the enhancement factors k_i of all the components have the same value k lets us write

$$\Phi_S = k^{\sum_{i=1}^{N} (1-L_i) \cdot x_i} \tag{40}$$

where the logical parameter L_i has been included for separating liquids ($T \geq T_{f,i}$ and $L_i = 1$) and solids ($T < T_{f,i}$ and $L_i = 0$) without affecting the limiting values of k_i as discussed above. The $T_{f,i}$ are freezing temperatures of component i. The exponent in Eq. 40 represents the fraction of components in solution. Thus, it is

$$\Phi_S(T) = k^{1-F(T)} \tag{41}$$

where $F(T)$ is the freezing point distribution of the mixture normalized between 0 and 1. As discussed above, the enhancement factor depends on the amount of components in solution

$$k = a \cdot [F(T)]^n \tag{42}$$

If we assume that the enhancement factor is directly proportional to the freezing point distribution ($a = 1$, $n = 1$), the final equation for calculating the mixture viscosity is

$$\Phi(T) = \Phi_L(T) \cdot [F(T)]^{1-F(T)} \tag{43}$$

In practice, we need to have information about the amount of components in the mixture that have freeze points lower than the temperature at which we want to calculate the viscosity. At elevated temperature, when the temperature of the system is higher than the freeze point temperature of all the components in the mixtures $F(T) = 1$. Consequently, the actual viscosity equals the ideal liquid viscosity. Figure 9 shows the results of this new approach in comparison with some of the other methods discussed in this article applied to the vacuum gas oil (VGO) specified in Table 4 in Korsten (1997). Even without a high degree of structural information reasonable results can be obtained. The calculated viscosity curve shown in Figure 9 has been generated on the assumption that the freezing point distribution in mainly determined by the n-paraffins, and that this distribution is a normal distribution.

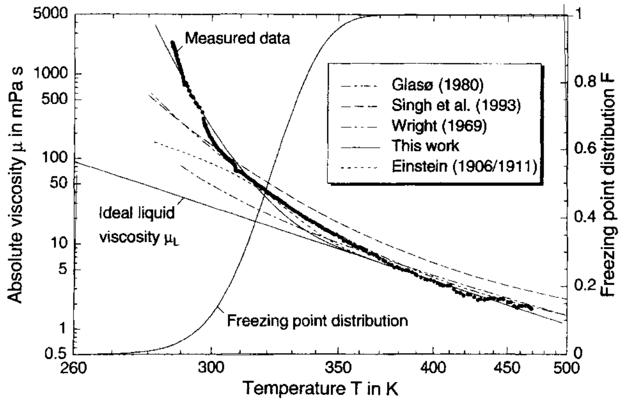

Figure 9. Viscosity of a VGO.

From the boiling point distribution, it can be concluded that the oil contains paraffins in the range between $C_{13}H_{28}$ and $C_{55}H_{112}$. The freezing temperatures T_f of n-paraffins in unit K can be calculated by Eq. 44

$$T_f = 473.5 - \frac{2,745}{\sqrt{M}} \tag{44}$$

Assuming a solution of large, spherical molecules in a solvent of small molecules, Einstein (1906, corrected 1911) showed that the viscosity can be described by the equation

$$\mu = \mu_L \cdot (1 + 2.5 \cdot \varphi) \tag{45}$$

where φ is the volume fraction of solids dissolved in the liquid. According to Einstein's assumptions, Eq. 45 is valid for low concentrations of solids dissolved in the liquid. At small solid concentrations, Eq. 45 is in good agreement with the experimental data and with the new model presented here, as shown in Figure 9.

It should be mentioned that full agreement between the experimental data and the new procedure can be obtained, if the freezing point distribution is slightly modified towards higher temperatures for the heavy components. Thus, a high

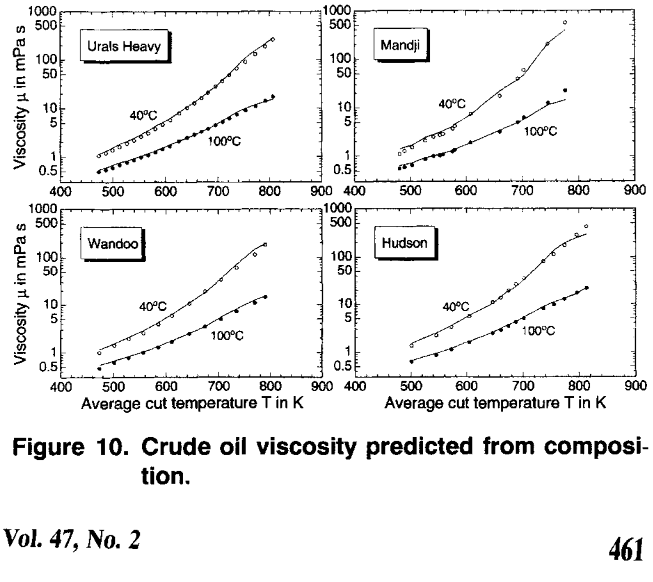

Figure 10. Crude oil viscosity predicted from composition.

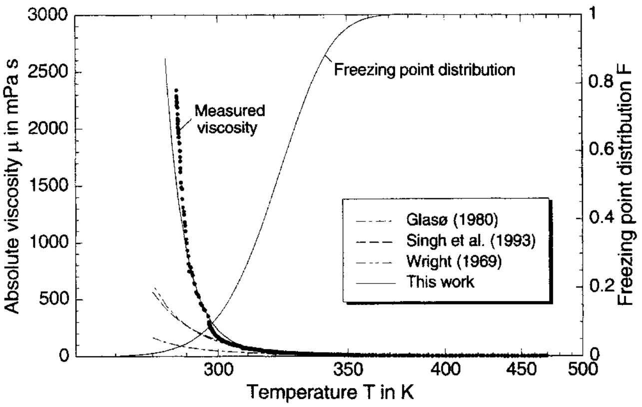

Figure 11. Freezing effect on low temperature viscosity.

degree of compositional information promises the ability to predict viscosities of complex mixtures like petroleum fractions with only minor deviations. We are applying the new models in conjunction with the high level of compositional information provided by "structure oriented lumping"(Quann and Jaffe, 1992). Some examples for predicting viscosities of various crude oils by this approach are shown in Figure 10. In practice, we are interested in the viscosity rather than in its logarithmic representation. As shown in Figure 11, the viscosity rises very rapidly with increasing amount of frozen components that are dissolved in the solvent oil. This happens within a very narrow temperature range, and it is well predicted even by incorporating the normal freezing point distribution of the *n*-paraffins as an approximation. Strictly speaking, Eq. 43 is applicable at temperatures above the cloud point temperature, because complete solution of the frozen components is assumed. At lower temperatures, the viscosity might be affected by the formation of wax visible as clouds. As shown above, the viscosity calculated by the model presented in this article increases rapidly towards infinity if the temperature is decreasing. Whether this model is able to represent the viscosity accurately enough at temperatures far below the cloud point may be a topic of further investigation. If necessary, Eq. 38 can be expanded by an additional parameter that accounts for the effects of visible solids in the mixture. The required solid concentration can be calculated by solid-liquid equilibrium calculations.

Literature Cited

Abbott, M. M., T. G. Kaufmann, and L. Domash, "A Correlation for Predicting Liquid Viscosities of Petroleum Fractions," *Canad. J. Chem. Eng.*, **49**, 379 (1971).

Chevalier, J. L. E., P. J. Petrino, and Y. H. Gaston-Bonhamme, "Viscosity and Density of Some Aliphatic, Cyclic, and Aromatic Hydrocarbons Binary Liquid Mixtures," *J. Chem. Eng. Data*, **35**, 206 (1990).

Christensen, G., M. R. Apelian, K. J. Hickey, and S. B. Jaffe, "Future Directions in Modeling the FCC Process: An Emphasis on Product Quality," *Chem. Eng. Sci.*, **54**, 2753 (1999).

Dymond, J. H., and H. A. Øye, "Viscosity of Selected Liquid n-Alkanes," *J. Phys. Chem. Ref. Data*, **23**, 41 (1994).

Einstein, A., "Eine neue Bestimmung der Moleküldimensionen," *Ann. D. Physik*, **19**, 289 (1906).

Einstein, A., "Berichtigung zu meiner Arbeit: 'Eine neue Bestimmung der Moleküldimensionen," *Ann. Der Physik*, **24**, 591 (1911).

Ely, J. F., and H. J. M. Hanley, "Prediction of Transport Properties. 1. Viscosity of Fluids and Mixtures," *Ind. Eng. Chem. Fundam.*, **20**, 323 (1981).

Eyring, H., "Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates," *J. Chem. Phys.*, **4**, 283 (1936).

Glasø, Ø., "Generalized Pressure-Volume-Temperature Correlations," *J. Petr. Tech.*, **32**, 785 (1980).

Heric, E. L., and J. G. Brewer, "Viscosity of some Binary Liquid Nonelectrolyte Mixtures," *J. Chem. Eng. Data*, **12**, 574 (1967).

Hildebrand, J. H., *Viscosity and Diffusivity. A Predictive Treatment*, Wiley, New York (1977).

Hwang, M.-J., and W. B. Whiting, "A Corresponding States Treatment for the Viscosity of Polar Fluids," *Ind. Eng. Chem. Res.*, **26**, 1758 (1987).

Katzer, J. R., M. P. Ramage, and A. Sapre, "Petroleum Refining: Poised for Profound Changes,"*Chem. Eng. Prog.*, **96**, 41 (July, 2000).

Kendall, J., and K. P. Monroe, "The Viscosity of Liquids: II. The Viscosity-Composition Curve for Ideal Liquid Mixtures," *J. Am. Chem. Soc.*, **39**, 1787 (1917).

Kincaid, J. F., H. Eyring, and A. E. Stearn, "The Theory of Absolute Reaction Rates and its Application to Viscosity and Diffusion in the Liquid State," *Chem. Rev.*, **28**, 301 (1941).

Korsten, H., "Characterization of Hydrocarbon Systems by DBE Concept," *AIChE J.*, **43**, 1559 (1997).

Korsten, H., "Critical Properties of Hydrocarbon Systems," *Chem. Eng. Technol.*, **21**, 3 (1998).

Korsten, H., "Internally Consistent Prediction of Vapor Pressure and Related Properties," *Ind. Eng. Chem. Res.*, **39**, 813 (2000).

Letsou, A., and L. I. Stiel, "Viscosity of Saturated Nonpolar Liquids at Elevated Pressures," *AIChE J.*, **19**, 409 (1973).

Madsen, H. E. L., and R. Boistelle, "Solubility of Octacosane and Hexatriacontane in different n-Alkane Solvents," *Chem. Soc., London: J. Faraday Trans. I*, **75**, 1254 (1979).

Mehrotra, A. K., "Correlation and Prediction of the Viscosity of Pure Hydrocarbons," *Canad. J. Chem. Eng.*, **72**, 554 (1994).

Monnery, W. D., W. Y. Svrcek, and A. K. Mehrotra, "Viscosity: A. Critical Review of Practical Predictive and Correlative Methods," *Canad. J. Chem. Eng.*, **73**, 3 (1995).

Pachaiyappan, V., S. H. Ibrahim, and N. R. Kuloor, "Simple Correlation for Determining Viscosity of Organic Liquids," *Chem. Eng.*, **74**, 193 (May 22, 1967).

Papaloannou, D., T. Evangelou, and C. Panayiotou, "Dynamic Viscosity of Multicomponent Liquid Mixtures," *J. Chem. Eng. Data*, **36**, 43 (1991).

Quann, R. J., and S. B. Jaffe, "Structure-Oriented Lumping: Describing the Chemistry of Complex Hydrocarbon Mixtures," *Ind. Eng. Chem. Res.*, **31**, 2483 (1992).

Rackett, H. G., "Equation of State for Saturated Liquids," *J. Chem. Eng. Data*, **15**, 514 (1970).

Ratcliff, G. A., and M. A. Khan, "Prediction of the Viscosities of Liquid Mixtures by a Group Solution Model," *Can. J. Chem. Eng.*, **49**, 125 (1971).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases & Liquids*, 4th ed., McGraw-Hill, New York (1987).

Singh, B., A. Miadonye, and V. R. Puttagunta, "Heavy Oil Viscosity Range from one Test," *Hydrocarb. Proc.*, **72**, 157 (Aug. 1993).

Spencer, C. F., and R. P. Danner, "Improved Equation for Prediction of Saturated Liquid Density," *J. Chem. Eng. Data*, **17**, 236 (1972).

Tham, M. J., and K. E. Gubbins, "Correspondence Principle for Transport Properties of Dense Fluids. Nonpolar Polyatomic Fluids," *Ind. Eng. Chem. Fundam.*, **9**, 63 (1970).

van Velzen, D., R. Lopes Cardozo, and H. Langenkamp, "A Liquid Viscosity-Temperature-Chemical Constitution Relation for Organic Compounds," *Ind. Eng. Chem. Fundam.*, **11**, 20 (1972).

Watson, K. M., "Thermodynamics of the Liquid State," *Ind. Eng. Chem.*, **35**, 398 (1943).

Wright, W. A., "An Improved Viscosity-Temperature Chart for Hydrocarbons," *J. Mater., JMSLA*, **4**, 19 (March 1969).

Manuscript received Jan. 3, 2000, and revision received Aug. 21, 2000.