validity of the assumptions underlying the theory.

The assumption of no mean voidage fluctuation is a reasonable one for analyzing the Rayleigh–Taylor instability modes, because allowance of mean voidage fluctuations only leads to appearance of additional dilation instability modes, e.g., instability voidage waves (see Pigford and Baron, 1965; Anderson and Jackson, 1968; and Homsy et al., 1980). The quasi-static assumption well describes the experimental conditions when the shock is far from both the top and the base of the bed and is a valid one, considering the long experimental residence times of our experiments. The assumption of Newtonian constitutive equation for the stress at very high particle concentrations, is therefore a questionable one.

We interpret our first type of experiment as follows: over the voidage range covered, the particulate phase exhibits a yield stress; i.e., it will not flow under applied stress until a critical level is reached. In a carefully controlled experiment, the fluctuations which may drive an instability are presumably small, and therefore do not result in stresses above the yield value. This would account for the observed high degree of stability. The theory ignores this effect and predicts a high degree of instability for reasonable values of the material parameters. It is easy to show, however, that any linear instability theory containing a finite yield stress will predict *no instability*, in agreement with our observations. The presence of a finite yield stress is also in accord with widely accepted behaviors of cohesionless granular materials; see Homsy (1979) for a partial discussion and references. It is clear that if this yield stress is due to particle kinematics alone and not due to forces of electrostatic, molecular, or capillary origin, it should vanish above a certain voidage. Due to the flow distribution described earlier, we were not able to examine the conjecture experimentally.

It remains to account for our second type of experiment, in which gravitational instabilities *were* observed. We interpret these as follows: after the large increase in flow, sufficient pressure exists at the base of the unsaturated bed to lift it off the distributor. As the saturation front propagates into the packed section, uniform sedimentation

occurs until the point that the layer is dilated above the void fraction for which the yield stress vanishes. Rayleigh–Taylor instability then rapidly develops, leading to vigorous macroscopic mixing in the saturated region.

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Prediction of Transport Properties. 1. Viscosity of Fluids and Mixtures

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A model for the prediction of the viscosity of nonpolar fluid mixtures over the entire range of *PVT* states is presented. The model is an extension of an earlier version (Hanley, 1976) to molecular weights which roughly correspond to that of C_{20}. The proposed model is based on an extended corresponding states principle and requires only critical constants and Pitzer's acentric factor for each component as input. Extensive comparisons with experimental data for pure fluids and binary mixtures are presented. The average deviation between experiment and prediction is 8% for pure species and 7% for mixtures.

Introduction

The purpose of this article is to present a reliable self-consistent method for predicting the viscosity of nonpolar fluids and their mixtures over a wide range of thermodynamic states from the dilute gas to the dense liquid. We

stress that the method is predictive and, in principle, the number of mixture components is unrestricted.

In general, engineering calculations of transport properties are based on empirical correlations, limited to narrow ranges of temperature and pressure and often to pure

fluids. A review of these methods is given by Reid et al. (1978). Methods with more theoretical foundations (other than for the dilute gas) include those of Tham and Gubbins (1970) and Doan and Brunet (1972). Both of these, however, are limited to liquid phases and the latter requires structural parameters which are usually not readily available for the types of fluids encountered in practice. Many variants of the Eyring approach and the Enskog approach (Hirschfelder et al., 1964) have been presented but, again, they are usually limited as to the type of fluid and to a limited range of experimental conditions.

A procedure has been presented recently, however, (Mo and Gubbins, 1974; Hanley, 1976; Haile et al., 1976), to estimate the transport properties of natural gas and similar mixtures which is based on the corresponding states principle and the conformal solution, one-fluid concept. It is predictive and requires only the critical parameters and Pitzer's acentric factor of each mixture component as input: no mixture properties or transport data of the components of the mixture are required. The basic idea is relatively straightforward. It is assumed that the configurational properties of a single-phase mixture can be equated to those of a hypothetical pure fluid. The properties of this hypothetical pure fluid are then evaluated via corresponding states with respect to a given reference fluid.

The theoretical foundation of the approach is well defined for a conformal system in equilibrium (Henderson and Leonard, 1971). It is less understood for a nonconformal system (i.e., a system in which the mixture components do not interact with the same intermolecular potential, e.g., polyatomic molecules) and for a system in nonequilibrium, although Mo and Gubbins (1976) and Evans and Hanley (1979) have recently discussed the assumptions in the latter example. Nevertheless, we have found by experience that the method gave very good agreement—typically less than 10% uncertainty—for the transport properties of liquefied natural gas (LNG) like fluids (i.e., polyatomic nonpolar species). Further, even though the procedure in our earlier work was optimized for the C_1 to C_5 hydrocarbons and common inorganics, it gave acceptable results–typically 10–40% uncertainty—for a diverse number of more complex pure components and their mixtures. These results for fluids that were well beyond the intended scope of the original model encouraged us to explore a systematic extension of the method to more complex systems.

In this paper we report results for the viscosity of pure paraffins, alkenes, aromatics, and naphthenes in the C_1 to C_{20} molecular weight range, and their mixtures. Carbon dioxide is included as a common inorganic. In discussing the broadened approach, we point out some general problems of applied corresponding states over a very wide range of conditions. The thermal conductivity has also been discussed previously (Hanley, 1976) and our recent work in this area will be reported subsequently.

The One-Fluid Model and Equations

In our procedure, the viscosity (η) of a mixture at density, ρ, and temperature, T, and composition $\{x_\alpha\}$ is equated to the viscosity of a hypothetical pure fluid, i.e., $\eta_{\mathrm{mix}}(\rho,T)$ = $\eta_x(\rho,T)$. Then, via the corresponding states argument

$$\eta_x(\rho,T) = \eta_0(\rho_0,T_0) F_\eta \qquad (1)$$

where

$$F_\eta = \left(\frac{M_x}{M_0}\right)^{1/2} f_{x,0}^{1/2} h_{x,0}^{-2/3} \qquad (2)$$

where x refers to the fluid of interest, pure fluid or mixture,

and 0 refers to the reference fluid. M is the molecular weight and T_0 and ρ_0 are defined by the ratios

$$T_0 = T/f_{x,0}$$

$$\rho_0 = \rho h_{x,0} \qquad (3)$$

where $f_{x,0}$ and $h_{x,0}$ are, in general, functions of the critical parameters and acentric factor. In the special case of two-parameter corresponding states between two pure fluids α and 0, they reduce to the well known ratios of critical constants

$$f_{\alpha,0} = T_\alpha^c/T_0^c$$

$$h_{\alpha,0} = V_\alpha^c/V_0^c \qquad (4)$$

$$\equiv \rho_0^c/\rho_\alpha^c$$

where V is the volume and superscript c indicates the critical value.

Note that for the special case of two parameter corresponding states for which $Z_\alpha^c = Z_0^c$, the factor F_η can be written in terms of the common viscosity reducing parameter ζ_α

$$\zeta_\alpha = T_\alpha^{c1/6}/(M_\alpha^{1/2}p_\alpha^{c2/3}) \qquad (5)$$

so

$$F_\eta = \zeta_0/\zeta_\alpha \qquad (6)$$

where p is the pressure. Note that eq 1 is written in terms of the temperature and density rather than the temperature and pressure. Density is a convenient variable from the statistical mechanical viewpoint and the temperature dependence of the viscosity at constant density is small whereas the temperature dependence at constant pressure can be very large. Hence a correlation of viscosity in terms of the density is both theoretically convenient and mathematically simpler in practice. Calculation of the density given the pressure and temperature presents no difficulty in our procedure.

Extended Corresponding States

The range of applicability of corresponding states in general, and of eq 1 in particular, can be broadened considerably by introducing the extended corresponding states model (Leland et al., 1968; Rowlinson and Watson, 1969). Here the two-parameter corresponding states formalism is maintained except that the equivalent substance reducing parameters become, using the special case of the pure as an example

$$f_{\alpha,0} = (T_\alpha^c/T_0^c)\theta_{\alpha,0}(T_\alpha{}^*, V_\alpha{}^*,\omega_\alpha) \qquad (7)$$

$$h_{\alpha,0} = (V_\alpha^c/V_0^c)\phi_{\alpha,0}(T_\alpha{}^*, V_\alpha{}^*, \omega_\alpha) \qquad (8)$$

where $\theta_{\alpha,0}$ and $\phi_{\alpha,0}$ are the so-called shape factors (Leach and Leland, 1968) which are functions of Pitzer's acentric factor ω_α and of the reduced variables $T_\alpha{}^*$ and $V_\alpha{}^*$ where the asterisk indicates reduction by the critical point value.

In principle, the shape factors can be determined exactly for any pure fluid with respect to a reference fluid by simultaneous solution of the conformal solution equations (Rowlinson and Watson, 1969)

$$A_\alpha^{\mathrm{conf}}(V,T) = f_{\alpha,0}A_0^{\mathrm{conf}}(V/h_{\alpha,0}, T/f_{\alpha,0}) - RT \ln h_{\alpha,0} \qquad (9)$$

and

$$Z_\alpha(V_\alpha,T_\alpha) = Z_0(V_\alpha/h_{\alpha,0}, T_\alpha/f_{\alpha,0}) \qquad (10)$$

the superscript conf indicates the configurational contribution, i.e., the contribution which is due to the volume dependence of the statistical mechanical partition function.

One could ensure that pure fluid α maps exactly with the reference fluid on a PVT surface via the shape factors. However, it is much more convenient to have some generalized analytical relationship for θ and ϕ. Leach and Leland (1968) have solved eq 9 and 10 for the pure normal paraffins C_1–C_{15} with essentially a methane reference fluid 0. Their results are generalized as follows

$$\theta_{\alpha,0}(T_\alpha^*, V_\alpha^*, \omega_\alpha) = 1 + (\omega_\alpha - \omega_0)\, F(T_\alpha^*, V_\alpha^*) \quad (11)$$

and

$$\phi_{\alpha,0}(T_\alpha^*, V_\alpha^*, \omega_\alpha) =$$
$$[1 + (\omega_\alpha - \omega_0)\, G(T_\alpha^*, V_\alpha^*)]\, Z_0^c/Z_\alpha^c \quad (12)$$

where

$$F(T_\alpha^*, V_\alpha^*) =$$
$$a_1 + b_1 \ln T_\alpha^+ + (c_1 + d_1/T_\alpha^+)(V_\alpha^+ - 0.5) \quad (13)$$

and

$$G(T_\alpha^*, V_\alpha^*) = a_2(V_\alpha^+ + b_2) + c_2(V_\alpha^+ + d_2)\ln T_\alpha^+ \quad (14)$$

$$T_\alpha^+ = \min\{2, \max\{T_\alpha^*, 0.5\}\} \quad (15)$$

and

$$V_\alpha^+ = \min\{2, \max\{V_\alpha^*, 0.5\}\} \quad (16)$$

Mixing Rules and Comments on the Assumptions

There are two basic assumptions of the theory: (1) A pure fluid and a reference fluid obey two parameter classical corresponding states formalism and, for a mixture, that all interactions in the mixture follow this principle. (2) The mixture can be represented by a hypothetical pure fluid which implies mixing rules exist to evaluate the reducing ratios. Clearly it has been assumed that the introduction of extended corresponding states allows these assumptions to be upheld.

As we pointed out in the Introduction, the assumptions have been discussed for the system in equilibrium but have received less attention for a system in nonequilibrium, especially for polyatomic molecules. It is at once apparent that the one-fluid concept is formally weak for transport since the transport properties can contain contributions unique to the mixture—the diffusion coefficient, for example. There is also the difficulty in formulating a consistent mass mixing rule which is unnecessary for equilibrium properties but is required for both eq 2 and the equivalent equation for the thermal conductivity.

These problems were examined by Evans and Hanley (1979) and by Hanley and Evans (1981) and we repeat here very briefly the results of those studies. Following Henderson and Leonard (1971), the potential contribution to the energy, E_u, is written down for a pure fluid and for a mixture, respectively

$$E_u = 2\pi N \frac{N}{V} \int u(r) g(r) r^2 \, dr \quad (17)$$

and

$$E_u = 2\pi N \frac{N}{V} \sum_\alpha \sum_\beta x_\alpha x_\beta \int u_{\alpha\beta}(r) g_{\alpha\beta}(r) r^2 \, dr \quad (18)$$

where N is the number of molecules in volume V, $u(r)$ is the pair potential as a function of intermolecular separation, r, and $g(r)$ is the radial distribution function. If all species in a mixture obey corresponding states and thus obey the force law $u = \epsilon u^*(r/\sigma)$ and if the radial distribution functions scale as

$$g_{\alpha\alpha}(r/\sigma_{\alpha\alpha}) = g_{\alpha\beta}(r/\sigma_{\alpha\beta}) = g_{\beta\beta}(r/\sigma_{\beta\beta}) \quad (19)$$

then eq 18 can be written in the reduced form

$$E_u =$$
$$2N\left(\frac{N}{V}\right)\sum_\alpha \sum_\beta x_\alpha x_\beta \epsilon_{\alpha\beta}\sigma_{\alpha\beta}^3 \int u^*(r_{\alpha\beta}^*) g(r_{\alpha\beta}^*) r_{\alpha\beta}^{*2} \, dr_{\alpha\beta}^* \quad (20)$$

where $u^* = u/\epsilon$ and $r^* = r/\sigma$: ϵ and σ are the usual potential parameters where $\epsilon \sim T^c$ and $\sigma^{-3} \sim \rho^c$. One then writes eq 17 in similar form and compares with eq 20. The results of this comparison are that the mixture behaves as a hypothetical pure fluid with parameters σ_x and ϵ_x defined by

$$\epsilon_x \sigma_x^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta \epsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \quad (21)$$

We then write this expression in terms of the critical parameters to obtain

$$f_{x,0} = h_{x,0}^{-1} \sum_\alpha \sum_\beta x_\alpha x_\beta f_{\alpha\beta,0} h_{\alpha\beta,0} \quad (22)$$

Following Leland et al. (1968), the mixture size parameter is defined as

$$\sigma_x^3 = \sum_\alpha \sum_\beta x_\alpha x_\beta \sigma_{\alpha\beta}^3$$

or in terms of the critical parameters

$$h_{x,0} = \sum_\alpha \sum_\beta x_\alpha x_\beta h_{\alpha\beta} \quad (23)$$

These rules, "the so-called van der Waals one (vdW1)" mixing rules allow for the calculation of the pseudo critical constants for the mixture and the shape factors. It should be pointed out, however, that the ratios, eq 7 and 8, could in principle be solved for the mixture via eq 9 and 10, but this is almost an impossible task given the lack of experimental data and the infinite number of possible mixture combinations.

The radial distribution function for a fluid in nonequilibrium due to the presence of a shear is given by Green (1952)

$$g(\mathbf{r}, \gamma^{0s}) = g_0(r) + \nu(r)\mathbf{T} : \gamma^{0s} + \ldots \quad (24)$$

where γ^{0s} is the symmetric traceless strain rate, $\mathbf{T}$ is a tensor, and $\nu(r)$ is a scalar function of the intermolecular separation (r), temperature and density, which has units of inverse time. $g_0(r)$ is the equilibrium function as in eq 17. Given eq 24, one can show that the potential contribution to the viscosity η_u can be written in a form similar to eq 17 and 18, namely

$$\eta_u = \frac{2\pi}{15}\left(\frac{N}{V}\right)^2 \int r^3 \frac{du}{dr} \nu(r) \, dr \quad (25)$$

and for a mixture

$$\eta_u = \frac{2\pi}{15}\left(\frac{N}{V}\right)^2 \sum_\alpha \sum_\beta x_\alpha x_\beta \int r^3 \frac{du_{\alpha\beta}}{dr} \nu_{\alpha\beta}(r) \, dr \quad (25a)$$

By scaling the equations one obtains

$$\sigma_x^4 (\epsilon_x M_x)^{1/2} = \sum_\alpha \sum_\beta x_\alpha x_\beta \sigma_{\alpha\beta}^4 (\epsilon_{\alpha\beta} M_{\alpha\beta})^{1/2} \quad (26)$$

which we then write in terms of the ratios f and h to yield

$$h_{x,0}^{4/3} f_{x,0}^{1/2} M_x^{1/2} = \sum_\alpha \sum_\beta x_\alpha x_\beta h_{\alpha\beta,0}^{4/3} f_{\alpha\beta,0}^{1/2} M_{\alpha\beta}^{1/2} \quad (27)$$

We note that this mass mixing rule differs from that derived by Mo and Gubbins (1976) by considering the generalized Enskog theory. This difference arises because the Enskog theory essentially applies to the kinetic regime and therefore scales as $\epsilon^{1/2} M^{1/2} \sigma^{-2}$. Hence eq 22, 23, and 27 are

the mixing rules required to evaluate the ratios of eq 7 and 8, and hence the viscosity, eq 1. Combining rules are needed finally and these were selected to be

$$f_{\alpha\beta,0} = (f_{\alpha,0}f_{\beta,0})^{1/2}(1 - k_{\alpha\beta}) \qquad (28)$$

$$h_{\alpha\beta,0} = \frac{1}{8}(h_{\alpha,0}^{1/3} + h_{\beta,0}^{1/3})^3(1 - l_{\alpha\beta}) \qquad (29)$$

and

$$M_{\alpha\beta} = 2M_\alpha M_\beta/(M_\alpha + M_\beta) \qquad (30)$$

where $k_{\alpha\beta}$ and $l_{\alpha\beta}$ are correction factors or binary interaction parameters with values close to zero. Although it is well known that thermodynamic calculations (especially phase equilibria) can be sensitive to their numerical value, this does not appear to be true for the viscosity; hence they were set equal to zero for the results reported in this article.

Evans and Hanley (1979) examined formally the assumptions of the conformal solution theory and tested the mixing rules via computer simulation. For the purposes of this work the conclusions were that, although they are not exact, the vdWl mixing rules are satisfactory if the components of a mixture are not too dissimilar; i.e., the appropriate critical parameters are within about a factor of *two*. However, *even* if two parameter corresponding states is obeyed *exactly*, the radial distribution functions g and ν do not obey equations such as eq 13 if this factor is exceeded. Hence the one-fluid model breaks down. This result is confirmed by experience since we have found that, although our approach works remarkably well over a wide experimental range for a wide class of systems, some difficulty is apparent in representing mixtures whose species differ by a size factor greater than *three* in the critical volume. The methane–decane system is an example and is discussed further in a later section.

Summary of the Calculation Procedure

A summary of the calculation procedure to evaluate a viscosity from eq 1 is as follows. Input parameters are the critical temperature, density or volume, pressure, acentric factor, and molecular weight of each component of the mixture of interest. These parameters for the reference fluid are required with an equation of state and some functional form of the viscosity for this fluid.

Typical experimental input would be the pressure, temperature, and mixture composition. The density of the fluid or mixture is obtained by finding the equivalent pressure of the reference substance via the ratio $p_0 = p_x h_{x,0}/f_{x,0}$ from the corresponding pressure in the mixture, p_x. Initially the shape factors in the ratios 7 and 8 are set to unity. Given $p_0 = p(\rho_0,T_0)$, the density ρ_0 follows. Thus, a first guess of the density is that from eq 3. Repeated iterations using eq 11 and 12 give the final density. Having, therefore, final values of ρ, $f_{x,0}$, and $h_{x,0}$, one can evaluate F_η of eq 2 and ρ_0 and T_0 and hence $\eta_0(\rho_0,T_0)$ of eq 1, thereby obtaining a value for $\eta_x(\rho,T)$.

The Reference Fluid: Extended Equations for Methane

It should be stressed that the procedure outlined in the previous section does not in principle place restrictions on the choice of the reference fluid and, especially, the reference fluid does not have to be a component of the mixture. Nonetheless, common sense suggests that the reference fluid should be similar to the systems of interest. Methane was chosen for the earlier work because we were concerned mainly with the properties of LNG and the light hydrocarbons. Since the object of this work is to study the heavy hydrocarbons in particular, it would seem appropriate to select a fluid such as hexane or decane, or say
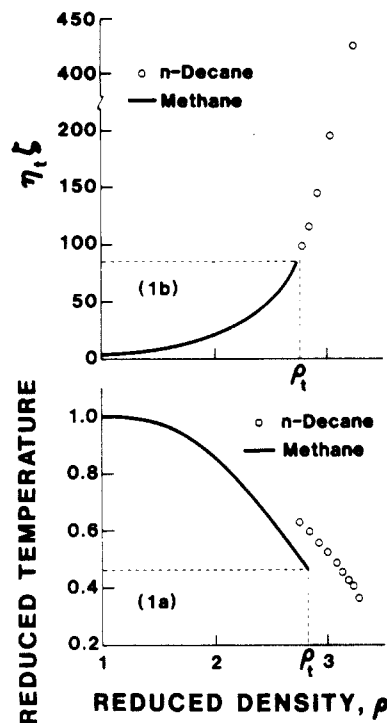

Figure 1. (a) Comparison of reduced density of methane and *n*-decane as a function of reduced temperature. (b) Comparison of scaled viscosity of methane and *n*-decane as a function of reduced density. ζ is defined eq 5. Note the broken scale on the $\eta\zeta$ axis above 200.

benzene if the mixtures contained a high proportion of aromatics, for the reference fluid. Unfortunately, at this time, methane is the only fluid which has sufficient reliable data correlated over a wide range of experimental conditions for the equation of state, the viscosity, and the thermal conductivity. Methane was therefore selected as the reference for this work. One can anticipate problems; for example, lack of conformality between methane and the mixutres, effects of internal degrees of freedom, of hindered rotation, and so on. In practice, a more obvious difficulty occurs: methane freezes at a reduced temperature of 0.48 which is well above the reduced temperatures commonly encountered for the liquid states of fluids as simple as propane. This is demonstrated in Figure 1a where we plot the saturated liquid density for methane and *n*-decane in terms of T^* and ρ^*. One sees that the range of states of *n*-decane is simply not covered by those of methane, and similarly for the viscosity as is shown in Figure 1b in which $\eta(\rho,T)\zeta$ is plotted vs. ρ^*, where ζ was defined by eq 5. Again the data for liquid methane terminate due to freezing well before the freezing point of decane is reached.

PVT. To overcome these difficulties an extended methane equation of state was constructed. The basic form of this equation is the 32 term BWR type proposed by Jacobsen and Stewart (1973) which has been extensively used by McCarty (1974). In order to force this equation to extrapolate properly to low temperatures and high pressures, the vapor pressure, orthobaric densities, and heat capacity of saturated liquid methane were extrapolated to 40 K and fitted with the data tabulated by Goodwin (1974). In addition, the recent data of Trappeniers et al. (1979) which extend to 2600 bar were included in the fitting process. The functional form of the equation of state and the resulting coefficients are given in Table I. The average absolute deviation between the calculated and experimental densities obtained in this procedure was less than 0.2% over the entire, extended *PVT* surface.

Table I. Reference Fluid Equation of State Coefficients[a]

$$p = \sum_{n=1}^{9} a_n(T)\rho^n + \sum_{n=10}^{15} a_n(T)\rho^{2n-17}e^{-\gamma\rho^2}$$

$a_1 = RT$

$a_2 = N_1 T + N_2 T^{1/2} + N_3 + N_4/T + N_5/T^2$

$a_3 = N_6 T + N_7 + N_8/T + N_9/T^2$

$a_4 = N_{10}T + N_{11} + N_{12}/T$

$a_5 = N_{13}$

$a_6 = N_{14}/T + N_{15}/T^2$

$a_7 = N_{16}/T$

$a_8 = N_{17}/T + N_{18}/T^2$

$a_9 = N_{19}/T^2$

$a_{10} = N_{20}/T^2 + N_{21}/T^3$

$a_{11} = N_{22}/T^2 + N_{23}/T^4$

$a_{12} = N_{24}/T^2 + N_{25}/T^3$

$a_{13} = N_{26}/T^2 + N_{27}/T^4$

$a_{14} = N_{28}/T^2 + N_{29}/T^3$

$a_{15} = N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4$

i/N_i		i/N_i	
1	-1.184347314485E-2	17	1.071143181503E-5
2	7.540377272657E-1	18	-9.290851745353E-3
3	-1.225769717554E+1	19	1.610140169312E-4
4	6.260681393432E+2	20	3.469830970789E+4
5	-3.490654409121E+4	21	-1.370878559048E+6
6	5.301046385532E-4	22	1.790105676252E+2
7	-2.875764479978E-1	23	1.615880743238E+6
8	5.011947936427E+1	24	6.265306650288E-1
9	-2.821562800903E+4	25	1.820173769533E+1
10	-2.064957753744E+5	26	1.449888505811E-3
11	1.285951844828E-2	27	-3.159999123798E+1
12	-1.106266656726E+0	28	-5.290335668451E-6
13	+3.060813353408E-4	29	1.694350244152E-3
14	-3.174982181302E-3	30	8.612049038886E-9
15	5.191608004779E+0	31	-2.598235689063E-6
16	-3.074944210271E-4	32	3.153374374912E-5

[a] Units: p, atm; ρ, mol/L; T, K. γ = 0.0096; R = 0.08205616; 0.101325 MPa = 1 atm.

Viscosity. A simple extrapolation of the methane viscosity surface to high values of ρ^* was not possible because the derivative $(\partial\eta/\partial\rho)_T$ is very large if $\rho^* \gtrsim 2.5$. Note the scale in Figure 1b. It was therefore decided to calculate pseudo methane viscosity data in the high density region and then to fit the pseudo and real methane data to some functional form for η_0 of eq 1. Pseudo data were derived from eq 1 in the form

$$\eta_0'(\rho_0,T_0) = \eta_\alpha^{exp}(\rho_\alpha, T_\alpha)/F_\eta \qquad (31)$$

where η_0' is the pseudo or equivalent methane viscosity and η_α^{exp} is some selected value for a heavy hydrocarbon. We chose propane as the representative hydrocarbon, i.e., the α species.

Initial attempts produced results such as those illustrated in Figure 2 which shows the deviation between the pseudo methane values from eq 31 and our previous "exact" correlation (Hanley et al., 1974) plotted against equivalent methane density. Two features are apparent: (1) an apparent noncorrespondence in the viscosity to equivalent densities of $\rho = 27.5$ mol/L, and (2) definite breakdown of the original methane correlation if it is extrapolated below the triple point. Similar figures were observed with other hydrocarbons selected for α fluid. In fact it was interesting to observe how similar the figures were for the wide range of carbon numbers C_3–C_{20}. It is impossible to differentiate a priori between a failure in the viscosity to correspond or in a failure of the density to correspond since obviously a failure in the latter will automatically distort the viscosity evaluation. Failures in the
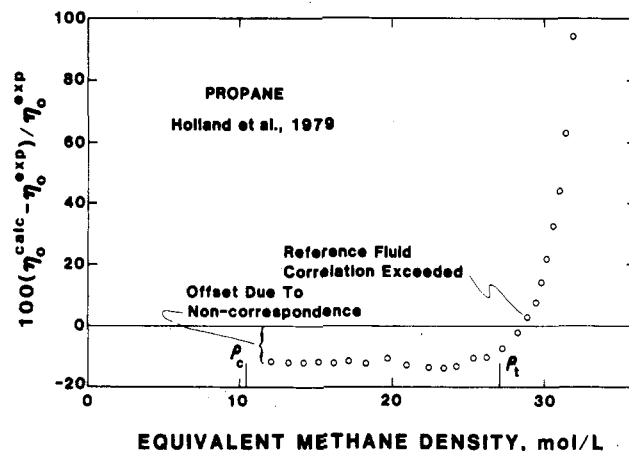

Figure 2. Comparison of calculated and pseudo methane viscosity data for propane. The propane data used in this calculation came from the correlation of Holland et al. (1979).

Table II. Coefficients for Shape Factor Correlations

θ coefficients (eq 13)	ϕ coefficients (eq 14)
$a_1 = 0.090569$	$a_2 = 0.394901$
$b_1 = -0.862762$	$b_2 = -1.023545$
$c_1 = 0.316636$	$c_2 = -0.932813$
$d_1 = -0.465684$	$d_2 = -0.754639$

density should be considered possible because the Leland–Leach formulas are set equal to a constant at low reduced temperatures, eq 15–16. This possibility can essentially be eliminated as follows. Given the equation of state for methane and for the fluid α [propane (Goodwin, 1979)], eq 7 and 8 were solved simultaneously to obtain the reducing ratios $f_{\alpha,0}$ and $h_{\alpha,0}$. In addition, shape factors for the C_2–C_{20} normal paraffins were obtained by solving the ratios $\rho_0 = \rho_\alpha{}^\sigma h_{\alpha,0}$ and $p_0 = p_\alpha{}^\sigma h_{\alpha}/f_\alpha$ given densities and pressures at saturation, superscript σ. The shape factors from both sets of calculations (which incidently agreed very well with those predicted by the Leland-Leach correlations above reduced temperatures of 0.5) were then refit to the functional forms of eq 11 and 12 with the constraint on T^* (eq 15) eliminated. The resulting coefficients are given in Table II. Using these shape factors to calculate the equivalent methane viscosity and density gave almost identical curves as shown in figure 2, so we concluded that the offset in density to 27.5 mol/L was in fact due to a noncorrespondence in the viscosity.

That the viscosity does not correspond was discussed in a qualitative manner by Hanley (1976) who introduced an X_η factor in the viscosity equation and proposed a form for it based on the modified Enskog theory (Hanley et al., 1972). Here we have adopted a slightly simpler expression

$$X_\eta = \left\{ \left[1 - \psi\frac{T_x}{f_{x,0}}\left(\frac{\partial f_{x,0}}{\partial T_x}\right)_{V_x} \right] \frac{Z_x{}^c}{Z_0{}^c} \right\}^{1/2} \qquad (32)$$

where $\psi = 1.5$ and for a mixture $Z_x{}^c = \sum_\alpha x_\alpha Z_\alpha{}^c$. This expression, which is always close to unity, has a basis in the Enskog theory in that the density dependence of the viscosity is strongly dependent on the derivative $(\partial p/\partial T)_v$.

Following our earlier correlation for methane, we therefore proposed the functional form for the viscosity to be

$$\eta_0(\rho_0,T_0) = \eta_0{}^{(1)}(T_0) + \eta_0{}^{(2)}(T_0)\rho_0 + \Delta\eta_0(\rho_0,T_0)X_\eta \qquad (33)$$

where $\eta_0{}^{(1)}$ and $\eta_0{}^{(2)}$ represent the dilute gas and first density correction, respectively, while $\Delta\eta$ is a remainder which dominates the viscosity at high density.

Table III. Reference Fluid Viscosity Correlation[a] $(T, K; \rho, g/cm^3)$

$$\eta(\rho,T) = \eta_0(T) + \eta_1(T)\rho + \Delta\eta(\rho,T)$$

i	a_i	b_i	c_i
1	$-1.0239160427E+1$	$1.6969859271E+0$	$2.9077413Q7E+6$
2	$1.7422822961E+2$	$-1.3337234608E-1$	$-3.312874033E+6$
3	$1.7460545674E+1$	1.4	$1.608101838E+6$
4	$-2.8476328289E+3$	$1.68E+2$	$-4.331904871E+5$
5	$1.3368502192E-1$		$7.062481330E+4$
6	$1.4207239767E+2$		$-7.116620750E+3$
7	$5.0020669720E+3$		$4.325174400E+2$
8			$-1.445911210E+1$
9			$2.037119479E-1$

[a] $\eta_0 = \Sigma_{n=1}^9 c_n T^{(n-4)/3}; \eta_1 = b_1 + b_2[b_3 - \ln(T/b_4)]; \Delta\eta = \exp\{a_1 + a_2/T\}\{\exp[(a_3 + a_4/T^{3/2})\rho^{0.1} + (\rho/\rho_c - 1)\rho^{0.5}(a_5 + a_6/T + a_7/T^2)] - 1.0\}$.
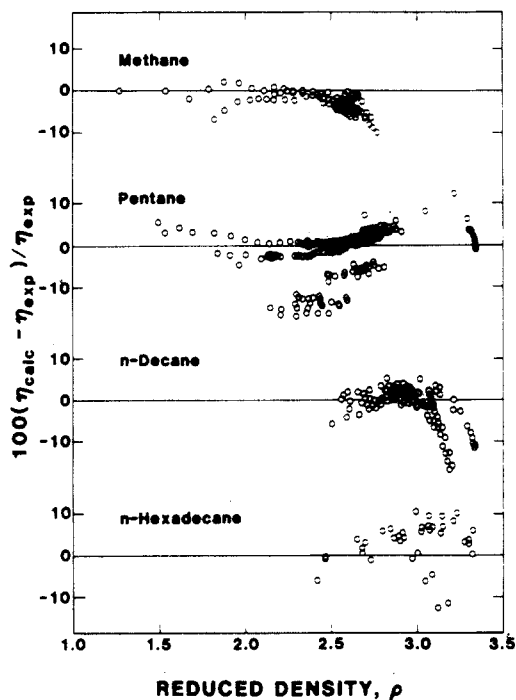

Figure 3. Comparison of calculated and experimental viscosity of methane, pentane, decane, and hexadecane as a function of reduced density. Literature references are given in Table IV.

Having selected the factor X_η, equivalent methane viscosities for $\Delta\eta_0$ were defined by

$$\Delta\eta_0(\rho_0,T_0) = [\eta_\alpha^{exp}(\rho_\alpha,T_\alpha)/F_\eta - \eta_0^{(1)}(T_0) - \eta_0^{(2)}(T_0)\rho_0]X_\eta^{-1} \quad (34)$$

and were calculated for approximately 200 data points for the normal paraffins C_1-C_{14}. Final coefficients for the methane viscosity are given in Table III.

Results for Pure Fluids

Having, therefore, the reference equation of state for methane, Table I and the equation for the viscosity, Table III, it was straightforward to calculate the viscosity of pure species α by eq 1. A considerable data base was assembled to provide a thorough test of the procedure and Table IV lists the fluids and appropriate references. The data were evaluated as far as possible for accuracy and internal consistency. One should point out that in general the data situation is not too satisfactory in that more recent accurate experimental techniques, such as the oscillating piezoelectric crystal have not been applied to many organic liquids other than methane, and recently to ethane and propane (Diller, 1981). A realistic guess as to the accuracy of the data quoted is 5-15% and probably much worse for the very heavy species.
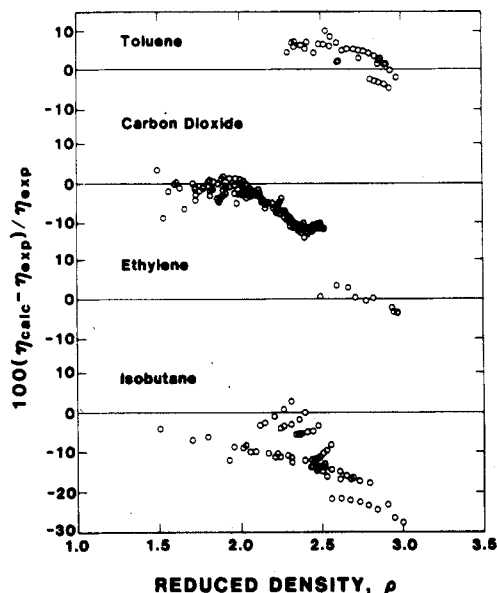

Figure 4. Comparison of calculated and experimental viscosity for toluene, carbon dioxide, ethylene, and isobutane. See Table IV for literature references.

The results are summarized in Table V and in Figures 3 and 4. Results from the method of Jossi et al. (1962) are included in Table V because this latter method is fairly standard for pure hydrocarbon liquids, so one can obtain a feel for the agreements from our method. Shown are the average absolute percent deviation, AAD, the average percentage error, BIAS, and the maximum error, MAX. Unfortunately, the maximum error is not a good measure of the reliability of the method since it usually reflects the high degree of uncertainty in some of the experimental data.

The overall deviations between experiment and eq 1 are very satisfactory. They become somewhat worse, and negative, as the freezing point of the fluid is approached. It is not clear why this should be the case but one can say that there is a good chance that the fluids become non-Newtonian in this region and that pre-freezing nucleation effects are important. One also observes that the results are maredly worse for highly branched alkanes and for the naphthenes. We attribute this to a failure of the corresponding states model to represent adequately the effect of the internal degrees of freedom on the transport coefficient. In spite of these limitations the overall results are excellent, especially considering the limited input $(T_c, p_c, V_c,$ and $\omega)$ needed to make the predictions.

Results for Mixtures

The main objective of this work was to develop a procedure to predict the transport properties of mixtures: there is a real need for such a procedure, yet none exists

Table IV. Pure Fluid Viscosity Data Sources

fluid	sources
CH_4	Huang et al. (1966); Boon et al. (1967); Haynes (1973)
C_2H_6	Van Itterbeek and Van Pamael (1941); Gerf and Galkov (1941); Gerf and Galkov (1940); Swift et al. (1960)
C_3H_8	Swift et al. (1959, 1960); Lipkin et al. (1942); Gerf and Galkov (1941); Evans (1938); Carmichael et al. (1964); Huang et al. (1966)
n-C_4H_{10}	Dolan et al. (1963); Swift et al. (1960); Lipkin et al. (1942); Kuenen and Wisser (1913); Eakin (1962); Sage et al. (1939)
i-C_4H_{10}	Lipkin et al. (1942); Sage et al. (1939); Gonzalez and Lee (1966)
n-C_5H_{12}	Thorpe and Rodger (1894); Vargaftik (1975); Giller and Drickamer (1949); Reamer et al. (1959); Agaev and Golubev (1963); Lee et al. (1965)
neo-C_5H_{12}	Gonzalez and Lee (1968); Phibbs (1951); Van Wijk et al (1940)
n-C_6H_{14}	Medani and Hason (1977); Vargaftik (1975); Thorpe and Rodger (1894); Khalilov (1939); Eicher and Zwolinski (1972); Giller and Drickamer (1949)
i-C_6H_{14}	Thorpe and Rodger (1894)
n-C_7H_{16}	Vargaftik (1975); Thorpe and Rodger (1894); Khalilov (1939); Johnston and LeTourneau (1953); Giller and Drickamer (1949); Agaev and Golubov (1963)
n-C_8H_{18}	Agaev and Golubov (1963); Vargaftik (1975); Thorpe and Rodger (1894); Schmidt et al. (1941); Doolittle and Peterson (1951); Giller and Drickamer (1949)
n-C_9H_{20}	Doolittle and Peterson (1951); Bingham and Fornwalt (1930); Rastorguyev and Keramidi (1974)
n-$C_{10}H_{22}$	Lee and Ellington (1965); Giller and Drickamer (1949); Rastorguyev and Keramidi (1974)
n-$C_{11}H_{24}$	Doolittle and Peterson (1951); Bingham and Fornwalt (1930); Schmidt et al. (1941)
n-$C_{12}H_{26}$	Evans (1938); Bingham and Fornwalt (1930); Hogenboon et al. (1967); Giller and Drickamer (1949); Dixon et al. (1967)
n-$C_{13}H_{28}$	Doolittle and Peterson (1951); Schmidt et al. (1941); Rastorguyev and Keramidi (1974)
n-$C_{14}H_{30}$	Rastorguyev and Keramidi (1974); Ubbelohde and Agthe (1913); Giller and Drickamer (1949)
n-$C_{15}H_{32}$	Hogenboom et al. (1967); Dixon et al. (1967)
n-$C_{16}H_{34}$	Nederbragt and Boelhouwer (1956); Ubbelohde and Agthe (1913); Evans (1938); Rastorguyev and Keramidi (1974)
n-$C_{17}H_{36}$	Doolittle and Peterson (1951); Schmidt et al. (1941)
n-$C_{18}H_{38}$	Hogenboom et al. (1967); Ubbelohde and Agthe (1913); Dixon et al. (1967)
n-$C_{20}H_{42}$	Dixon et al. (1967); Vargaftik (1975)
C_2H_4	Gerf and Galkov (1940); Comings et al. (1944)
C_3H_6	Gerf and Galkov (1940, 1941)
3-methyl-1-butene	Thorpe and Rodger (1894)
C_6H_{12}	Vargaftik (1975); Weight (1961)
cyclohexane	Friend and Hargreaves (1944); Evans (1938); Kuss (1955); Jonas et al (1980)
methylcyclohexane	Friend and Hargreaves (1944); Eyring (1936)
ethylcyclohexane	Geist and Cannon (1946); Caozier (1955); Ubbelohde and Agthe (1913)
cyclopentane	Evans (1938); Chavahne and ven Ryssegham (1922)
benzene	Vargaftik (1975); Kuss (1955); Medani and Hasan (1977); Heiks and Orban (1956)
toluene	Medani and Hasan (1977); Heydweiller (1895); Thorpe and Rodger (1895); Kyropoylous (1932); Vargaftik (1975)
m-xylene	Mamedov et al. (1966)
propylbenzene	Evans (1938)
butylbenzene	Evans (1938)
carbon dioxide	Herreman et al. (1970)

which does not require in some way transport data of the pure components. Our method, however, avoids this and the mixture evaluations are no more complicated than those for the pures, given the mixing rules, eq 22, 23, and 27. It is also worth remarking that the procedure also gives the mixture density automatically.

One further refinement was considered for mixtures. We introduced an X_η factor in eq 32 to account for lack of correspondence between the reference fluid and a pure fluid of interest. For mixtures, however, the X_η will act as a correction not only for lack of correspondence between reference fluid 0 and the hypothetical pure fluid x, but should also account for the basic lack of conformality in the mixture. It turns out that although most of the mixtures studied cannot be conformal, the procedure works reasonably well with $X_\eta \simeq 1.0$. Our results did show, however, a systematic diagreement with experiment in one special case, namely when the components of the mixture differed substantially in effective size, e.g., in the values of the critical volume. In particular, initial calculations for the methane/n-decane mixture viscosity (Lee et al., 1966) showed large deviations at high densities as the mole fraction of methane increased. In effect, the contribution of methane to the mixture viscosity was negligible until $x_{CH_4} \approx 0.9$ and the procedure over estimated it. For this system $(V_{dec}/V_{CH_4}) \approx 6$.

A plausible explanation of this behavior, and similar failures due to lack of conformality, follows from some nonequilibrium molecular dynamic studies of mixtures (Hanley and Evans, 1981). It was shown that the local or ambient mole fractions in a mixture with large molecular size differences can be substantially different from the bulk or average value. For instance, it was shown that a simulated 50/50 mixture of methane/n-decane corresponded to an effective 15/85 decane-rich mixture. Moreover, the thermophysical properties of such a mixture including the viscosity are controlled by the local, not by the average mole fractions. This is because the properties of the system depend largely on short range molecular forces.

Since a methane/decane type mixture is relatively common, we attempted to account for the size effect empirically in the present model. The correction factor X_η was modified to become

$$X_\eta = \left\{ \left[1 - \psi \frac{T_x}{f_{x,0}} \left(\frac{\partial f_{x,0}}{\partial T_x} \right)_{V_x} \right] \frac{Z_x^c}{Z_0^c} \right\}^{1/2} \left\{ \frac{a + b\bar{R}}{1 + c\bar{R}} \right\} \quad (35)$$

where

$$\bar{R}^{-1} = \sum_\alpha x_\alpha (V_\alpha^c / V_{min}^c)^{1/3} \quad (36)$$

and $a = 0.16129$, $b = -4.51613$, and $c = -5.35484$. V_{min}^c

Table V. Summary of Calculated Results for Pure Fluids (AAD = Average Absolute Percent Deviation; BIAS = Percentage Bias)

| fluid	N	this work			Jossi, Stiel, Thodos		
		AAD	BIAS	MAX	AAD	BIAS	MAX
methane	76	3.03	−2.89	−10.11	5.73	−1.25	31.85
ethane	48	12.31	9.99	25.27	10.09	4.76	25.40
propane	146	6.56	−5.10	21.65	13.24	−11.99	−83.02
n-butane	200	3.39	−2.80	9.77	5.23	−3.59	−14.79
isobutane	68	11.49	−11.39	−27.80	5.77	−3.87	−53.53
n-pentane	195	4.15	−1.49	−16.84	9.99	−7.03	−15.30
neopentane	75	32.83	−32.83	−49.21	37.90	−37.57	−47.98
n-hexane	66	3.30	2.16	13.76	6.90	−5.49	37.47
isohexane	12	3.09	−3.09	−3.75	10.28	−10.28	−12.26
n-heptane	78	6.31	3.45	−19.6	10.14	−6.00	−49.85
n-octane	52	6.22	4.30	19.73	7.56	−5.22	−28.05
n-nonane	46	2.89	1.54	−9.00	6.45	−5.56	−21.04
n-decane	107	3.25	−1.56	−16.68	16.32	−16.32	−35.12
n-undecane	19	3.47	1.29	−8.96	21.09	−21.09	−34.70
n-dodecane	41	5.12	1.19	19.87	27.24	−27.24	−42.00
n-tridecane	58	4.69	−1.12	−22.76	33.88	−33.88	−50.39
n-tetradecane	53	5.04	−2.97	−25.59	44.11	−44.11	−60.42
n-pentadecane	18	5.37	−2.23	−13.53	48.51	−48.51	−55.80
n-hexadecane	39	5.33	2.08	−18.67	52.82	−52.82	−60.17
n-heptadecane	15	6.11	3.56	−10.11	60.83	−60.83	−67.91
n-octadecane	28	9.66	5.89	22.09	66.57	−66.57	−75.29
n-eicosane	16	6.37	3.89	10.72	78.43	−78.43	−83.38
ethylene	10	2.02	−0.61	−3.81	21.72	−21.72	−38.64
propylene	13	9.72	3.18	24.67	32.52	−31.74	−72.34
3-methyl-1-butene	8	5.53	−5.53	−6.92	8.64	8.64	13.97
1-hexene	27	17.19	17.19	22.17	3.90	2.81	9.04
cyclohexane	48	49.25	−49.25	−69.33	48.57	−48.57	−66.88
methylcyclohexane	14	30.69	−30.69	−41.02	38.12	−38.12	−49.12
ethylcyclohexane	17	30.81	−30.81	−37.77	36.84	−36.84	−46.13
cyclopentane	10	29.20	−29.20	−31.91	28.89	−28.89	−31.44
benzene	82	8.39	−8.33	−30.01	14.16	−13.85	−35.81
toluene	47	4.13	3.17	9.52	15.06	−15.06	−24.91
m-xylene	16	20.35	20.35	27.02	3.70	0.22	9.41
propylbenzene	5	8.16	8.16	10.89	10.32	10.32	14.65
butylbenzene	5	12.12	12.12	14.73	13.76	13.76	19.03
carbon dioxide	111	4.75	−4.75	−13.77	7.04	−5.14	17.59
overall	1869	8.42	−4.10		17.71	−15.71	
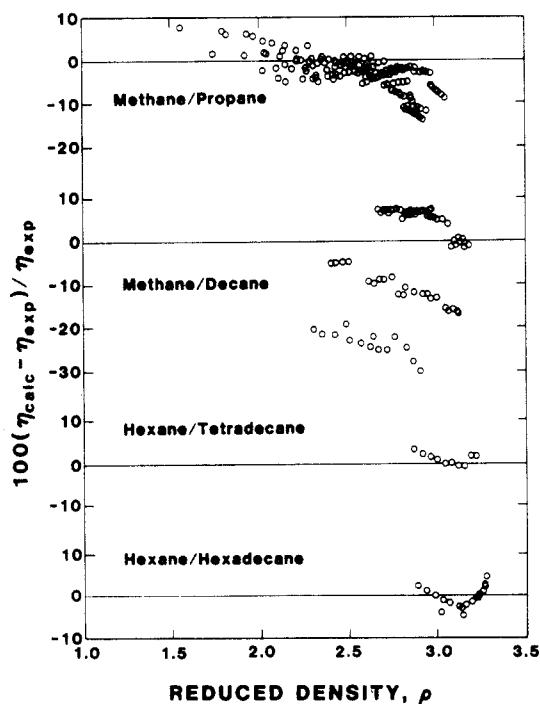
Figure 5. Comparison of calculated and experimental viscosity of selected paraffin binary mixtures as a function of reduced density. See Table VI for literature references.

is the critical volume of the smallest component in the mixture. It should be noted that for most mixtures, results
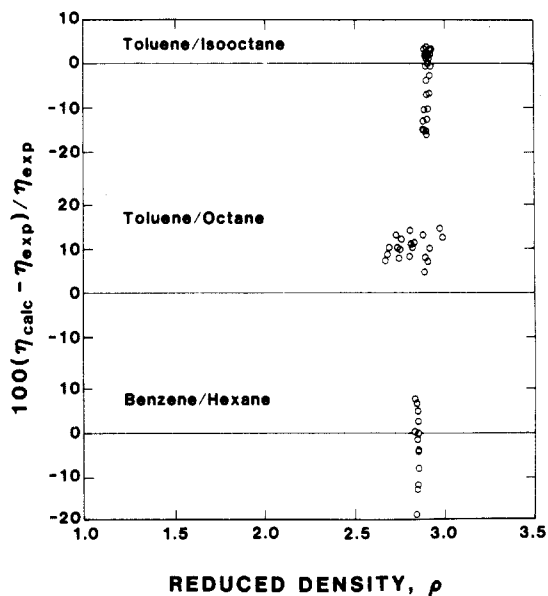
Figure 6. Comparison of calculated and experimental viscosity of selected aromatic/paraffin binary mixtures.

from eq 35 are very close to that from eq 32 and in fact that X_η is often ≈ 1.

Table VI lists the mixtures, data sources, number of points considered, and the ADD and BIAS between experiment and our procedure. Figures 5 and 6 are typical of the deviations observed. In general, the results are

Table VI. Summary of Literature References and Results for Binary Mixtures

component 1	component 2	source(s)	N	AAD	BIAS
methane	propane	Huang et al. (1967)	134	3.86	−2.85
	n-nonane	Bennett (1966)	32	9.56	8.12
	n-decane	Lee et al. (1966)	71	10.62	−5.80
2,3-dimethylbutane	n-octane	Dixon (1959)	2	5.04	−5.04
n-hexane	2,3-dimethylbutane	Dixon (1959)	2	5.19	5.19
	n-tetradecane	Heric and Brewer (1967)	10	1.23	0.99
	n-hexadecane	Dixon (1959); Heric and Brewer (1967)	26	1.84	−0.58
n-heptane	n-dodecane	Trevoy and Drickamer (1949)	3	4.32	4.32
	n-tetradecane	Trevoy and Drickamer (1949)	3	2.47	2.47
	n-hexadecane	Trevoy and Drickamer (1949)	3	1.96	−0.24
	n-octadecane	Trevoy and Drickamer (1949)	2	1.73	0.27
	methylcyclohexane	Mussche and Verhoeye (1975)	24	17.31	−16.51
2,2,3-trimethylbutane	2,3,3-trimethylpentane	Dixon (1959)	2	29.93	−29.93
n-octane	n-decane	Dixon (1959)	2	3.83	3.83
n-tetradecane	n-hexadecane	Heric and Brewer (1967)	11	2.73	2.53
benzene	n-hexane	Heric and Brewer (1967)	15	6.02	−1.58
	n-heptane	Trevoy and Drickamer (1949)	3	6.58	6.56
	2,2,4-trimethylpentane	Mussche and Verhoeye (1975)	26	11.21	−11.21
	n-decane	Trevoy and Drickamer (1949)	3	5.68	4.00
	n-dodecane	Trevoy and Drickamer (1949)	3	7.04	7.04
	n-tetradecane	Trevoy and Drickamer (1949)	3	3.41	3.27
	n-hexadecane	Trevoy and Drickamer (1949)	3	3.57	2.46
	n-octadecane	Trevoy and Drickamer (1949)	3	2.79	2.79
toluene	n-heptane	Mussche and Verhoeye (1975)	21	6.09	6.09
	n-octane	Ling and Van Winkle (1958)	20	10.14	10.14
	2,2,4-trimethylpentane	Mussche and Verhoeye (1975)	28	5.87	−3.40
overall			455	6.95	−2.07

excellent with an average absolute percent deviation of approximately 7%. An assessment of the method should, however, bring to mind that the data situation for mixtures is not very good; an assignment of 5–20% on the accuracy of the data is reasonable.

Conclusion

We have presented a predictive procedure to estimate the viscosity of nonpolar pure fluids and mixtures over the entire range of fluid states, from the dilute gas to the dense liquid. Extensive comparisons with data show that the viscosity of a range of pure fluids—C_1–C_{20}, aromatics and others—is predicted to within an absolute percent deviation of about 8% and a similar range of mixtures shows that the viscosity is represented to within about 7%. Not shown in this paper are comparisons for the density, which is also predicted, and for the viscosity of the dilute gas. In general, the density is predicted to better than 1% and the dilute gas viscosity is predicted to within 5–10%.

The basis of the method is the one-fluid corresponding states concept with the extended corresponding states approach included. The method is *predictive* and requires only the common characterization parameters of the pures as input: T^c, p^c, V^c, ω, and M. The number of components of a mixture which can be considered is, in princple, unrestricted.

The thermal conductivity will be discussed in another paper. The application of the approach to polar fluids and to molecules with a structure which could cause hindered rotation and stearic effects is under investigation.

Computer Program

A computer program for predicting the transport properties (viscosity and thermal conductivity) and the density of pure fluids and their mixtures is available from the Gas Processors Association, Tulsa, Oklahoma, at a nominal cost. The program is essentially that used to generate the results reported here.

Acknowledgment

Nomenclature

A = Helmholtz free energy
E = internal energy
F = dimensional scaling factor for viscosity
M = molecular weight
N = number of molecules in a system
R = universal gas constant
$\bar{R}$ = average size ratio in a mixture, eq 34
T = absolute temperature
V = volume
X = viscosity noncorrespondence correction
Z = compressibility factor, pV/RT
$a, b, c, ...$ = correlation parameters
f = equivalent substance temperature reducing ratio
g = equilibrium radial distribution function
h = equivalent substance volume reducing ratio
k = energy binary interaction constant
l = volume binary interaction constant
p = absolute pressure
r = intermolecular separation
u = intermolecular pair potential function
x = mole fraction

Greek Letters

γ = strain rate
ϵ = intermolecular potential well depth
ζ = classical corresponding states viscosity scaling parameter
η = viscosity
θ = energy shape factor
ν = non-equilibrium radial distribution function
ρ = density
σ = intermolecular potential size parameter (hard sphere diameter)
ϕ = size shape factor
ψ = parameter in viscosity non-correspondence function eq 32

ω = Pitzer's acentric factor

Subscripts

α, β, ... = pure components or species in a mixture
$\alpha\beta$ = binary pair in a mixture
0 = reference fluid value
x = fluid of interest, mixture or pure
u = potential contribution

Superscripts

c = critical value
conf = configurational property
exp = experimental value
σ = saturation value
* = reduced by value at critical point

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