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Viscosity of Defined and Undefined Hydrocarbon Liquids Calculated Using an Extended Corresponding-States Model[1]

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We predict the viscosity of petroleum fractions using extended corresponding states. Our model builds upon the TRAPP procedure, which is the most advanced approach to predict transport properties of straight-chain nonpolar hydrocarbons and their mixtures. We perform comparisons with experimental viscosity data for pure hydrocarbons, treating them as nonstandard components; we find deviations of 10–15%. We also extend the model to predict the transport properties of petroleum fractions and compare with an experimental database of more than 80 crude oils, including highly aromatic petroleum fractions. The model predicts the viscosity of the crude oil fractions within experimental uncertainty.

KEY WORDS: corresponding states; petroleum fractions; viscosity prediction.

1. INTRODUCTION

Transport properties, such as viscosity, are important for petroleum reservoir simulation and design of oil production, transportation, and processing equipment for the chemical and petroleum industry. A viscosity model applicable to a wide range of compositions, temperatures, and pressures, including both the gaseous and the liquid phases, is highly desirable. This paper presents a reliable, self-consistent method to predict the viscosity of heavy petroleum fractions over a wide range of thermodynamic states from the dilute gas to the dense liquid.

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2. EXTENDED CORRESPONDING-STATES VISCOSITY MODEL

The power and versatility of corresponding states as a predictive tool for transport properties of both pure fluids and their mixtures have already been well demonstrated [1–4]. In the TRAPP corresponding-states model [3,4], the viscosity of a fluid η_i at density ρ and temperature T is related to the viscosity of a reference fluid η_0 at a corresponding-state point (ρ_0, T_0) by

$$\eta_i(\rho, T) = \eta_0(\rho_0, T_0)\, F_\eta \tag{1}$$

where

$$F_\eta = \sqrt{\frac{M_i}{M_0}}\, f_i^{1/2} h_i^{-2/3} \tag{2}$$

The subscript 0 refers to the reference fluid, the subscript i denotes the fluid of interest, and M is the molecular mass. The state points T_0 and ρ_0 are defined by

$$\begin{aligned} T_0 &= T/f_i \\ \rho_0 &= \rho h_i \end{aligned} \tag{3}$$

where f_i and h_i are equivalent substance reducing ratios, defined by

$$f_i = (T_{c,i}/T_{c,0})\, \theta_i(T_{r,i}, \rho_{r,i}, w_i) \tag{4}$$

$$h_i = (\rho_{c,0}/\rho_{c,i})\, \phi_i(T_{r,i}, \rho_{r,i}, w_i) \tag{5}$$

θ_i and ϕ_i are the shape factors which are functions of the reduced temperature $T_r = T/T_c$, reduced density $\rho_r = \rho/\rho_c$, and the acentric factor w. The subscript c denotes the critical point.

It is important to have a very thorough representation of the *PVT* surface of the reference fluid, and also to have an accurate method of determining the shape factors. For the reference fluid, we use a 32-term MBWBR equation of state for propane [5] that, except very near the critical region, is accurate in density to 0.1–0.2%. The use of shape factors [6] in corresponding-states models is known as "extended" corresponding states. For simple molecules such as argon, methane, and neon, the shape factors are 1, and the equivalent substance reducing ratios are simply ratios of the critical parameters. In principle, given detailed information about the Helmholtz energy and *PVT* surface of the pure fluid involved, shape factors may be determined *exactly* [7]. One also may use generalized expressions for θ and ϕ [3,4]. Here we apply an *approximate* method for determining the shape factors, which assumes that they are functions of temperature only [8], and force the saturation boundary of the pure fluids to match

$$\rho_i^{\mathrm{sat,liq}}(T) = \rho_0^{\mathrm{sat,liq}}(T/f_i)\, h_i \tag{6}$$

$$p_i^{\mathrm{sat}}(T) = p_0^{\mathrm{sat}}(T/f_i)\, \frac{f_i}{h_i} \tag{7}$$

A correlation for p^{sat} and $\rho^{\mathrm{sat,\,liq}}$ is used with Eqs. (6) and (7) to solve numerically for f and h.

3. EXTENSION OF THE MODEL TO PETROLEUM FRACTIONS

The corresponding-states procedure is very flexible and requires only minimal input about a fluid (the critical point, molecular mass, and the Pitzer acentric factor). Although many process streams are mixtures of defined hydrocarbons, an equally large percentage is characterized only as petroleum fractions. For these undefined (or nonstandard) fluids, very little in the way of exact physical properties is available; typically, only specific gravity and some type of average boiling point will be known. We follow an approach similar to that developed by Baltatu and co-workers [9, 10] and use *only* the mean average boiling point [11] and the specific gravity as input to our procedure. All other information used in our program (critical point, molecular mass, vapor pressures, acentric factor, and saturated liquid density) is generated from correlations described in the following paragraph.

We investigate three methods for estimating the critical point and the molecular mass: the Riazi [12], the Lee and Kesler [13], and the Twu [14] correlations. The Riazi correlations are based only on data for defined hydrocarbons but work very well for petroleum fractions and are recommended by the API Technical Data Book [15] as a standard estimation method. For vapor pressures, we use the Lee and Kesler [16] reformulation of the Maxwell–Bonnell [17] correlation, which is especially accurate for heavy hydrocarbons. For saturated liquid density, we use the COSTALD correlation [18]. Although developed for pure hydrocarbons, it is suitable for the calculation of the density of crude oil fractions as well. For consistency in our model, we calculate the acentric factor from its defenition using the vapor pressure correlation. Also, to reduce the uncertainty of the density predictions, we obtain the characteristic volume parameter V^* from the specific gravity as suggested by Baltatu and coworkers [19]. This method estimates the liquid density of petroleum fractions within about 0.3%.

4. RESULTS

Table I gives the results for viscosity of pure hydrocarbons treated as nonstandards (with only the normal boiling point and specific gravity as input) and also treated as defined hydrocarbons (with the critical point, acentric factor, and molecular mass as input). We define the average absolute deviation, aad, as $\sum \mathrm{Abs}[100(\eta_i^{\mathrm{calc}}-\eta_i^{\mathrm{exp}})/\eta_i^{\mathrm{exp}}]/n$, and the bias as $\sum[100\ (\eta_i^{\mathrm{calc}}-\eta_i^{\mathrm{exp}})/\eta^{\mathrm{exp}}]/n$, where n is the total number of points. A total of 1336 pure fluid points was used, including alkanes, alkenes, cycloalkanes, and alkylbenzenes; the references for the viscosity database are given in Ref. 20. The nonstandard viscosity predictions of all three methods for pure fluids are in close agreement and compare well with the results of the defined hydrocarbons. All of the models give predictions almost within the experimental uncertainty of the data. Unfortunately there is considerable inconsistency between different data sets for some fluids; the data sets themselves may differ as much as 15–20%. Figure 1 shows sample results for selected pure fluids (*n*-hexane, *n*-heptadecane, and *n*-eicosane) treated as nonstandard comonents using the Riazi method. There is agreement with experimental data regardless of the chain length of the paraffin (thus no upper limit on the boiling points).

Because of its simplicity, we used the Riazi method for the petroleum fraction work. The results for petroleum fraction cuts were generally good,

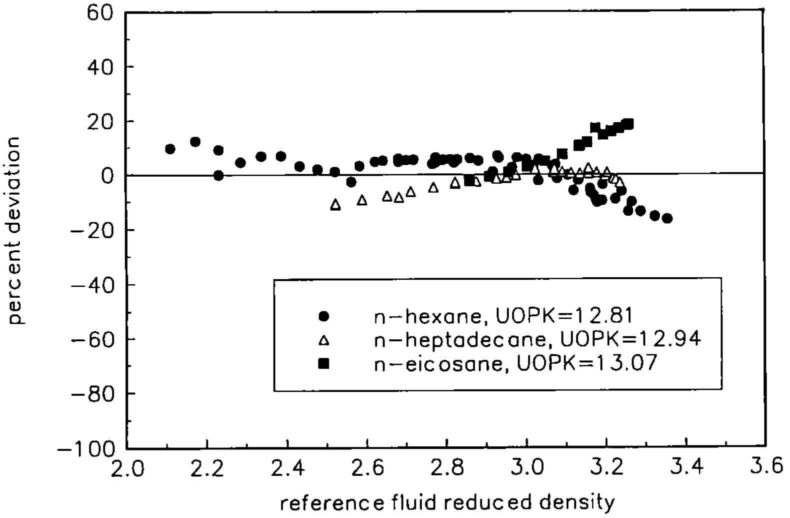

Fig. 1. Comparison of calculated and experimental viscosities for selected pure fluids treated as nonstandard components (input only specific gravity and boiling point).

Tabel I. Summary of Corresponding-States Results for Viscosity of Pure Hydrocarbons

				As undefined hydrocarbon mixtures (boiling point and specific gravity as input)								
	As defined hydrocarbons			Riazi			Twu			Lee–Kesler		
Fluid type	*n*	aad	bias	*n*	aad	bias	*n*	aad	bias	*n*	aad	bias
n-Paraffins	1301	4.89	−0.48	888	5.54	0.95	888	5.02	−0.21	884	5.48	−0.17
i-Paraffins	155	21.17	−21.17	315	23.10	−21.33	315	25.22	−18.6	311	26.71	−25.65
Alkenes	58	11.29	7.85	52	7.02	3.04	52	33.93	32.22	na	na	na
Cycloalkanes	89	40.56	−40.56	41	47.11	−47.11	41	47.24	−47.24	41	47.26	−47.26
Alkylbenzene	155	8.45	−0.69	40	7.02	3.04	40	4.09	1.00	40	6.51	2.18
Totals	1758	7.91	−1.14	1336	11.12	−5.93	1336	10.93	−6.01	1276	12.03	−8.33

although we noticed two problem areas, shown in Fig. 2. The first problem concerns the poor results for cyclohexane, even at relatively low densities. This can be attributed to the limitations of the model to represent adequately the effect of the internal degrees of freedom on the transport coefficients and can be corrected for pure hydrocarbons and their mixtures by means of a mass shape factor [20, 21]. This problem does not occur in petroleum fractions at low to moderate densities. We speculate that due to the tremendous number of discrete components in a petroleum fraction cut, the highly branched alkanes or naphthenes are dispersed between other molecules and their net effect on the viscosity of the whole crude is negligible at low densities. The second problem is related to prefreezing nucleation and is a function of the density and characteristics of the fraction such as aromaticity or naphthenicity. Figure 2 shows that for the naphthenic and aromatic petroleum fraction cuts, the calculated viscosity deviations increase dramatically with density at reduced densities of the reference fluid greater than 3. We observed the prefreezing nucleation effects to be proportional to the difference in the Watson characterization factor of the fraction and that of a straight-chain hydrocarbon with the same boiling point. This led us to develop a correction factor η_w such that Eq. (1) becomes

$$\eta_i(\rho, T) = [\eta_0(\rho_0, T_0)\, \eta_w(\Delta k_w, \rho_0)]\, F_\eta \tag{8}$$

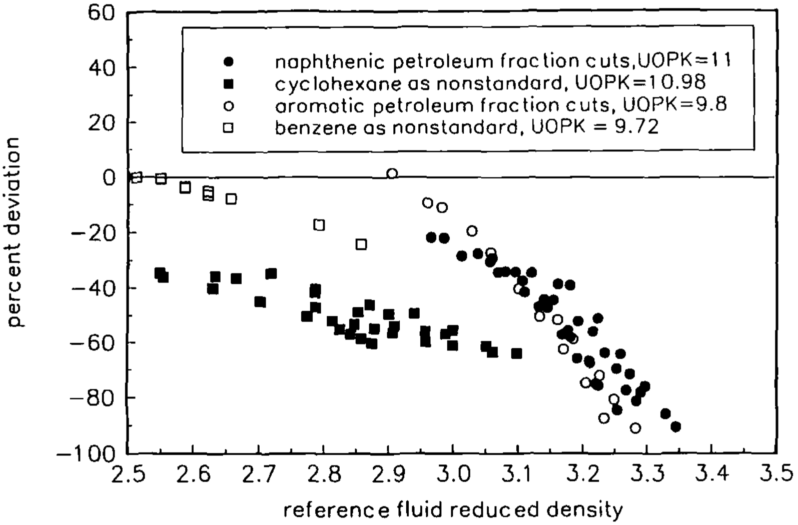

Fig. 2. Comparison of calculated and experimental viscosities for selected petroleum fraction cuts and nonstandard pure fluids with equivalent UOPK values.

with

$$\begin{aligned} \eta_{\mathrm{w}}(\Delta k_{\mathrm{w}}, \rho_0) &= (\Delta k_{\mathrm{w}})^3 \, (a_1 + a_2 \rho_{\mathrm{r},0} + a_3 (\rho_{\mathrm{r},0})^2) \\ \Delta k_{\mathrm{w}} &= 13.5 - k_{\mathrm{w}} \end{aligned} \tag{9}$$

In Eqs. (8) and (9) the Watson k factor (or UOPK factor) is $k_{\mathrm{w}} = (T_{\mathrm{b}}^{1/3}/\text{specific gravity})$ with T in °R, $\rho_{\mathrm{r},0}$, the reduced density of the reference fluid, $\rho_0/\rho_{0,\mathrm{c}}$, and the coefficients a_1, a_2, and a_3 are 5.7672, −3.9873, and 0.68932, respectively. We tested the model incorporating the correction factor given by Eqs. (8) and (9), using the Riazi method to estimate critical points and molecular mass, on over 2000 petroleum fraction data points. The crudes were chosen on the basis of geographical source and on whole crude oil specific gravity, with the objective of having as wide a variety as possible. The crude oil gravities range from −0.15 to 65° API with boiling points up to 910 K (1178°F). The results are summarized in Table II. Overall, the average absolute deviation is about 17%. This is actually good considering the large amount of inconsistency between different data sets (some sets differed from each other by as much as 40%) and the fact that viscosity is changing extremely rapidly as a function of density at high densities. Figure 3 demonstrates how the use of the correction factor in Eqs. (8) and (9) greatly improves the viscosity predictions at higher densities. This method gives results superior to existing viscosity prediction methods [31–34] and is applicable over the entire fluid range, not just in the liquid region. The method also is easily extended to mixtures through the use of mixing and combining rules.

Table II. Summary of Corresponding-States Results for Petroleum Fractions [22–30]

Fraction cut	No. points	Boiling point range (K)	API gravity range	aad	Bias
Midcontinent distillate	31	451–734	2.1–47.2	22.0	−6.2
Smackover distillate	8	505–676	21–33.1	13.4	7.7
Pennsylvania distillate/lube oils	11	518–744	28–43.4	15.5	11.4
fuel oils	11	516–573	29–37.8	15.9	−15.9
bottom and overhead stocks	99	435–628	16.5–49.9	34.2	−33.8
kerosene and gas oils	1	563	32.7	1.0	1.0
domestic crude oils	283	361–536	29.3–65.3	6.0	−5.3
foreign crude oils	282	353–672	25.7–62.2	9.2	6.2
domestic medium and high boiling pt. fractions	129	460–910	21.7–55.9	15.5	2.6
Arabian crude fractions	56	429–681	11.6–63.4	10.4	−7.5
misc. domestic and foreign crudes	145	404–869	17.3–36.6	25.4	−22.0
North Sea crudes	94	416–649	20.19–50.8	26.0	−17.7
South American oil fractions	6	486–726	21.8–53.6	26.6	0.1
Middle East crude fractions	768	421–876	22.2–52.1	19.5	7.9
US whole crudes	45	486–581	24.9–48.1	12.9	−6.9
ASME lube oils	30	663–814	20.1–50.1	29.6	−24.3
coal liquids	61	340–671	−0.15–64.1	30.6	−3.0
Total	2060	340–910	−0.15–65.3	17.4	−1.6

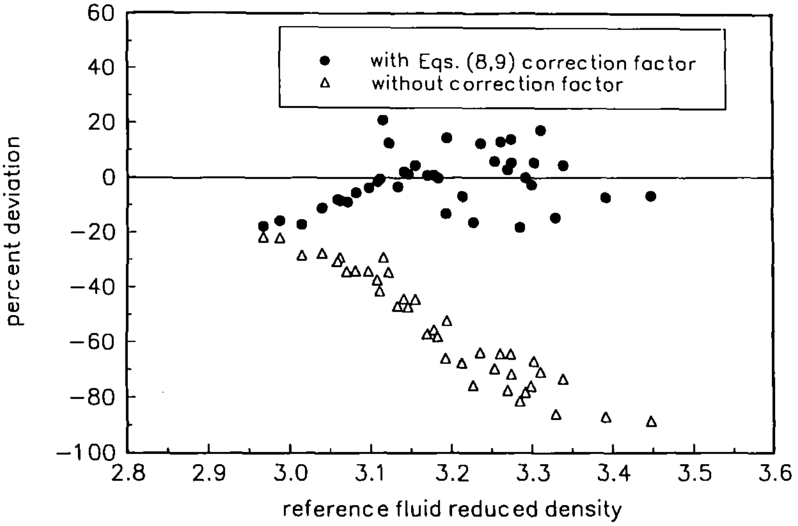

Fig. 3. Comparison of calculated and experimental viscosity for a crude oil fraction with UOPK = 11.2.

5. CONCLUSIONS

We have further extended the TRAPP extended corresponding-states viscosity model [3, 4] to predict the viscosity of heavy crude oil fractions. The model incorporates an improved scheme for calculating shape factors [9], as well as a new correction factor to account for anomalies in the behavior of heavy crudes at high densities. It is reliable and self-consistent, and requires only the specific gravity and mean average boiling point as input parameters. There is no limit on the magnitude of the boiling point range that can be considered. The viscosity of pure hydrocarbons, treated as nonstandard components, is predicted to within 10–15%. The viscosity of heavy crude fractions is predicted within about 17%. Future work will extend this model to predict viscosity of mixtures of hydrocarbons and petroleum fractions and also to predict the thermal conductivity of heavy petroleum fractions.

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