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Transport Properties of Petroleum Fractions[1]

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A corresponding-states model for the transport properties of petroleum fractions is presented. The model requires only the API specific gravity and the mean average boiling point as input parameters. The extended correspanding-states model uses propane as a reference fluid, and new generalized shape factor expressions that are functions of the acentric factor and the reduced temperature are presented. Also presented are new correlating functions for the viscosity and thermal conductivity of the reference fluid that can be extrapolated well below the freezing point of propane. The performance of the model is demonstrated by comparing with experimental data for viscosity and thermal conductivity of petroleum fractions.

KEY WORDS: corresponding states; petroleum fractions; propane; viscosity, thermal conductivity.

1. INTRODUCTION

In the design of oil processing equipment and in reservoir simulation studies, it is important to be able to predict accurate values of the viscosity and thermal conductivity of petroleum fractions over a wide range of temperatures and pressures. In this work we modify the TRAPP extended corresponding states model [1, 2] for application to petroleum fractions. This type of model is valid over a wide range of thermodynamic states, from the dilute gas to the dense fluid state.

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2. EXTENDED CORRESPONDING STATES MODEL

Various forms of extended corresponding states models have been used to predict the transport properties of standard hydrocarbons [3] and their mixtures, petroleum fractions [4, 5], as well as refrigerants and their mixtures [6, 7]. Following the original TRAPP corresponding states model [1, 2], 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 using

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

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, M is the molar mass, and f_i and h_i are functions called equivalent substance reducing ratios, that can depend upon both temperature and density.

The application of the model to thermal conductivity is very similar to that for the viscosity, except that we separate the thermal conductivity λ into two contributions: λ', arising from the transfer of energy from purely collisional or translational effects, and λ'', from the transfer of energy via internal degrees of freedom, such that $\lambda_i = \lambda'_i + \lambda''_i$. We apply the corresponding states assumption only to the translational contribution, such that

$$\lambda'_i(\rho, T) = \lambda'_0(\rho_0, T_0)\, F_\lambda X \tag{3}$$

where

$$F_\lambda = f_i^{1/2} h_i^{2/3} \sqrt{\frac{M_0}{M_i}}, \qquad X = X_\omega = \frac{1 + 2.18664(\omega - \omega_0)}{1 - 0.505(\omega - \omega_0)} \tag{4}$$

The factor X_ω is a correction factor used successfully for predicting hydrocarbon thermal conductivity [8], and ω is the acentric factor. In this work we found improved results if we also permitted the X correction factor to have density dependence, such that $X = X_\rho X_\omega$ with

$$X_\rho = 1 - 0.153\rho_{r,0} + 0.177\rho_{r,0}^2 - 0.04245\rho_{r,0}^3 \tag{5}$$

where $\rho_{r,0} = \rho_0/\rho_{c,0}$ is the reduced density of the reference fluid. We assume that λ'' is independent of density and is given by [2]

$$\frac{\lambda_i'' M_i}{\eta_i^*} = 1.32\left(C_p^{ig} - \frac{5R}{2}\right) \tag{6}$$

where η_i^* is the dilute gas viscosity of fluid i (which can be estimated using the method given in Ref. 1), C_p^{ig} is the ideal gas heat capacity, and R is the universal gas constant.

The state points T_0 and ρ_0 are defined by the relations $T_0 = T/f_i$ and $\rho_0 = \rho h_i$, where f_i and h_i are equivalent substance reducing ratios, defined by

$$f_i = (T_{c,i}/T_{c,0})\, \theta_i(T_{r,i}, \rho_{r,i}, \omega_i) \tag{7}$$

$$h_i = (\rho_{c,0}/\rho_{c,i})\, \phi_i(T_{r,i}, \rho_{r,i}, \omega_i) \tag{8}$$

and θ_i and ϕ_i are shape factors which are functions of the reduced temperature $T_{r,i} = T_i/T_{c,i}$, reduced density of the fluid $\rho_{r,i} = \rho_i/\rho_{c,i}$, and the acentric factor ω. The subscript c denotes the critical point.

Use of the model requires a very thorough representation of the PVT surface of the reference fluid and, also, an accurate method of determining the shape factors. For the reference fluid, we use a 32-term modified Benedict–Webb–Rubin (MBWR) equation of state for propane [10]. Propane was selected as a reference fluid because it has a very long saturation boundary, with a reduced triple point temperature of 0.24. The functional dependence of θ_i and ϕ_i in Eqs. (7) and (8), in contrast to constant factors, is a feature of "extended" corresponding states [11]. Various procedures have been used to determine shape factors [8, 11–13]. In this work, we use saturation boundary information about C_1 to C_{24} straight chain alkanes to obtain the following generalized expression for the shape factors:

$$\Theta_i(T_{r,i}, \omega_i) = 1 + (\omega_i - \omega_0)[\alpha_1 + \alpha_2 \ln(T_{r,i})] \tag{9}$$

$$\Phi_i(T_{r,i}, \omega_i) = \left[\frac{Z_{0,c}}{Z_{i,c}}\right] [1 + (\omega_i - \omega_0)(\beta_1 + \beta_2 \ln(T_{r,i}) + \beta_3 \ln(T_{r,i})^2)] \tag{10}$$

where we obtained new coefficients $\alpha_1 = 0.06354$, $\alpha_2 = -0.7256$, $\beta_1 = -0.2263$, $\beta_2 = 0.2831$, and $\beta_3 = 0.1184$. In earlier work [4, 5] saturation boundary information was used to obtain the shape factors, but an iterative method was used that sometimes failed to converge.

Following the model given in Refs. 4 and 5, we use *only* the mean average boiling point [14] and the specific gravity as input to our procedure. The definition of the dimensionless quantity API gravity (°A.P.I.) relates it to the specific gravity (60°F/60°F) using the relationship °A.P.I. = (141.5/specific gravity) − 131.5. We calculate all other property information required for the extended corresponding states model. For the critical point and the molar mass, we use the Riazi [15] correlations. For ideal gas heat capacities, we use procedure 7D4.2 of the API Technical Data book [16]. We compute the acentric factor using its definition and the Lee–Kesler vapor pressure equation [17].

It is also necessary to have correlations for transport properties of the propane reference fluid. The reference fluid viscosity is expressed as the sum, $\eta(\rho, T) = \eta^0(T) + \eta^1(T)\,\rho + \eta_{\text{high}}(\rho, T)$, where η^0 is the dilute gas contribution, η^1 is the first density correction, and η_{high} is the high-density contribution. In previous work [4, 5], the Younglove–Ely [10] correlation for viscosity was used for η_{high} and kinetic theory [9] was used for η^0. We wanted to use the very recent correlation for propane viscosity given by Vogel and Küchenmeister [18], which incorporates new experimental data. However, in extending the corresponding states model to heavy oil fractions, it sometimes is necessary to evaluate the reference fluid properties at temperatures as low as 50 K. The new viscosity fit of Vogel and Küchenmeister [18] is not appropriate for our purposes as its range is restricted to temperatures greater than the triple point; in particular, at very low temperatures and high densities a region of negative viscosities may be encountered. We therefore refit the propane viscosity data set recommended by Vogel to a new functional form for η_{high}:

$$\begin{aligned}
\eta_{\text{high}} &= \rho\beta_1 + \rho^2\left(\frac{\beta_2}{T_r^6} + \frac{\beta_3}{T_r^2} + \frac{\beta_4}{T_r^{0.5}}\right) + \rho^3\beta_5 + \beta_9\left[\exp\left(\beta_{10} T_H \frac{\rho}{\rho_f}\right) - 1\right] \\
T_H &= \beta_6 T_r + \beta_7 T_r^2 + \beta_8 T_r^3, \qquad T_r = T/T_c \\
\rho_f &= \rho_{00} - \rho, \qquad \rho_{00} = \beta_{14} E_{th} \\
E_{th} &= 1 + \beta_{11} T_r^{0.5} + \beta_{12} T_r^{1.5} + \beta_{13} T_r^{3.5}
\end{aligned} \tag{11}$$

The viscosity is obtained in mPa · s with the density in $\text{kg} \cdot \text{m}^{-3}$ the temperature in K, and the coefficients $\beta_1 = -0.116097$, $\beta_2 = 0.790917 \times 10^{-4}$, $\beta_3 = -0.498527 \times 10^{-2}$, $\beta_4 = -0.831120 \times 10^{-2}$, $\beta_5 = -0.750653 \times 10^{-2}$, $\beta_6 = -1.687856$, $\beta_7 = 0.454393$, $\beta_8 = 0.210490$, $\beta_9 = 28.8119$, $\beta_{10} = -0.193272 \times 10^{-1}$, $\beta_{11} = -0.436061$, $\beta_{12} = 1.0$, $\beta_{13} = -0.293449$, and $\beta_{14} = 3.8$. We compute the viscosity of propane using Eq. (11) for the high-density contribution, the Vogel and Küchenmeister expressions [18] for η^0

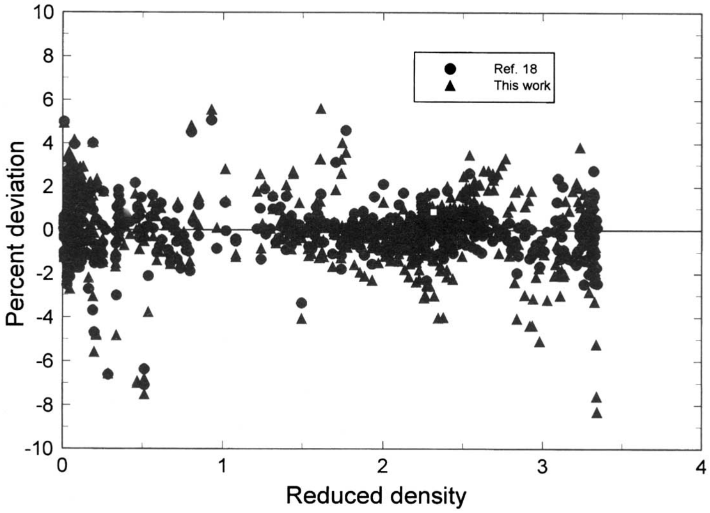

Fig. 1. Deviation plot for the representation of the viscosity of propane (reference fluid).

and η^{l}, and restrict ρ_{f}^{-1} to be greater than 0.1 kg · m^{-3}. Figure 1 shows the resulting percentage deviations (here defined as $100^*[(\eta_{\text{calc}}-\eta_{\text{exp}})/\eta_{\text{exp}}]$) of the present correlation and the Vogel and Küchenmeister [18] correlation with the recommended data set of Vogel as a function of reduced density. Both correlations fit the data very well. The Vogel and Küchenmeister [18] fit is slightly better, with an average absolute deviation (AAD) of 0.83%, a bias of −0.01%, and an RMS of 1.22%, compared with an AAD of 1.32%, a bias of −0.03%, and an RMS of 1.89% for the present model. However, for our purposes we need the ability to extrapolate well to low temperatures and high densities, and the new fit gives us that capability. We continue to work on finding a viscosity correlation function that can represent the experimental data to within experimental accuracy and that extrapolates well.

The reference fluid thermal conductivity is expressed as the sum $\lambda=\lambda^{0}+\lambda_{\text{high}}+\lambda_{\text{crit}}$, where the dilute gas contribution λ^{0} and a critical enhancement λ_{crit} are described in Ref. 5. We refit the data in Refs. 19–24 along with a few points generated by extrapolating thermal conductivity data below 90 K and obtained

$$\lambda_{\text{high}}=\frac{\rho}{\rho_c}\left[a_1+\left(a_2+\frac{\rho}{\rho_c}\left\{a_3+a_4\tau+\frac{\rho}{\rho_c}(a_5+a_6\tau)\right\}\right)\left(\frac{\rho}{\rho_c}\right)^2\right] \tag{12}$$

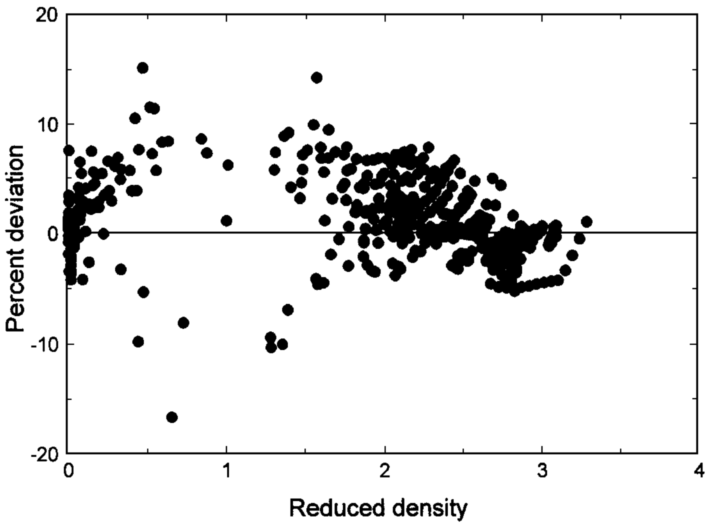

Fig. 2. Deviation plot for representation of the thermal conductivity of propane (reference fluid).

where $\tau = T_c/T$, and new parameters $a_1 = 20.53648$, $a_2 = -1.68353$, $a_3 = 2.34321$, $a_4 = -1.05427$, $a_5 = 6.92167 \times 10^{-2}$, and $a_6 = 0.252831$, and with the thermal conductivity in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$. We computed the thermal conductivity of propane using Eq. (12) for λ_{high} and the method in Ref. 5 for λ^0 and λ_{crit}. Figure 2 shows the resulting percentage deviations between our correlation and the data in Refs. 19–24; for these points, the AAD is 3.302%, the bias is −0.112%, and the RMS is 6.69%.

In earlier work [4] we found that adding a correction factor for aromaticity and napthenicity improves the viscosity predictions. In this work we use a mass shape factor, g_i, such that Eq. (2) becomes

$$F_\eta = \sqrt{\frac{M_i}{M_0}}\, f_i^{1/2} h_i^{-2/3} g_i^{1/2} \tag{13}$$

Mass shape factors have been used for pure hydrocarbons [3] as well as refrigerants [6]. Here, we obtain an expression specifically for petroleum fractions,

$$g_i = \left[b_1 + b_2 \exp \left[-0.5 \left[\frac{(\Delta k_w - b_3)}{b_4} \right]^2 + \left[\frac{(\Delta \rho - b_5)}{b_6} \right]^2 \right] \right]^2 \tag{14}$$

where $\Delta k_w = 13.9 - \text{UOPK}$ and $\Delta\rho = \rho_{0,r} - 2.9$. We found the coefficients $b_1 = 1.191014$, $b_2 = 157430.57$, $b_3 = 3.5311755$, $b_4 = 0.4906795$, $b_5 = 1.2279506$, and $b_6 = 0.20108099$. The variable k_w is the Watson characterization factor or UOPK, defined by $k_w = T_b^{1/3}/\text{specific gravity}$, and T_b is the boiling point temperature in °R.

3. RESULTS

In Table I we compare the viscosity calculated with our model to the experimental data bank we used in Ref. 4 for a wide variety of petroleum fractions. The overall average absolute deviation (AAD) for 2060 points is 17.4% with a bias of −6.3%, compared with an AAD of 29.0% and a bias of −28.3% when Eq. (14) is not used. In Fig. 3 we show comparisons of experimental data and the model with and without the correction factor in Eq. (14), demonstrating the improvement with Eq. (14).

In Table II we give the results of comparisons of thermal conductivity with a large variety of crude oils, petroleum fraction cuts, and coal-derived liquids from the data bank in Ref. 5. The data cover a wide range of API

Table I. Viscosity of Petroleum Fractions

Fraction	Number of points	BP (K)	API gravity	AAD (%)	Bias (%)
Midcontinent distillate	31	451–734	2.1–47.2	57.5	37.4
Smackover distillate	8	505–676	21.0–33.1	9.4	6.6
Pennsylvania distillate	11	518–744	28.0–43.4	29.8	−15.6
Diesel fuel	11	513–571	25.3–37.8	6.3	−2.4
Bottom & overhead stocks	99	417–624	16.5–55.0	38.2	−37.5
Kerosine and gas oil	1	557	32.7	16.1	−16.1
Domestic crudes	283	361–536	25.5–65.3	7.5	−2.1
Foreign crudes	276	353–672	25.4–71.5	11.4	9.6
Misc. crudes	72	429–681	21.7–51.8	9.9	1.3
Midcontinent crude fractions	133	364–869	−2.0–60.6	15.0	−9.6
North Sea crudes	94	416–649	20.2–50.8	39.5	−39.5
South American crudes	6	482–719	23.4–41.9	15.5	−15.5
Middle East crude fractions	902	419–876	13.6–55.8	16.5	−5.3
U.S. whole crudes	45	486–581	31.1–52.5	19.8	−19.8
ASME lube oils	30	661–806	16.1–28.6	43.0	−38.0
Coal liquids	58	340–671	−1.9–64.1	15.2	−7.4
All points	2060			17.4	−6.3

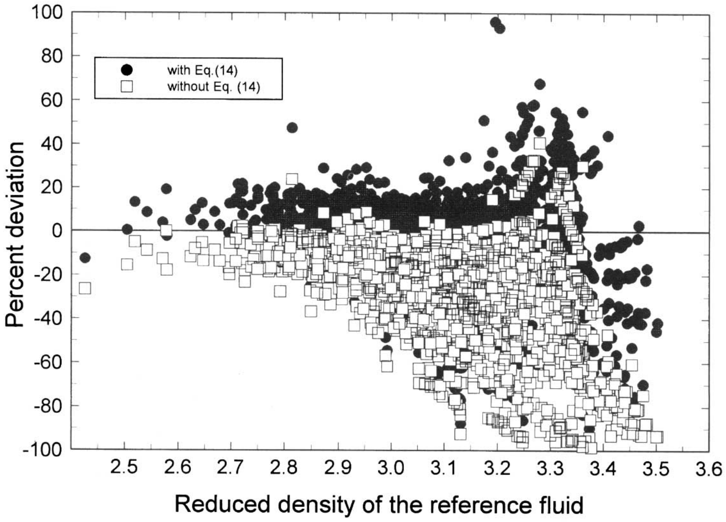

Fig. 3. Deviation plot for viscosity of petroleum fractions using the new model.

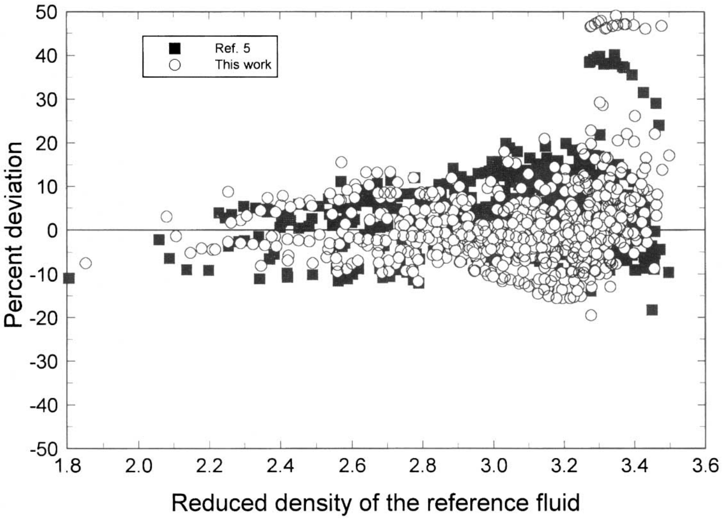

Fig. 4. Deviation plot for thermal conductivity of petroleum fractions using the new model.

specific gravity (−10.9 to 81.3) as well as awide range of boiling points (337 to 858 K). The AAD for a total of 713 points is 6.8% and the bias is 1.2%, which is within the experimental accuracy of the data. Figure 4 shows the percentage deviations in thermal conductivity as a function of the reduced density of the reference fluid.

Table II. Thermal Conductivity of Liquid Petroleum Fractions

Description	Number of points	API gravity	BP (K)	AAD (%)	Bias (%)
Oil fraction	64	16.9–71.2	355–632	5.5	0.4
Coal liquid	74	−10.9–52.2	372–750	4.2	−2.4
Alaska N. shore	8	18.4–43.3	469–755	4.2	3.7
San Joaquin Valley	24	11.8–34.3	469–755	3.4	−1.3
Altamont	8	36.8–53.5	469–755	12.2	−5.0
Undefined oils	172	16.7–50.2	388–766	9.6	5.5
SRC naptha	26	49.7–49.7	387–396	6.5	5.1
Utah coed distillate	23	29.4–29.4	473–473	6.2	−6.2
Coolant and transformer oils	7	23.0–32.2	592–672	3.0	−3.0
Malgobek and Anastasevesk	30	20.0–70.5	338–811	6.1	2.8
Acid-refined napthenic oil	2	19.4–19.4	732–732	7.0	7.0
Atmospheric residue	2	16.9	758	14.1	14.1
Paraffin oil	5	28.2–31.3	693–693	5.8	5.8
Cable oil	1	28.7–28.7	715–715	7.3	7.3
Diesel and fuel oils	20	27.1–41.7	505–689	4.4	−2.1
Dewaxed oil	3	26.2–26.2	694–753	8.3	4.8
Heat transfer oil	3	17.2–17.2	621–621	2.4	−0.1
Hydraulic oil	11	26.5–29.6	681–730	10.7	10.7
Kerosene	19	33.2–49.2	411–534	5.0	−2.0
Lubricating oil	35	9.3–38.5	622–794	9.7	8.3
Gasoline	14	33.2–49.2	411–534	4.1	−0.6
Residual	3	22.8–29.8	662–858	37.0	28.3
Solvent refined paraffinic oil	4	28.0–28.0	726–726	5.1	4.9
Misc. industrial	4	29.6–31.8	640–663	6.8	6.8
Waxy distillate	3	18.5–18.5	728–728	15.7	15.7
White spirit	2	53.8–53.8	434–434	2.0	1.0
Russian distillate fractions	36	22.9–81.3	337–746	5.7	−5.4
Russian crude	29	15.9–45.0	439–686	10.4	−10.2
Misc. oils	7	24.9–33.5	626–763	7.1	7.1
Diphenyl mix	39	1.2–1.2	531–531	2.0	−2.0
Gazoil	15	34.0–34.0	507–507	6.0	−6.0
PAB	20	10.5–10.5	600–600	2.4	2.2
All points	713	−10.9–81.3	337–858	6.8	1.2

4. CONCLUSIONS

We have further modified the TRAPP extended corresponding states model [1, 2] to predict the transport properties of heavy crude oil fractions. The model requires only the specific gravity and mean average boiling point as input parameters. The model presents several new features including a noniterative scheme for calculating shape factors, new propane viscosity and thermal conductivity correlations that extrapolate well to low temperatures, and a new correction factor to improve the viscosity prediction for heavy crudes.

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