J. Chem. Eng. Data **2005,** *50,* 1−5

Reviews

Generalized Correlation for the Viscosity of Hydrocarbons Based on Corresponding States Principles and Molar Refraction

M. R. Riazi,* K. A. Mahdi,[†] and M. Alqallaf

Chemical Engineering Department, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait

A generalized correlation in terms of the reduced molar refraction (parameter *r*) is proposed for the calculation of the viscosity of dense hydrocarbon fluids. The input parameters are the refractive index and density at 20 °C, molecular weight, critical temperature, and pressure. For more than 2600 data points used for the evaluation of the proposed correlations, the average deviation for liquids for hydrocarbons from C_1 to C_{20} is about 8%. For saturated gases ($P_r < 1$), the absolute average deviation is 3.5%, whereas for high-pressure gases ($1 < P_r < 10$) and for hydrocarbons from C_1 to C_{10} the average deviation is about 11%. A comparison with similar generalized correlations shows that molar refraction is a suitable third parameter for the generalized correlation of transport properties of dense hydrocarbons.

Introduction

The viscosity of hydrocarbon fluids under elevated pressure conditions is an important transport property to use in predicting the movement of oils and reservoir fluids and their mobility in the petroleum reservoirs as well as estimating other transport properties. The nature of viscosity and the complexity of petroleum mixtures make viscosity one of most difficult properties to estimate, especially for dense petroleum fluids. The viscosity of gases at low pressure is well predicted through the kinetic theory of gases. However, for liquids and dense gases the predictive theories are less developed. Deviations from experimental values as high as 50% or even 100% are not unusual in predicting the viscosity of liquid oils. Most predictive methods for viscosity and transport properties of hydrocarbons and petroleum fractions are based on the corresponding states principle.[1−5]

In many of these correlations, the acentric factor has been used as a third parameter in addition to reduced temperature and pressure.[4−6] In generalized correlations, usually a physical or thermodynamic property is calculated through a reduced property. For example, in the API TDB[4] the following relation is recommended for estimating the viscosity of dense liquid hydrocarbons through procedure 11A5.1:

$$\eta_r = \eta_r^{(0)} + \eta_r^{(1)} \tag{1}$$

where η_r is the reduced viscosity ($= \eta/\eta_c$) in which η_c is the critical viscosity and ω is the acentric factor. $\eta_r^{(0)}$ and $\eta_r^{(1)}$ are reduced viscosities for simple and acentric fluids, respectively. Graphical correlations and alternative complex equations for calculating $\eta_r^{(0)}$ and $\eta_r^{(1)}$ in terms of reduced temperature, T_r ($= T/T_c$), and reduced pressure, P_r ($= P/P_c$), are given by the API.[4] For example, $\eta_r^{(0)}$ is calculated from

$$\eta_r^{(0)} = A_1(\log P_r) + A_2(\log P_r)^2 + A_3P_r + A_4P_r^2 + A_5 \tag{2}$$

where coefficients A_i are given in terms of T_r through similar polynomial relations. For $\eta_r^{(1)}$, similar relations are given for two ranges of P_r. In general, a total of 67 numerical constants are given for the calculations of $\eta_r^{(0)}$ and $\eta_r^{(1)}$ for $P_r < 1$. Values of η_c are given for a limited number of hydrocarbons[4] and may be calculated from eq 1 when the viscosity is available for at least one temperature and pressure. For dense hydrocarbon gases, the following relation is recommended in the API as the most accurate method under procedure 11B4.1.[4]

$$(\eta - \eta_0)\xi = 10.08 \times 10^{-5}[\exp(1.439\rho_r) - \exp(-1.11\rho_r^{1.858})] \tag{3}$$

$$\xi = 1.0876\frac{T_c^{1/6}}{M^{1/2}P_c^{2/3}}$$

where η_0 is viscosity at low pressure (atmospheric) in mPa·s and ρ_r is the reduced density ($= V_c/V$). V_c is the critical molar volume, and V is the molar volume. T_c and P_c are in K and bar, respectively. If T_c is in K and P_c is in atm, then the numerical value of 1.0876 should be replaced by 1.000. In any case, the calculated value of ξ according to eq 3 has units of $(\text{mPa·s})^{-1}$. The value of V can be determined from the experimental value of the density or can be calculated from a generalized correlation.

The acentric factor is a defined parameter based on critical constants and may not be calculated accurately for heavy hydrocarbons,[5] whereas the refractive index is known for many hydrocarbon compounds or it can be accurately estimated.[7] Use of the refractive index in

---

* Corresponding author: E-mail: riazi@kuc01.kuniv.edu.kw.

[†] E-mail: k_mahdi@kuc01.kuniv.edu.kw.

10.1021/je049832t CCC: $30.25

Table 1. Critical Properties, Reduced Molar Refraction, and Acentric Factor of Pure Hydrocarbons[a]

compound	formula	T_c/K	P_c/bar	V_c/cm^3·mol^{-1}	η_c/mPa·s	M	r	ω
methane	CH_4	190.5	46.41	98.63	0.016	16.04	1.00	0.011
ethane	C_2H_6	305.5	49.13	145.48	0.021	30.07	1.62	0.099
propane	C_3H_8	370.0	42.64	200.14	0.023	44.09	2.26	0.152
butane	C_4H_{10}	425.1	37.96	255.07	0.024	58.12	2.93	0.200
pentane	C_5H_{12}	469.6	33.69	313.04	0.024	72.15	3.60	0.251
hexane	C_6H_{14}	507.4	30.31	371.22	0.025	86.18	4.28	0.301
heptane	C_7H_{16}	540.6	27.36	427.90	0.025	100.19	4.94	0.349
octane	C_8H_{18}	568.8	24.86	486.34	0.025	114.22	5.61	0.399
nonane	C_9H_{20}	594.6	22.89	543.67	0.026	128.26	6.27	0.443
decane	$C_{10}H_{22}$	617.6	20.96	599.59	0.026	142.30	6.93	0.492
undecane	$C_{11}H_{24}$	638.8	19.70	658.67	0.026	156.31	7.60	0.530
dodecane	$C_{12}H_{26}$	658.3	18.20	715.66	0.026	170.34	8.23	0.576
tridecane	$C_{13}H_{28}$	675.8	17.20	774.61	0.026	184.37	8.88	0.617
tetradecane	$C_{14}H_{30}$	694.0	16.20	829.80	0.026	198.39	9.55	0.643
pentadecane	$C_{15}H_{32}$	707	15.20	888.48	0.026	212.42	10.2	0.686
hexadecane	$C_{16}H_{34}$	717	14.20	944.34	0.025	226.45	10.8	0.717
heptadecane	$C_{17}H_{36}$	733	13.20	999.84	0.026	240.47	11.5	0.769
octadecane	$C_{18}H_{38}$	745	12.10	1059.7	0.026	254.50	12.2	0.811
nonadecane	$C_{19}H_{40}$	756	11.2	1119.8	0.026	268.52	12.8	0.852
eicosane	$C_{20}H_{40}$	767	11.10	1169.5	0.026	282.56	13.5	0.906
isobutane	C_4H_{10}	408.1	36.47	262.69	0.023	58.12	2.95	0.180
isopentane	C_5H_{12}	460.4	33.80	305.83	0.024	72.14	3.61	0.227
propylene	C_3H_6	364.8	46.10	188.35	0.023	42.07	2.616	0.139
1,3 butadiene	C_4H_6	425.1	43.30	220.50	0.026	54.08	3.211	0.189
cyclopentane	C_5H_{10}	511.8	45.08	257.90	0.028	70.13	3.290	0.195
cyclohexane	C_6H_{12}	554.1	40.75	307.88	0.029	84.13	3.849	0.209
benzene	C_6H_6	562.6	49.24	258.92	0.031	78.10	3.752	0.210
tolune	C_7H_8	594.0	40.05	315.79	0.031	92.13	4.442	0.262
ethylbenzene	C_8H_{10}	617.1	36.61	373.81	0.030	106.2	5.114	0.302
o-xylene	C_8H_{10}	630.4	37.3	369.17	0.030	106.1	5.104	0.310
m-xylene	C_8H_{10}	617.0	35.43	375.80	0.030	106.1	5.146	0.326
p-xylene	C_8H_{10}	616.3	35.10	379.12	0.030	106.1	5.155	0.321

[a] Values of M, T_c, P_c, V_c, and ω are taken from API-TDB.[4] Values of r are taken from Riazi and Roomi.[7] Values of η_c are calculated with eq 9.

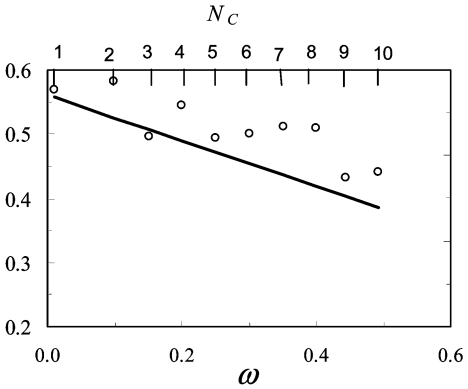

Figure 1. Variation of reduced viscosity (η_r) versus acentric factor ω at $P_r = 0.5$ and $T_r = 0.9$: −, estimated; ○, data.

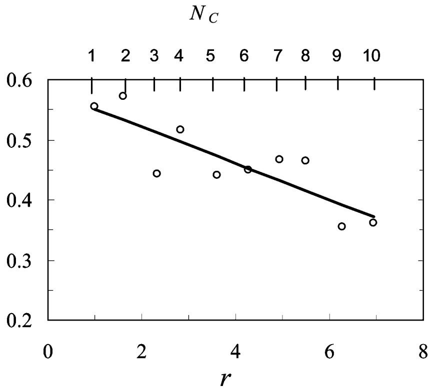

Figure 2. Variation of reduced viscosity (η_r) versus parameter r at $P_r = 0.5$ and $T_r = 0.9$: −, estimated; ○, data.

estimations of volumetric, thermal, and transport properties has been shown in previous publications.[7,8] In this paper, the use of molar refraction as an alternate third parameter for the correlation of transport properties of dense hydrocarbon fluids is investigated, and a generalized correlation for the estimation of the viscosity of hydrocarbons is proposed.

Technical Developments

Viscosity, like any other physical property, depends on intermolecular forces. For hydrocarbon and nonpolar compounds, the main molecular force is the London dispersion force, which is characterized by the polarizability, α. Parameter α is defined in terms of molar refraction, R, which is defined as[7,9]

$$R = VI = \frac{MI}{\rho} \tag{4}$$

where R is in cm^3·mol^{-1}, V is the liquid molar volume (cm^3·mol^{-1}), M is the molecular weight, and ρ is the absolute density in g·cm^{-3}. Parameter I is defined in terms of the refractive index as

$$I = \frac{n^2 - 1}{n^2 + 2} \tag{5}$$

in which n is the liquid refractive index at 20 °C and 101.3 kPa. Although both V and I vary with temperature, parameter R is nearly independent of temperature.[9] Because methane is the simplest hydrocarbon, it may be used as a reference fluid. The value of R for methane is 6.987. The reduced refraction, r, is then defined as

$$r = \frac{R}{6.987} \tag{6}$$

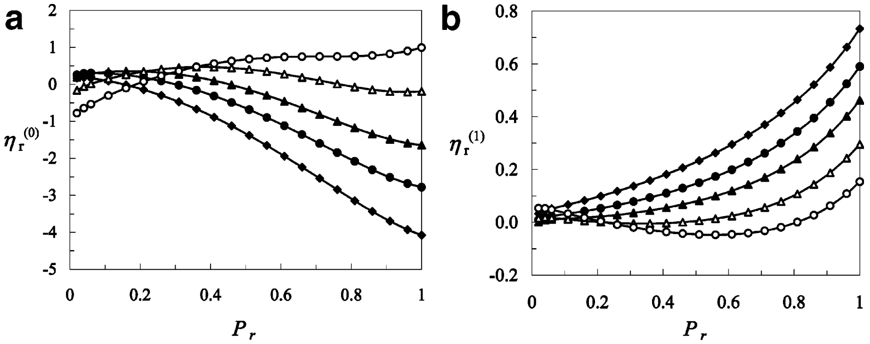

Figure 3. Graphical presentation of (a) $\eta_r^{(0)}$ and (b) $\eta_r^{(1)}$ in eq 7 for saturated vapors: ◆, $T_r = 0.5$; ●, $T_r = 0.6$; ▲, $T_r = 0.7$; Δ, $T_r = 0.85$; ○, $T_r = 1$.

Table 2. Data Bank Used in This Study

system	N_C, range	T_r, range	P_r, range	η/mPa·s, range	no. of data points	ref
sat. vapor	C_1 to C_{10}	0.58 to 2.06	0.02 to 7.64	4.5 to 55	202	11
gases at high press.	C_1 to C_{10}	0.47 to 2.2	1.0 to 24.1	1 to 983	2111	12, 13
sat. liquids	C_1 to C_{20}	0.58 to 0.99	0.02 to 1.0	19 to 4302	300	11, 14−15
total	C_1 to C_{20}	0.47 to 2.2	0.02 to 24.1	4.5 to 4302	2613	11−15

Table 3. Coefficients of Equation 8 for Hydrocarbon Systems

system	range	η_r	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9
sat. vapor	C_1-C_{10}	$\eta_r^{(0)}$	0.667	4.152	−7.148	−5.011	−4.431	12.288	−0.612	-1.6×10^{-3}	1.090
		$\eta_r^{(1)}$	0	−0.438	0.828	0.437	0.303	−1.225	0.076	$-2.8 \times 10-4$	0.173
sat. liquid	C_1-C_{10}	$\eta_r^{(0)}$	29.013	115.165	−115.33	−127.1	−28.296	157.05	−29.946	0.094	0
		$\eta_r^{(1)}$	0	−42.867	32.477	38.817	7.836	−43.914	7.949	$-9.2 \times 10-3$	0
gases	C_1-C_3	$\eta_r^{(0)}$	−9.717	2.241	0.817	3.034	0.0235	−0.897	6.061	−0.0086	0
$P_r < 11$		$\eta_r^{(1)}$	0	1.893	−0.474	−3.422	−0.0251	0.781	1.349	0.047	0
gases	C_4-C_{10}	$\eta_r^{(0)}$	−804.5	1108.2	−2.99	−517.4	0.0018	4.957	198.9	−0.064	0
$P_r < 24$		$\eta_r^{(1)}$	0	−8.13	0.88	10.056	0.00124	−1.396	1.565	0.0164	0
liquid	$C_{11}-C_{20}$	$\eta_r^{(0)}$	−4435.6	8146.02	0	−4870.1	0	0	791.01	0	0
$P = 101$ kPa		$\eta_r^{(1)}$	0	−99.096	0	102.268	0	0	13.671	0	0

Values of r for a number of hydrocarbons and methods of its estimation are given in an earlier publication.[7] For some hydrocarbons, values of r are given in Table 1. It has been shown that parameter r can be used instead of ω to obtain equation-of-state parameters.[7] The proposed generalized correlation for viscosity is given in the following form:

$$\eta_r = \frac{\eta}{\eta_c} = \eta_r^{(0)} + r\eta_r^{(1)} \tag{7}$$

η, η_r, and η_c are the absolute, reduced, and critical viscosity, respectively. $\eta_r^{(0)}$ and $\eta_r^{(1)}$ are functions of reduced temperature (T_r) and reduced pressure (P_r), as given by the following relation:

$$\eta_r^{(0)} \text{ or } \eta_r^{(1)} = a_1 + a_2T_r + a_3P_r + a_4T_r^2 + a_5P_r^2 + a_6P_rT_r + \frac{a_7}{T_r} + \frac{a_8}{P_r} + a_9P_r^6$$

$$T_r = \frac{T}{T_c} \qquad P_r = \frac{P}{P_c} \tag{8}$$

The relation for η_c is given by the following equation, as taken from Perry:[10]

$$\eta_c = 61.6 \times 10^{-4}\frac{(MT_c)^{1/2}}{V_c^{2/3}} \tag{9}$$

T_c, P_c, and V_c are the critical temperature, pressure, and volume in units of kelvin, kPa, and $cm^3 \cdot mol^{-1}$, respectively. η and η_c are both in mPa·s. Values of T_c, P_c, V_c, and η_c are given in Table 1.

The variation of η_r with ω for hydrocarbons from C_1 to C_{10} at $P_r = 0.05$ and $T_r = 0.9$ is shown in Figure 1, where N_C represents the carbon number of n-alkane hydrocarbons. The same data for the variation of η_r with parameter r is presented in Figure 2. The correlation coefficient for data shown in Figure 1 is 0.63, whereas that for data shown in Figure 2 is 0.70 (correlation coefficient = 1 for an exactly linear line). At this particular T_r and P_r, the advantage of parameter r over ω is not very significant, but when an evaluation is made over the entire range of T_r and P_r, the difference is more visible. Obviously, parameter r is not a suitable third parameter for polar, associated, and nonhydrocarbon compounds in which the polarizability alone cannot characterize intermolecular forces.

Coefficients a_1-a_9 in eq 8 have been determined for $\eta_r^{(0)}$ and $\eta_r^{(1)}$ for both liquids and vapors in the pressure range from 101 kPa to $P_r = 24$ for pure hydrocarbons from C_1 to C_{10}. Data on the viscosity of saturated liquid and vapor hydrocarbons from paraffins, olefins, naphthenes, and aromatics have been used to obtain the coefficients.[11−15] A summary of the data bank used in this study is given in Table 2. Sets of coefficients determined for use in eqs 7 and 8 for both liquid and vapor viscosity are given in Table 3. For liquid hydrocarbons in the range of $C_{11}-C_{20}$, data at 101 kPa were available, and for this reason, the coefficients of the P_r terms in eq 8 are all zero. Graphical presentations of $\eta_r^{(0)}$ and $\eta_r^{(1)}$ based on eq 8 for two cases are shown in Figures 3 and 4. Figure 3 shows the variation

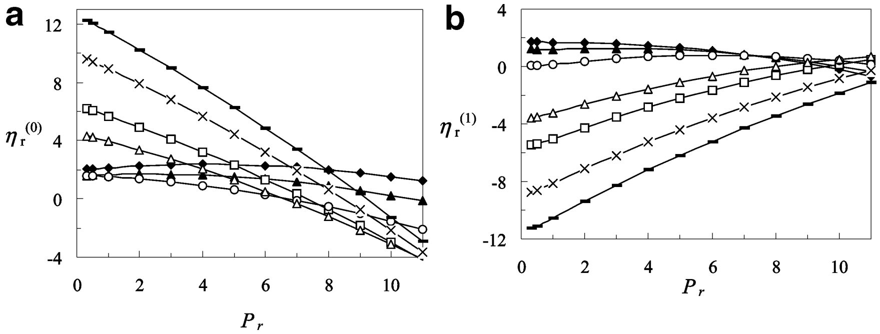

Figure 4. Graphical presentation of (a) $\eta_r^{(0)}$ and (b) $\eta_r^{(1)}$ in eq 7 for gases at high pressures: ◆, $T_r = 0.7$; ▲, $T_r = 0.8$; ○, $T_r = 1$; Δ, $T_r = 1.5$; □, $T_r = 1.7$; ×, $T_r = 2.0$; –, $T_r = 2.2$.

Table 4. Evaluation of Proposed Methods for the Viscosity Prediction of Pure Hydrocarbons[a]

system	N_C, range	no. of data points	eq 7 AAD%	eq 7 MAD%	API methods AAD%	API methods MAD%
sat. vapor ($P_r < 1$)	C_1–C_{10}	199	3.6	22	19.3	83.7
sat. liquid ($P_r < 1$)	C_1–C_{10}	214	8.0	14	17.5	84.3
gases ($0.3 < P_r < 11$)	C_1–C_3	435	3.5	16	13.2	38.8
gases ($0.03 < P_r < 24$)	C_4–C_{10}	1677	11.6	87	33.4	58.7
liquids ($P = 101$ kPa)	C_{11}–C_{20}	83	8.3	49	8.6	24.2
total	C_1–C_{20}	2608	9.2	87	26.9	84.3

[a] AAD%: average absolute percent deviation. MAD%: maximum absolute percent deviation. AAD% = (1/number of data points) × 100 Σ|predicted value − experimental value|/experimental value.

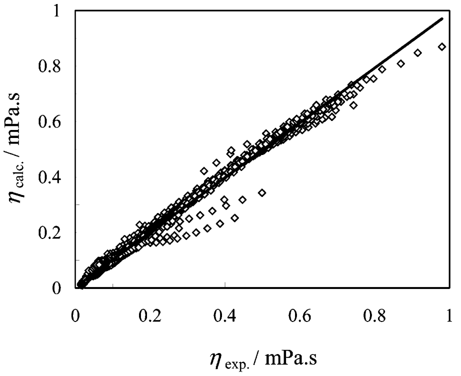

Figure 5. Evaluation of eq 7 for the viscosity prediction of liquid hydrocarbons C_1–C_{10}.

of $\eta_r^{(0)}$ and $\eta_r^{(1)}$ with T_r and P_r for saturated vapors ($P_r < 1$), and Figure 4 shows reduced viscosity for high-pressure gases where $P_r > 1$.

Viscosity data used in this study are taken from various sources with a measured accuracy of ±1%.[14–15] Measurements of temperature have an accuracy of ±2 K, whereas the accuracy in the measurement of pressure was about ±0.001 MPa. When newly measured data[16] on viscosity were compared with the previous data bank,[15] deviations were generally less than 1%. A comparison between the measured viscosity data by Aucejo et al.[16] and those reported by Baltazar and Barrufet[14] also shows an average deviation of about 1%.[16]

An evaluation of the proposed method is shown in Table 4. The API methods generally gave errors as much as twice those for the proposed method. For example, for the viscosity of gases at high pressures the API method gives an average deviation of about 30% for some 2000 data points. Graphical presentations of evaluations for both the API method and the proposed method are shown in Figures 5, 6, and 7. The proposed method may be extended to hydrocarbon mixtures and complex petroleum fractions. For such mixtures, parameter *r* can be estimated from the method given in the ref 7. One major advantages of the proposed method (eq 7) with the use of molar refraction over the traditional form of corresponding states with the use of the acentric factor (eq 1) is the possibility of an accurate estimation of parameter *r* for very heavy hydrocarbons and undefined petroleum mixtures. The reason for

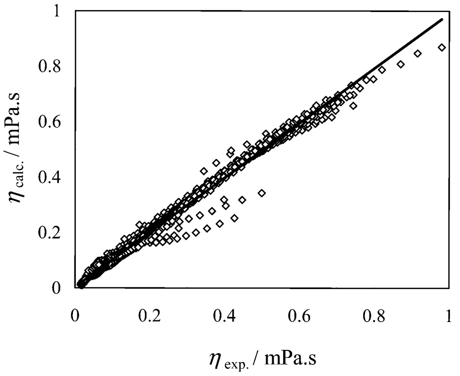

Figure 6. Evaluation of eq 7 for the viscosity prediction of hydrocarbon gases C_1–C_4.

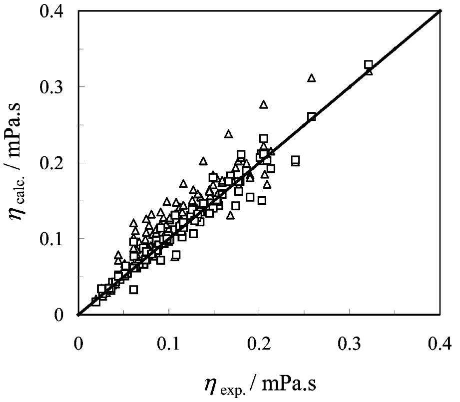

Figure 7. Comparison of the prediction of viscosity from two methods for liquid hydrocarbons C_1–C_{10}: Δ, calculated from the API method (eq 1); □, calculated from the proposed method (eq 7).

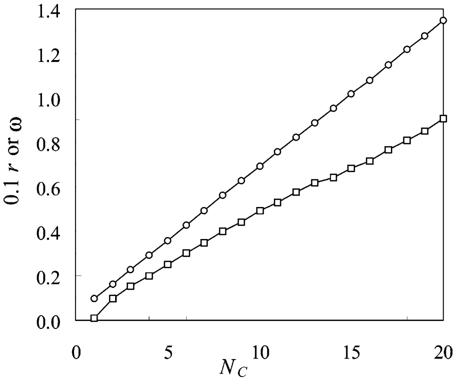

Figure 8. Variation of parameter r and ω with carbon number, N_C, for n-alkanes: ○, 0.1r; □, ω.

such a possibility is best presented in Figure 8, where for n-alkanes from C_1 to C_{20} the variation of both r and ω versus carbon number (N_C) is shown. Values of r presented in this figure have been divided by 10 so that they vary within the same range of values as ω and a better comparison can be presented. As shown in this figure, parameter r varies nearly linearly with carbon number, whereas the variation of ω with carbon number is not linear and for heavier hydrocarbons it tends to show less variation with carbon number. This behavior shows that one can get a better estimate of values of r for heavy hydrocarbons by linear extrapolation of values of r from light hydrocarbons. This simple extrapolation to obtain values of ω for heavy hydrocarbons is not possible.

Conclusions

In this paper, a new third parameter in the form of reduced molar refraction is used to develop a three-parameter generalized corresponding states correlation for the estimation of the viscosity of dense liquids and gases for nonpolar systems. The proposed method shows better predictive capability when compared with traditional third parameters for hydrocarbon systems. The proposed third parameter can be directly determined from experimental data or may be estimated from existing methods with good accuracy. Such direct measurement is not possible for existing third parameters such as the acentric factor.

Literature Cited

(1) Pedersen, K. S.; Fredenslund, A. An Improved Corresponding States Model for the Prediction of Oil and Gas Viscosities and Thermal Conductivities. *Chem. Eng. Sci.* **1987**, *42*, 182−186.
(2) Chung, T. H.; Ajlan, M.; Lee, L. L.; Starling, K. E. Generalized Multiparameter Correlation for Nonpolar and Polar Fluid Transport Properties. *Ind. Eng. Chem. Res.* **1988**, *27*, 671−679.
(3) Ozdogan, S.; Yucel, G. Correlations Towards Prediction of Petroleum Fraction Viscosities: A Semi-Theoretical Approach. *Fuel* **2000**, *79*, 1209−1214.
(4) *API Technical Data Book − Petroleum Refining*, 6th ed.; API: Washington, DC, 1997.
(5) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw Hill: New York, 2000.
(6) Riazi, M. R.;Faghri, A. Prediction of Thermal Conductivity of Gases at High Pressures. *AIChE J.* **1985**, *31*, 164−167.
(7) Riazi, M. R.; Roomi, Y. Use of the Refractive Index in the Estimation of Thermophysical Properties of Hydrocarbons and Their Mixtures. *Ind. Eng. Chem. Res.* **2001**, *40*, 1975−1984.
(8) Riazi, M. R.; Al-Otaibi, G. N. Estimation of Viscosity of Petroleum Fractions. *Fuel* **2001**, *80*, 27−32.
(9) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
(10) Perry, R. H.; Chilton, C. H. *Chemical Engineering Handbook*, 5th ed.; McGraw Hill: New York, 1973; p 229.
(11) *Physical Property Data for Design the Engineer*; Beaton, C. F., Hewitt, G. F., Eds.; Taylor and Francis: New York, 1989.
(12) Diehl, J.; Gondouin, M.; Houpeurt, A.; Neoschil, J.; Zurawsky, R. *Viscosity & Density of Light Paraffins, Nitrogen and Carbon Dioxide*; EditionsTechnip: Paris, 1970; pp 80−118.
(13) Guo, X. Q.; Wang, L. S.; Rong, S. X.; Guo, T. M. Viscosity Model Based on Equations of State for Hydrocarbon Liquid and Gases. *Fluid Phase Equilib.* **1997**, *39*, 405−421.
(14) Baltazar, A. E.; Barrufet, M. A. Liquid Viscosities of Pentane + Decane from 298.15 to 373.15 K and up to 25 MPa. *J. Chem. Eng. Data* **1998**, *43*, 601−604.
(15) Viswanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Taylor and Francis: New York, 1989 (absolute viscosity data table).
(16) Aucejo, A.; Burguet, M. C.; Munoz, R.; Marques, J. L. Densities, Viscosities, and Refractive Indices of Some n-Alkane Bianry Liquid Systems at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 141−147.

Received for review May 1, 2004. Accepted October 17, 2004.

JE049832T