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Tests of Predictive Viscosity Models for Pure Liquids[1]

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It is of considerable importance to be able to predict accurately the viscosity of liquids over a wide range of conditions. In the present work, the ability of the three-parameter generalized corresponding states principle (GCSP) for the prediction of the viscosity of pure liquids is demonstrated. The viscosity of six different classes of pure liquids, *viz.*, alkanes (19 compounds; 207 data points), cycloalkanes (6 compounds; 74 data points), alkenes (9 compounds; 146 data points), aromatics (4 compounds; 123 data points), alkanols (8 compounds; 89 data points), and esters (4 compounds; 28 data points) have been predicted over a wide range of temperatures using the three-parameter (T_c, P_c, θ) GCSP. Five options for the third parameter (θ) were studied, *viz.*, Pitzer's acentric factor ω, molar mass M, characteristic viscosity η^*, critical compressibility factor Z_c, and modified acentric factor Ω, in addition to groups ωZ_c and ΩZ_c being treated as composite third parameters. Pressure effects were neglected. Good agreement between experimental and predicted values of viscosity was obtained, especially with either ω or η^* being used as the third parameter. Furthermore, the viscosities of alkanes predicted by the TRAPP method and an empirical, generalized one-parameter model for liquid hydrocarbons provide comparisons with the more accurate GCSP method. The GCSP provides a simple and yet a powerful technique for the correlation and prediction of viscosities of a variety of pure liquids over a wide range of temperatures.

KEY WORDS: alkanes; alkanols; alkenes; aromatics; corresponding states; cycloalkanes; esters; liquids; viscosity.

1. INTRODUCTION

Transport properties are important quantities required in engineering design for production, transportation and processing. For example,

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viscosity is an important property for the determination of pressure drops in pipe flow required in pipeline sizing and the power required to pump fluids through it. Viscosity also enters into heat-exchanger and separation equipment sizing and is a critical parameter for the recovery efficiency of reservoir oils. Since it is unlikely that experimental measurements of all viscosities of interest can be found in the literature, it is of considerable importance to be able to predict accurately the viscosity of liquids over a wide range of conditions.

Progress on the development of a general predictive theory for the viscosity of liquids has not been rapid despite years of concentrated effort aimed at understanding the mechanism of momentum transfer in liquids. Theoretical description of liquids is difficult due to various types of intermolecular forces, and there is no widely accepted simple theoretical method for liquid viscosity [1]. Predictive methods in the literature are generally empirical and require an extensive knowledge of input parameters, which are difficult to measure [2–7].

Semitheoretical methods based on the principle of corresponding states have been widely used for the determination of the viscosity of simple liquids [8]. The applicability of corresponding states was broadened considerably by the introduction of state-dependent shape factors to include substances of more complicated molecules [9–11]. The extended corresponding states model [10,11], TRAPP, is predictive and requires only the common characterization parameters (critical constants, acentric factor, and molar mass) as input. Results are satisfactory for *n*-paraffins, with average absolute deviations (AADs) typically within 5–10%, but are markedly poor for isomeric paraffins and naphthenes, with AADs as high as 55% [12]. Attempts have been made to improve the method by using viscosity as a conformal equation and/or making empirical modifications to the shape factors [12, 13]. A similar approach has been proposed using methane as the reference fluid for hydrocarbon and crude oil viscosities [14]. All of these corresponding-states methods are based on the known properties of one spherical reference fluid.

An alternative formulation of the corresponding states principle is based on the known properties of two nonspherical reference fluids [15, 16]. This three-parameter (critical temperature, critical pressure, and acentric factor) generalized corresponding states principle (GCSP) method is simple to use, involves no iterations, and is capable of systematic improvement and extension as wide reduced temperature range viscosity data for the reference fluids become available [17]. Instead of the acentric factor, a characteristic viscosity [18, 19] and molar mass [20] have also been used as third parameters in the GCSP method. A four-parameter corresponding states method involving three fixed reference fluids (CH_4, n-C_8H_{18}, and

H_2O) was developed recently for the calculation of viscosity of nonpolar and polar fluids [21].

Of special interest are some recent empirical methods developed exclusively for the correlation and prediction of the viscosity of liquid hydrocarbons [22–26]. A generalized, one-parameter viscosity-temperature equation for heavy hydrocarbons [22] was extended to correlate the viscosity of light and medium liquid hydrocarbons [23]. The single parameter is generalized for each hydrocarbon family in terms of molar mass, normal boiling point, critical temperature, and acentric factor. An effective carbon number (ECN) approach [24] was combined with the one-parameter equation [22, 23] to provide a simple relationship between ECN and the parameter, which can be extrapolated reliably to heavier hydrocarbons [25].

In the present work, the viscosity of six classes of pure liquids, *viz.*, alkanes, cycloalkanes, alkenes, aromatics, alkanols, and esters, have been predicted over a wide range of temperatures using the three-parameter GCSP. Five different options for the third parameter were studied. Pressure effects were neglected. Furthermore, the viscosities of alkanes predicted by the TRAPP method and an empirical, generalized one-parameter model for liquid hydrocarbons [22, 23] provide comparisons with the more accurate GCSP method. The ability of the GCSP method to use different reference fluids offers a tremendous advantage in the prediction of viscosities of a variety of liquids over a wide range of temperatures.

2. MODELS

2.1. The GCSP Model

The GCSP for any reduced (dimensionless) configurational property X can be written [15]

$$X(T_r, P_r, \theta) = X^{r1}(T_r, P_r, \theta^{r1}) + \left[\frac{\theta - \theta^{r1}}{\theta^{r2} - \theta^{r1}}\right] [X^{r2}(T_r, P_r, \theta^{r2}) - X^{r1}(T_r, P_r, \theta^{r1})] \tag{1}$$

where T_r is the reduced temperature, P_r is the reduced pressure, and the superscripts r1 and r2 refer to two reference fluids which are similar to the pure components of interest.

For viscosity calculations

$$X = \ln(\eta/H) \tag{2}$$

where

$$H = m^{1/2} P_c^{2/3} / (k_B T_c)^{1/6} \tag{3}$$

η is the viscosity in mPa · s, T_c is the critical temperature in K, P_c is the critical pressure in bar, m is the molecular mass (M/N$_A$), and k_B is the Boltzmann constant. A common choice for the third parameter θ has been the Pitzer acentric factor ω [16, 17]. In this work, in addition to using ω, the following alternative choices for the third parameter were examined: critical compressibility factor Z_c, molar mass M, the characteristic viscosity η^* (the reduced viscosity at $T_r = 0.6$) [18, 19], and a modified acentric factor Ω defined as [27]

$$\Omega = -\log P_r^s \text{ (at } T_r = 0.5) - \ln 10 \tag{4}$$

where P_r^s is the reduced vapor pressure. After Valderrama et al. [28], who used the group ωZ_c as a correlating parameter in equations of state for polar fluids, the groups ωZ_c and ΩZ_c have also been employed in the present work as alternative composite third parameters in the GCSP.

2.2. The TRAPP Model

The extended corresponding states model TRAPP is given by [10,11]

$$\eta_i(\rho, T) = \eta_o(\rho h_{i,o}, T/f_{i,o})(M_i/M_o)^{1/2} h_{i,o}^{-2/3} f_{i,o}^{1/2} \tag{5}$$

where ρ is the density and T is the temperature. The subscript i refers to the fluid of interest, and the subscript o refers to the reference fluid.

$$h_{i,o} = (v_{c,i}/v_{c,o})\, \phi_{i,o} \tag{6}$$

$$f_{i,o} = (T_{c,i}/T_{c,o})\, \theta_{i,o} \tag{7}$$

where v_c is the critical volume and $\phi_{i,o}$ and $\theta_{i,o}$ are shape factors. To calculate the viscosity, reference fluid (methane) viscosity and density correlations are required along with the critical properties, acentric factor and molar mass. The available computer program and reference fluid property correlations [10, 11] were used.

2.3. Empirical One-Parameter Model

The one-parameter viscosity–temperature equation is given by [22]

$$\log(\eta + 0.8) = 100\,(0.01T)^b \tag{8}$$

where η is in mPa·s and T is in K. Parameter b was generalized in terms of the normal boiling point T_b, M, T_c, or ω for individual families of hydrocarbons [23]. This resulted in a predictive method for the viscosity of hydrocarbons.

3. RESULTS AND DISCUSSION

Tables I through VI give the results (AAD%) obtained with the GCSP method using different options for the third parameter (θ), *viz.*, ω, M, η^*, Z_c, Ω, ωZ_c, and ΩZ_c, for alkanes (19 compounds, 207 data points), cycloalkanes (6 compounds, 74 data points), alkenes (9 compounds, 146 data points), aromatics (4 compounds, 123 data points),

Table I. Viscosity Predictions for the Alkanes Using Different Models

			GCSP parameter θ								
Alkane	No. of data	Temp. range (K)	ω	M	η^*	Z_c	Ω	ωZ_c	ΩZ_c	TRAPP	Empirical
			AAD (%)								
			Reference fluids: *n*-nonane, *n*-hexadecane								
Methane[a]	6	121–152	2.24	4.49	0.49	11.08	3.19	13.37	13.29	0.96	—
Ethane[a]	9	206–265	2.18	3.30	1.52	8.50	2.79	10.13	10.09	2.70	—
Propane[a]	12	230–301	0.91	1.65	0.92	6.85	1.24	8.43	8.39	2.53	—
n-Butane	4	248–270	0.37	0.95	0.32	6.91	0.42	8.66	8.63	2.59	3.38
Isopentane	8	236–292	0.40	1.46	0.09	6.85	0.26	8.59	8.55	4.33	8.08
n-Pentane	7	258–299	1.29	2.25	0.37	7.35	1.83	8.72	8.69	6.00	8.67
n-Hexane	10	271–331	0.75	1.56	0.41	5.49	1.18	6.58	6.55	4.49	9.34
n-Heptane	14	267–363	0.83	1.29	0.13	4.06	1.09	4.79	4.78	5.35	12.34
n-Octane	12	288–379	0.52	0.68	0.15	2.12	0.62	2.46	2.46	5.33	10.15
n-Decane	14	334–446	0.28	0.36	0.03	1.47	0.31	1.80	1.81	2.16	11.01
n-Undecane	9	394–469	0.15	0.24	0.14	2.20	0.23	2.74	2.76	1.78	9.49
n-Dodecane	12	383–479	0.29	0.38	0.05	3.73	0.37	4.56	4.60	1.77	10.16
n-Tridecane	10	413–498	0.08	0.21	0.10	4.52	0.27	5.58	5.58	2.43	9.34
n-Tetradecane	13	417–522	2.02	0.08	0.07	5.44	0.25	6.30	6.73	8.31	10.70
n-Pentadecane	10	472–552	0.04	0.08	0.10	5.81	0.11	7.09	7.17	1.98	12.29
n-Heptadecane	6	436–472	0.07	0.25	0.02	10.37	0.34	12.58	12.69	0.61	4.24
n-Octadecane[b]	15	314–467	0.59	1.91	0.27	1.41	0.79	0.14	0.43	—	20.13
n-Nonadecane[b]	25	376–567	0.29	0.78	0.26	2.35	0.28	0.84	0.73	—	12.58
n-Eicosane[b]	11	461–559	2.17	1.78	0.13	1.03	2.31	1.53	1.77	—	7.79
Total	207		0.81	1.24	0.29	5.13	0.94	6.04	6.08	3.33	9.98

[a] Large deviation in lowvalue viscosities obtained by the empirical method.

[b] Critical volume required in TRAPP unavailable.

Table II. Viscosity Predictions for the Cycloalkanes Using the GCSP Model

Cycloalkane	No. of data	Temp. range (K)	AAD (%), Parameter θ						
			ω	M	η^*	Z_c	Ω	ωZ_c	ΩZ_c
Reference fluids: cyclopentane, *n*-propylcyclopentane									
Cyclopropane	8	267–315	8.25	8.24	9.90	8.29	8.23	8.24	8.21
Cyclobutane	8	301–360	6.46	6.47	5.75	6.45	6.43	6.46	6.43
Methylcyclopentane	15	253–349	0.68	0.78	0.31	0.52	0.80	0.74	0.92
Cyclohexane	15	345–470	2.16	2.24	2.82	2.15	2.19	2.16	2.21
Methylcyclohexane	15	276–382	2.39	2.83	0.72	2.39	2.53	2.42	2.61
n-Propylcyclohexane	13	295–384	1.97	3.29	0.69	12.96	2.80	0.36	1.41
Total	74		3.65	3.97	3.36	5.46	3.83	3.39	3.58

alkanols (8 compounds, 89 data points), and esters (4 compounds, 28 data points) over a wide range of temperatures. Pressure effects were neglected. The appropriate pairs of reference fluids used were *n*-nonane/*n*-hexadecane for alkanes, cyclopentane/*n*-propylcyclopentane for cycloalkanes, 2-methylpropene/1-nonene for alkenes, benzene/*p*-xylene for aromatics, 1-propanol/1-butanol for alkanols, and ethylacetate/ethylbutyrate for esters. The temperature variation of the viscosity of reference fluids was represented by

$$\ln \eta = A + BT^{-1} + CT + DT^2 \tag{9}$$

Table III. Viscosity Predictions for the Alkenes Using the GCSP Model

Alkene	No. of data	Temp. range (K)	AAD (%), Parameter θ						
			ω	M	η^*	Z_c	Ω	ωZ_c	ΩZ_c
Reference fluids: 2-methylpropene, 1-nonene									
Ethene	10	167–243	2.09	1.95	4.93	8.86	1.99	2.26	2.44
Propene	16	201–316	1.38	1.36	2.83	7.77	1.35	2.56	2.62
1-Butene	23	198–389	2.74	2.61	1.76	5.34	2.66	1.74	1.74
1,3-Butadiene	28	200–415	1.40	1.47	1.48	6.31	1.41	1.94	1.92
1-Pentene	10	201–266	5.88	5.78	1.08	12.09	6.14	7.86	8.05
1-Hexene	17	216–336	2.03	2.11	0.51	4.75	1.99	2.74	2.71
1-Heptene	10	285–365	0.94	0.63	0.55	2.65	0.59	1.45	0.99
1-Octene	18	282–394	0.37	0.41	0.30	0.30	0.43	0.46	0.52
1-Decene	14	287–383	2.42	2.80	0.59	4.11	2.62	2.93	3.07
Total	146		2.13	2.12	1.55	5.79	2.13	2.66	2.67

Table IV. Viscosity Predictions for the Aromatics Using the GCSP Model

Aromatic	No. of data	Temp. range (K)	AAD (%), Parameter θ						
			ω	M	η^*	Z_c	Ω	ωZ_c	ΩZ_c
		Reference fluids: benzene, *p*-xylene							
Toluene	28	247–559	1.80	1.77	1.97	1.58	1.81	1.81	1.83
o-Xylene	27	263–599	0.68	0.96	1.39	0.62	0.73	0.72	0.78
m-Xylene	30	245–613	0.74	0.79	0.68	0.69	0.73	0.75	0.74
Ethylbenzene	38	235–603	0.67	0.67	0.57	0.68	0.62	0.67	0.61
Total	123		0.97	1.04	1.15	0.89	0.97	0.98	0.99

Table V. Viscosity Predictions for the Alkanols Using the GCSP Model

Alkanol	No. of data	Temp. range (K)	AAD (%), Parameter θ						
			ω	M	η^*	Z_c	Ω	ωZ_c	ΩZ_c
		Reference fluids: 1-propanol, 1-butanol							
Methanol	10	425–525	4.08	5.88	9.14	7.09	7.88	6.93	7.33
Ethanol	25	348–512	2.51	2.94	3.73	4.63	4.32	0.64	4.32
2-Propanol	9	310–360	2.89	5.32	7.57	3.23	11.49	2.78	8.01
2-Butanol	9	321–378	10.18	8.77	7.07	5.70	10.66	14.12	8.62
1-Pentanol	14	288–399	2.16	1.38	0.77	2.65	2.59	1.73	2.61
1-Hexanol	5	297–329	9.55	8.81	6.37	4.82	10.42	13.41	8.12
1-Heptanol	8	298–346	7.51	6.08	4.51	9.34	8.11	5.90	8.61
1-Octanol	9	299–362	11.39	9.44	8.39	11.58	11.30	11.22	11.41
Total	89		6.28	6.07	5.94	6.12	8.34	7.09	7.37

Table VI. Viscosity Predictions for the Esters Using the GCSP Model

Ester	No. of data	Temp. range (K)	AAD (%), Parameter θ						
			ω	M	η^*	Z_c	Ω	ωZ_c	ΩZ_c
		Reference fluids: ethyl acetate, ethyl butyrate							
Methyl formate	4	279–298	0.65	0.76	0.02	3.95	0.94	1.16	0.13
Ethyl formate	8	283–331	0.23	0.40	0.01	2.73	1.13	0.19	0.31
Propyl formate	9	285–349	1.19	0.13	0.13	1.71	1.38	0.79	0.75
Methyl acetate	7	282–330	1.68	1.32	0.13	2.98	0.97	1.88	1.41
Total	28		0.93	0.65	0.07	2.84	1.10	1.00	0.64

where η is in mPa · s and T in K. Model parameters (T_c, P_c, Z_c, M, ω) and the correlated viscosity data were taken from the literature [29]. Extensive compilations of vapor pressure data [27, 30, 31] were used to calculate the parameter Ω.

Although good predictions result with the use of either ω or η^* as the third parameter in the GCSP formulation, the method based on η^*, in general, leads to marginally better predictions than that based on ω. This is not surprising considering that η^* is a characterization parameter based on viscosity itself, whereas ω is a parameter based on vapor pressure. However, since use of η^* requires a datum value of viscosity at $T_r = 0.6$ for the fluid of interest, the method loses its predictive character in absence of the required viscosity datum. In contrast, the use of ω does offer the advantage that the same characterization parameter is used for both thermodynamic and transport property predictions.

Table I also includes the results for alkanes obtained with the TRAPP and the one-parameter empirical method. In comparison to these, the GCSP method is observed to give better predictions. It is interesting to note that only T_c, P_c, and θ are required in the GCSP model, while the TRAPP method requires T_c, P_c, v_c, ω, and M.

4. CONCLUSIONS

In conclusion, the GCSP has been demonstrated to be a simple and yet a powerful technique for the correlation and prediction of viscosities of a variety of pure liquids over a wide range of temperatures. The ability of the GCSP method to use different reference fluids offers a tremendous advantage in the prediction of viscosities of components for which the shape factors are not valid. In general, the predictions of the GCSP method are better than those of the TRAPP method. However, the TRAPP method can be used over the entire fluid region, while the present GCSP model is applicable only for liquids and in the range where the empirical temperature function Eq. (9) applies. TRAPP can also be used with different reference fluids. Nevertheless, convergence difficulties have been reported with the TRAPP method for higher molar mass substances, e.g., octadecane and eicosane [14]. Thus, application of the TRAPP method to high-boiling heavy hydrocarbons may lead to large errors. Moreover, the TRAPP method is not applicable to polar systems; it predicts gas-like viscosities (and large errors) for polar liquids [19].

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