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Generalized One-Parameter Viscosity Equation for Light and Medium Liquid Hydrocarbons

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The applicability of a viscosity-temperature equation, proposed recently for heavy hydrocarbons, is extended to light and medium hydrocarbons. The one-parameter equation, $\log(\mu + 0.8) = 100(0.01T)^b$, was developed for the viscosity of heavy hydrocarbons, including branched/unbranched paraffins/olefins and nonfused/fused aromatic/naphthenic compounds. This generalized equation is demonstrated to be capable of modeling the viscosity of light and medium hydrocarbons ($30 < M < 300$ g/mol) that belong to paraffin (alkane), olefin (alkene), (*n*-alkyl)cyclopentane, (*n*-alkyl)cyclohexane, and aromatic families. Average deviations from the generalized viscosity equation are between 5 and 15% for most hydrocarbons. Parameter "*b*" is correlated well ($|r| > 0.99$) with molar mass (*M*), inverse of normal boiling point ($1/T_b$), critical temperature (T_c), and acentric factor (ω) of the hydrocarbons in each family. The results of this study combined with those reported previously yield a generalized one-parameter method for predicting the viscosity of light, medium, and heavy liquid hydrocarbons.

Numerous calculation methods for the effect of temperature on liquid viscosity are available in the literature (Perry et al., 1984; Reid et al., 1977, 1986). The viscosity prediction methods developed by Ely and Hanley (1981), Teja and Rice (1981), and Pedersen et al. (1984) have been successful for certain liquid hydrocarbons. Several empirical correlations have been proposed for viscosity-temperature variation of liquids, of which the following four were evaluated by Reid et al. (1986): eq 1 by Andrade or de Guzman, eq 2 by Vogel, eq 3 for the Lewis-Squires chart, and eq 4 by van Velzen-Cardozo-Langenkamp.

$$\ln \mu = A + B/T \quad (1)$$

$$\ln \mu = A + B/(T + C) \quad (2)$$

$$\mu^{-0.2861} = \mu_K^{-0.2861} + (T - T_K)/233 \quad (3)$$

$$\log \mu = B(T^{-1} - T_0^{-1}) \quad (4)$$

In eqs 1-4, μ denotes the dynamic and/or kinematic viscosity (mPa·s and mm²/s) at temperature *T* (K). The above correlations involve two or three empirical parameters that may be determined from viscosity measurements at two or more temperatures. For eq 3, the data for viscosity (μ_K) at a temperature T_K are needed. Equation 1, used commonly for liquid viscosity, was shown to be inadequate for pure heavy hydrocarbons (Mehrotra, 1991). Equation 4 was obtained by eliminating constant *A* from eq 1, via temperature T_0 , at which the viscosity is 1 mPa·s or 1 cP exactly. In addition, van Velzen et al. (1972) provided an "equivalent chain length" approach for estimating parameters *B* and T_0 in eq 4.

Another two-parameter viscosity equation, used commonly for crude oils, is the Walther (1931) or ASTM (1981) correlation, which in an antilogarithmic form is (Mehrotra, 1991)

$$\log(\mu + 0.8) = 10^{b_1 T^{b_2}} \quad (5)$$

For 273 pure heavy hydrocarbons in API (1966), including branched and/or unbranched paraffins and olefins, nonfused and/or fused ring aromatics, and nonfused and/or fused ring naphthenes, a linear cross-correlation between parameters b_1 and b_2 was demonstrated and used to derive the following one-parameter equation (Mehrotra, 1991):

$$\log(\mu + 0.8) = 100(0.01T)^b \quad (6)$$

where 0.01 and 100 are generalized constants for 273 pure heavy hydrocarbons in API (1966). Furthermore, for each of the six families of heavy hydrocarbons in API (1966), parameter "*b*" was shown to be related to the logarithm of molar mass and the inverse of boiling point at 10 mmHg.

The objective of this study is to extend the use of eq 6 for the viscosity of a wider variety of hydrocarbons. For the light and medium hydrocarbons, parameter *b* in eq 6 is correlated with other properties, namely, the molar mass (*M*), the normal boiling point (T_b), the critical temperature (T_c), and the acentric factor (ω). These correlations provide useful predictive capabilities to the generalized one-parameter viscosity equation (eq 6).

The Database. Table I lists the 89 pure light and medium hydrocarbons included in the database. Also indicated in Table I are the number of data points and the temperature range along with *M*, T_b , T_c , and ω for each hydrocarbon. These hydrocarbons, with $30 < M < 300$ g/mol, are classified into the following five groups: paraffins or alkanes, 1-olefins or 1-alkenes, (*n*-alkyl)cyclopentanes, (*n*-alkyl)cyclohexanes, and alkylbenzenes or aromatics. The viscosity-temperature data for 45 of the database hydrocarbons were compiled by Monnery et al. (1991) from two main sources: TRC (1986) and Vargaftik (1975). For the remaining 44 compounds, the data were obtained from Rossini et al. (1953) and Vargaftik (1975).

Due to the logarithmic term, eqs 5 and 6 cannot be used for liquids with a viscosity of less than 0.2 mPa·s over the range of temperature. For some of the lighter members of the paraffin and olefin families, however, the viscosity falls below 0.2 mPa·s at higher temperatures. Hence, the maximum temperature for those compounds was selected such that the lowest viscosity value was above 0.3 mPa·s. Note that the viscosity range of 0.2-0.3 mPa·s was excluded mainly to avoid possible regression errors due to a divergence of the $\log(\mu + 0.8)$ term. Thus, the viscosity calculation method involving eq 5 or 6 is not recommended for μ much below 0.3 mPa·s; such low viscosities, however, are encountered only for the lightest hydrocarbons.

Discussion of Results

Regression of Viscosity-Temperature Data with Equation 5. The viscosity-temperature data for each

Table I. Results of Correlation and Prediction of Viscosity-Temperature Data for Light and Medium Liquid Hydrocarbons^a

compound	<i>M</i> , g/mol	<i>T</i> _b , K	<i>T</i> _c , K	ω	<i>N</i>	temp range, K	two-parameter correlation (eq 5)			one-parameter equation (eq 6)		
							<i>b</i> ₁	<i>b</i> ₂	AAD, %	<i>b</i>	AAD, %	AVR
Paraffins												
ethane	30.1	184.6	305.3	0.100	5	103–143	9.061	–4.835	2.0			
propane	44.1	231.1	369.8	0.154	9	100–183	7.254	–3.703	4.1			
isobutane	58.1	261.4	408.2	0.183	6	193–243	12.022	–5.605	2.2	–9.161	16.1	0.89
<i>n</i> -butane	58.1	272.2	425.2	0.200	6	183–233	10.326	–4.913	1.8	–9.709	24.1	1.10
isopentane	72.2	301.0	460.4	0.227	5	223–263	14.130	–6.387	1.5	–8.067	5.4	1.01
<i>n</i> -pentane	72.2	309.2	469.8	0.251	9	183–263	10.051	–4.698	2.6	–8.681	37.9	1.20
<i>n</i> -hexane	86.2	341.9	507.9	0.298	12	183–293	10.057	–4.599	3.4	–7.763	21.4	1.00
<i>n</i> -heptane	100.2	371.6	540.1	0.350	15	183–323	10.185	–4.566	4.5	–7.053	20.0	1.09
<i>n</i> -octane	114.2	398.8	568.8	0.400	14	223–353	11.270	–4.941	4.2	–6.313	18.6	0.95
<i>n</i> -nonane	128.3	424.0	594.6	0.445	16	223–373	11.144	–4.830	4.8	–5.956	20.2	1.09
<i>n</i> -decane	142.3	447.3	617.6	0.489	15	253–393	11.706	–5.002	4.0	–5.602	8.8	1.03
<i>n</i> -undecane	156.3	469.1	638.7	0.530	15	253–413	11.508	–4.880	4.8	–5.386	9.7	1.03
<i>n</i> -dodecane	170.3	489.5	658.3	0.571	14	273–433	11.909	–5.000	5.0	–5.176	6.1	1.01
<i>n</i> -tridecane	184.4	508.6	676.2	0.610	15	273–453	11.770	–4.914	5.4	–5.022	6.4	1.01
<i>n</i> -tetradecane	198.4	526.7	693.0	0.644	14	283–453	11.543	–4.794	4.5	–4.875	5.1	1.01
<i>n</i> -pentadecane	212.4	543.8	706.8	0.692	15	283–473	11.590	–4.788	5.5	–4.764	5.3	1.00
<i>n</i> -hexadecane	226.5	560.0	720.6	0.731	15	293–493	11.837	–4.862	6.0	–4.664	4.9	1.00
<i>n</i> -heptadecane	240.5	575.2	733.4	0.762	15	303–513	12.101	–4.944	6.6	–4.577	5.2	0.99
<i>n</i> -octadecane	254.5	589.5	748.2	0.790	15	303–513	11.639	–4.745	5.7	–4.489	4.5	0.99
<i>n</i> -nonadecane	268.5	603.1	756.0	0.827	15	313–533	11.852	–4.810	6.0	–4.422	5.2	0.99
<i>n</i> -eicosane	282.6	617.0	767.0	0.907	15	313–533	11.525	–4.668	5.6	–4.349	4.7	0.99
1-Olefins												
ethene	28.1	169.3	282.4	0.085	3	113–133	11.053	–5.832	1.3			
propene	42.1	225.5	364.9	0.144	8	103–173	8.415	–4.267	3.3			
1-butene	56.1	266.9	419.6	0.187	6	173–223	10.905	–5.221	1.9	–10.511	28.5	1.14
1-pentene	70.1	303.1	464.7	0.245	8	183–253	10.942	–5.114	3.2	–9.016	30.5	1.15
1-hexene	84.2	336.6	504.0	0.285	6	223–273	11.500	–5.236	1.4	–7.717	10.1	1.03
1-heptene	98.2	366.8	537.2	0.358	8	273–308	13.503	–5.965	0.4	–6.889	1.6	1.00
1-octene	112.2	394.4	566.6	0.386	14	273–338	13.236	–5.764	1.3	–6.372	2.7	1.00
1-nonene	126.2	420.0	592.0	0.430	19	273–363	12.614	–5.443	1.9	–5.990	3.7	1.01
1-decene	140.3	443.7	615.0	0.491	24	273–388	12.313	–5.266	2.5	–5.694	4.4	1.01
1-undecene	154.3	465.8	637.0	0.518	24	273–388	11.433	–4.867	1.9	–5.454	5.4	1.01
1-dodecene	168.3	486.5	657.0	0.558	24	273–388	11.031	–4.668	1.9	–5.262	6.1	1.02
1-tridecene	182.4	505.9	674.0	0.598	24	273–388	10.603	–4.464	1.5	–5.096	6.8	1.02
1-tetradecene	196.4	524.3	689.0	0.644	24	273–388	10.322	–4.323	1.3	–4.956	7.4	1.02
1-pentadecene	210.4	541.5	704.0	0.682	24	273–388	9.584	–4.001	2.4	–4.832	7.7	1.02
1-hexadecene	224.4	558.0	717.0	0.721	23	278–388	9.975	–4.137	1.3	–4.718	7.3	1.02
1-heptadecene	238.5	573.4	732.2	0.714†	21	288–388	9.944	–4.105	1.3	–4.612	11.2	1.01
1-octadecene	252.5	588.0	739.0	0.807	20	293–388	9.806	–4.032	1.0	–4.520	5.5	1.01
1-nonadecene	266.5	602.2	755.0	0.780†	19	298–388	9.752	–3.994	0.9	–4.437	4.9	1.01
1-eicosene	280.5	615.5	765.2	0.808†	17	308–388	9.704	–3.959	0.8	–4.358	3.9	1.01
(n-Alkyl)cyclopentanes												
cyclopentane	70.1	322.4	511.7	0.196	8	253–353	11.866	–5.236	2.1	–6.566	7.0	1.02
methylcyclopentane	84.2	345.0	532.7	0.231	10	253–343	12.382	–5.410	3.5	–6.343	7.1	1.02
ethylcyclopentane	98.2	376.6	569.5	0.271	11	253–353	11.580	–5.055	3.5	–6.159	9.5	1.03
<i>n</i> -propylcyclopentane	112.2	404.1	596.2	0.335	13	253–373	10.458	–4.554	1.7	–5.893	12.1	1.04
<i>n</i> -butylcyclopentane	126.2	429.8	621.2	0.372†	27	253–383	10.425	–4.491	2.6	–5.618	12.4	1.04
<i>n</i> -pentylcyclopentane	140.3	453.7	643.8	0.415†	27	253–383	10.010	–4.279	2.4	–5.391	13.7	1.05
<i>n</i> -hexylcyclopentane	154.3	476.3	660.1	0.476	27	253–383	9.774	–4.146	2.7	–5.196	14.9	1.05
<i>n</i> -heptylcyclopentane	168.3	497.3	679.0	0.515	27	253–383	9.443	–3.981	3.3	–5.036	16.9	1.06
<i>n</i> -octylcyclopentane	182.4	516.9	694.0	0.564	27	253–383	9.248	–3.876	3.8	–4.898	18.4	1.07
<i>n</i> -nonylcyclopentane	196.4	535.3	710.5	0.610	27	253–383	9.090	–3.789	4.3	–4.780	19.8	1.08
<i>n</i> -decylcyclopentane	210.4	552.5	723.8	0.654	27	253–383	8.934	–3.707	4.8	–4.677	21.2	1.08
<i>n</i> -undecylcyclopentane	224.4	569.0	742.2	0.619†	25	263–383	9.097	–3.752	3.7	–4.564	15.6	1.05
<i>n</i> -dodecylcyclopentane	238.5	584.1	754.4	0.719	24	268–383	9.081	–3.729	3.2	–4.473	13.8	1.04
<i>n</i> -tridecylcyclopentane	252.5	599.1	765.6	0.661†	22	278–383	9.223	–3.769	2.3	–4.384	9.9	1.03
<i>n</i> -tetradecylcyclopentane	266.5	599.0	772.0	0.789	21	283–383	9.231	–3.759	2.0	–4.313	8.5	1.02
<i>n</i> -pentadecylcyclopentane	280.5	625.0	780.0	0.833	19	293–383	9.306	–3.775	1.3	–4.242	6.2	1.01
<i>n</i> -hexadecylcyclopentane	294.6	637.0	791.0	0.861	18	298–383	9.305	–3.764	1.1	–4.184	5.3	1.01
(n-Alkyl)cyclohexanes												
cyclohexane	84.2	353.8	553.5	0.212	8	283–353	13.556	–5.738	1.8	–5.578	1.8	1.00
methylcyclohexane	98.2	374.1	572.2	0.236	13	253–373	12.415	–5.338	4.8	–5.874	7.7	1.02
ethylcyclohexane	112.2	404.9	609.0	0.243	13	253–373	10.339	–4.465	2.0	–5.682	12.8	1.04
<i>n</i> -propylcyclohexane	126.2	432.4	639.0	0.258	13	253–373	10.151	–4.357	1.5	–5.515	13.2	1.04
<i>n</i> -butylcyclohexane	140.3	454.1	667.0	0.362	7	253–313	9.407	–4.013	1.1	–5.390	12.2	1.03
<i>n</i> -pentylcyclohexane	154.3	476.8	669.0	0.426†	25	263–383	10.408	–4.381	1.4	–5.087	8.7	1.02
<i>n</i> -hexylcyclohexane	168.3	497.9	687.7	0.462†	25	263–383	10.282	–4.299	1.9	–4.929	8.8	1.03
<i>n</i> -heptylcyclohexane	182.4	518.1	704.7	0.501†	25	263–383	10.137	–4.214	2.2	–4.795	9.1	1.03
<i>n</i> -octylcyclohexane	196.4	536.8	720.3	0.534†	25	263–383	10.035	–4.150	2.8	–4.679	9.3	1.03
<i>n</i> -nonylcyclohexane	210.4	554.7	734.6	0.568†	25	263–383	9.917	–4.083	3.2	–4.579	9.5	1.03
<i>n</i> -decylcyclohexane	224.4	570.8	750.0	0.583	23	273–383	10.036	–4.112	2.6	–4.479	6.6	1.02

Table I (Continued)

compound	<i>M</i> , g/mol	<i>T_b</i> , K	<i>T_c</i> , K	ω	<i>N</i>	temp range, K	two-parameter correlation (eq 5)			one-parameter equation (eq 6)		
							<i>b</i> ₁	<i>b</i> ₂	AAD, %	<i>b</i>	AAD, %	AVR
<i>n</i> -undecylcyclohexane	238.5	586.4	759.9	0.615†	21	283–383	10.127	-4.131	2.2	-4.392	4.5	1.01
<i>n</i> -dodecylcyclohexane	252.5	601.1	771.1	0.631†	20	288–373	10.134	-4.119	2.3	-4.319	3.8	1.01
<i>n</i> -tridecylcyclohexane	266.5	615.1	781.5	0.652†	19	293–383	10.137	-4.107	2.4	-4.253	3.3	1.00
<i>n</i> -tetradecylcyclohexane	280.5	628.2	791.2	0.661†	18	298–383	10.162	-4.105	2.4	-4.194	2.8	1.00
<i>n</i> -pentadecylcyclohexane	294.6	641.2	800.2	0.685†	17	303–383	10.176	-4.099	2.4	-4.140	2.5	1.00
<i>n</i> -hexadecylcyclohexane	308.6	653.2	808.5	0.696†	16	308–383	10.224	-4.107	2.4	-4.090	2.4	1.00
Aromatics												
benzene	78.1	353.2	562.2	0.212	8	283–353	14.497	-6.197	1.8	-5.991	1.6	1.00
toluene	92.1	383.8	591.8	0.263	11	253–353	11.830	-5.146	2.7	-6.120	8.0	1.02
ethylbenzene	106.2	409.3	617.2	0.302	13	253–373	11.330	-4.911	3.4	-5.925	10.2	1.03
<i>m</i> -xylene	106.2	412.3	617.1	0.325	10	273–363	11.877	-5.148	2.0	-5.990	5.3	1.01
<i>o</i> -xylene	106.2	417.6	630.3	0.310	12	273–383	11.904	-5.102	2.8	-5.691	5.5	1.01
<i>p</i> -xylene	106.2	411.5	616.2	0.321	8	293–363	12.861	-5.530	1.4	-5.919	2.2	1.00
cumene	120.2	425.6	631.0	0.335	5	273–313	10.166	-4.403	0.2	-5.780	5.5	1.01
isopropylbenzene	120.2	425.6	651.0	0.326	7	273–333	10.532	-4.552	0.6	-5.749	6.3	1.01
<i>n</i> -propylbenzene	120.2	432.4	638.3	0.344	15	253–393	11.493	-4.930	4.1	-5.670	9.9	1.03
<i>n</i> -butylbenzene	134.2	456.5	660.5	0.393	17	253–413	11.449	-4.878	4.7	-5.482	10.1	1.04
<i>n</i> -hexylbenzene	162.3	499.3	696.3	0.482†	30	253–398	10.518	-4.425	2.1	-5.087	10.7	1.03
<i>n</i> -octylbenzene	190.3	537.6	726.9	0.557†	30	253–398	10.116	-4.212	1.9	-4.824	11.8	1.04
<i>n</i> -decylbenzene	218.4	571.0	752.8	0.615†	29	258–398	9.876	-4.075	1.7	-4.615	11.1	1.04
<i>n</i> -dodecylbenzene	246.4	600.8	774.8	0.656†	26	273–398	9.762	-3.996	1.8	-4.437	8.2	1.02
naphthalene	128.2	491.1	748.4	0.269	4	353–393	10.639	-4.414	0.2	-4.749	1.1	1.00

^a *N* = number of viscosity data points; AAD = $(1/N) \sum |\mu_{\text{exp}} - \mu_{\text{cal}}| / \mu_{\text{exp}}$; AVR = $(1/N) \sum (\mu_{\text{cal}} / \mu_{\text{exp}})$. Values marked with a dagger are calculated.

Table II. Summary of Viscosity Calculation Results for the Five Hydrocarbon Families^a

hydrocarbon family	<i>n</i>	two-parameter eq (5) overall AAD, %	one-parameter eq (6) overall AAD, %
paraffins	21	4.3	12.1
1-olefins	19	1.7	8.1
(<i>n</i> -alkyl)cyclopentanes	17	2.8	12.5
(<i>n</i> -alkyl)cyclohexanes	17	2.3	7.0
aromatics	15	2.1	6.6
average		2.7	9.4

^a *n* = number of compounds; overall AAD = $(1/n) \sum [(1/N) \sum |\mu_{\text{exp}} - \mu_{\text{cal}}| / \mu_{\text{exp}}]$.

compound were regressed individually by use of Walther's two-parameter correlation, eq 5, with the results summarized in Table I. The average absolute deviations (AADs) are very satisfactory as they are generally below 5%. In Table II, the overall AADs for the five families of hydrocarbons range from 1.7% for 1-olefins to 4.3% for paraffins. Overall, the average deviations for light and medium hydrocarbons with eq 5 are similar to those obtained by Mehrotra (1991) for heavy hydrocarbons.

Cross-Correlation between Parameters *b*₁ and *b*₂. A cross plot of the two parameters in eq 5 for all database compounds is presented as Figure 1. Despite some scatter, the points suggest a linear cross correlation in the parameter values. Consequently, the regression of viscosity-temperature data for each compound individually with eq 5 may not be appropriate.

Regression of Viscosity Data with the Generalized Equation (Equation 6). Regression calculations for each hydrocarbon in the database were performed with the one-parameter equation (eq 6). To maintain consistency with the previous study on the viscosity of heavy hydrocarbons (Mehrotra, 1991), no attempt was made to reevaluate the generalized constants 0.01 and 100 in eq 6. The "optimum" values of parameter *b* and the corresponding AAD for the database hydrocarbons are given in Table I. The average deviation for most compounds in Table I is 5–15%, which is within the level of reliability for literature

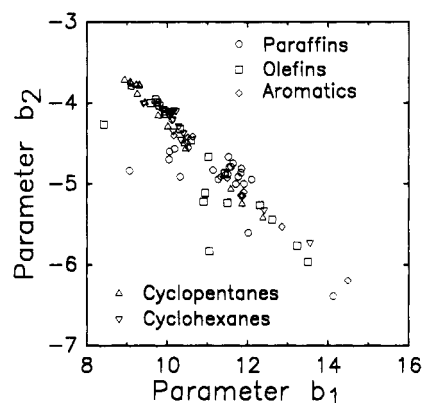


Figure 1. Cross correlation between parameters *b*₁ and *b*₂ for light and medium hydrocarbons in Walther's two-parameter correlation (eq 5).

viscosity data (Ely and Hanley, 1981).

In Table II, the overall AADs for the one-parameter equation range from 6.6% for the aromatics to 12.5% for (*n*-alkyl)cyclopentanes. As expected, the AADs for the generalized equation (eq 6) are larger than those for the two-parameter Walther's correlation (eq 5). Nonetheless, the magnitude of deviations with eq 6 is indeed very satisfactory in view of the generalization involving a wide variety of light and medium hydrocarbons. It is pointed out that the deviations for ethane, propane, ethene, and propene (i.e. the first two members of the paraffin and 1-olefin families) were high (AAD > 50%) due to their low viscosity at very low temperatures (i.e. *T* < 180 K); hence, the use of eq 6 is not recommended for the very light hydrocarbons.

Dependence of Parameter *b* on Hydrocarbon Properties. For the heavy hydrocarbons in API (1966), it was shown that parameter *b* could be predicted from molar mass and the boiling temperature (Mehrotra, 1991). For this study on light and medium hydrocarbons, the four properties selected are the molar mass (*M*), the normal boiling point (*T_b*), the critical temperature (*T_c*), and the acentric factor (ω).

Table III. Correlation of Parameter b and Molar Mass (M) with Equation 7

hydrocarbon family	regression constants			
	B_0^m	B_1^m	B_2^m	$ r $
paraffins	-6.351×10	4.664×10	-9.189	0.999
1-olefins	-6.972×10	5.245×10	-1.054×10	0.997
(<i>n</i> -alkyl)cyclopentanes	-1.604×10	5.836	-4.098×10^{-1}	0.998
(<i>n</i> -alkyl)cyclohexanes	-2.163×10	1.116×10	-1.646	0.997
aromatics	-1.403×10	3.955	2.884×10^{-2}	0.990

Table IV. Correlation of Parameter b and Normal Boiling Point (T_b) with Equation 8

hydrocarbon family	regression constants			
	B_0^t	B_1^t	B_2^t	$ r $
paraffins	-1.396	-1.358×10^3	-2.588×10^5	0.998
1-olefins	-3.075	9.987×10	-5.610×10^5	0.999
(<i>n</i> -alkyl)cyclopentanes	5.372×10^{-1}	-3.692×10^3	4.504×10^5	0.999
(<i>n</i> -alkyl)cyclohexanes	1.668×10^{-1}	-3.398×10^3	4.189×10^5	0.998
aromatics	1.093×10^{-1}	-3.284×10^3	3.368×10^5	0.995

Table V. Correlation of Parameter b and Critical Temperature (T_c) with Equation 9

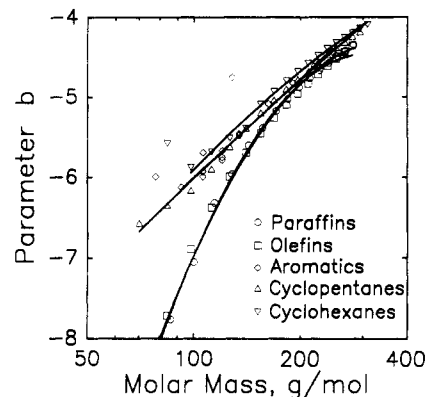
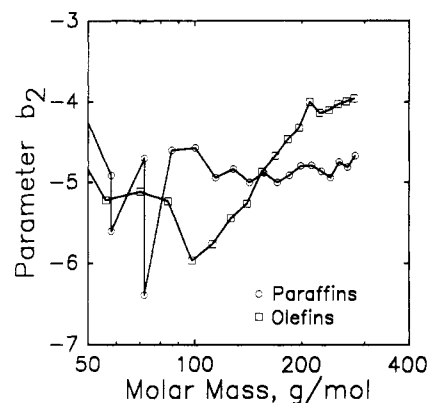
hydrocarbon family	regression constants			
	B_0^c	B_1^c	B_2^c	$ r $
paraffins	-2.879×10	6.075×10^{-2}	-3.777×10^{-5}	0.999
1-olefins	-3.033×10	6.571×10^{-2}	-4.173×10^{-5}	0.997
(<i>n</i> -alkyl)cyclopentanes	-1.242×10	1.305×10^{-2}	-3.296×10^{-6}	0.998
(<i>n</i> -alkyl)cyclohexanes	-1.155×10	1.092×10^{-2}	-2.022×10^{-6}	0.991
aromatics	-1.298×10	1.300×10^{-2}	-2.499×10^{-6}	0.993

Parameter b and Molar Mass (M). Figure 2 shows the dependence of parameter b on molar mass (M) for all database compounds. The value of parameter b is noted to increase with an increase in molar mass. The b and M values were regressed with the following polynomial.

$$b = B_0^m + B_1^m[\log M] + B_2^m[\log M]^2 \quad (7)$$

The results of regression calculations, summarized in Table III, were used to plot the curves in Figure 2. Note that the curves for paraffins and 1-olefins follow an almost identical behavior in Figure 2. In contrast, no consistent trends were found when the parameter b_2 in eq 5 was correlated with M , as is evident in Figure 3 for the same two hydrocarbon families. A comparison of the results in Figures 2 and 3 indicates the obvious superiority of the one-parameter equation (eq 6) over the two-parameter correlation (eq 5).

In obtaining the regression constants for all four correlations (eqs 7–10), the following six compounds were excluded because they did not follow the trends shown by other members in the respective hydrocarbon families: isobutane, isopentane, cyclopentane, cyclohexane, benzene, and naphthalene. Of these six compounds, the first two are isoalkanes and the next three are the first members (all without an alkyl group) of three families involving branched cyclic or aromatic structures. Thus, all of these

**Figure 2. Correlation of parameter b (in eq 6) with molar mass (M) for the five families of hydrocarbons.****Figure 3. Variation of parameter b_2 in Walther's two-parameter correlation (eq 5) with molar mass (M) for paraffins and olefins.**

compounds are structurally different from other members in the respective families. Large deviations for the first members of many homologous series were also found by van Velzen et al. (1972).

Parameter b and Normal Boiling Point (T_b). The values of parameter b and the inverse of normal boiling point ($1/T_b$) were regressed by use of the following polynomial.

$$b = B_0^t + B_1^t/T_b + B_2^t/T_b^2 \quad (8)$$

The values of B_0^t , B_1^t , and B_2^t for the five families of hydrocarbons are provided in Table IV. The correlation coefficients for all cases are impressive ($|r| > 0.99$) and similar to those in Table III.

Parameter b and Critical Temperature (T_c). Equation 9 was used to correlate parameter b and T_c .

$$b = B_0^c + B_1^c/T_c + B_2^c/T_c^2 \quad (9)$$

with the values of B_0^c , B_1^c , and B_2^c given in Table V. The correlation coefficients are again fairly satisfactory for all five families of hydrocarbons.

Parameter b and Acentric Factor (ω). For approximately 25% of the database hydrocarbons, no tabulated values of acentric factor (ω) could be located. For those cases, the values reported in Table I (identified by a

Table VI. Correlation of Parameter b and Acentric Factor (ω) with Equation 10

hydrocarbon family	regression constants				
	B_0^ω	B_1^ω	B_2^ω	B_3^ω	$ r $
paraffins	-1.596×10	4.019×10	-4.920×10	2.103×10	0.999
1-olefins	-1.779×10	5.283×10	-7.556×10	3.802×10	0.996
(<i>n</i> -alkyl)cyclopentanes	-7.908	7.499	-3.697		0.996
(<i>n</i> -alkyl)cyclohexanes	-6.521	3.201	4.396×10^{-1}		0.995
aromatics	-7.618	6.321	-2.286		0.988

Table VII. Comparison of Calculated Viscosities of Five Selected Hydrocarbons at 323.15 K

	<i>n</i> -undecane	1-undecene	<i>n</i> -hexylcyclopentane	<i>n</i> -pentylcyclohexane	<i>n</i> -hexylbenzene	average dev, ^a %
μ , mPa·s	0.760	0.680	0.938	1.026	1.035	
Reported Viscosity at 323.15 K						
Viscosities Calculated with Parameters in Table I						
Two-Parameter (Equation 5)						
μ , mPa·s	0.724	0.665	0.916	1.018	1.017	
dev, ^a %	4.8	2.2	2.4	0.8	1.7	2.4
One-Parameter (Equation 6)						
μ , mPa·s	0.715	0.668	0.881	1.004	1.004	
dev, ^a %	5.9	1.8	6.1	2.1	3.0	3.8
dev ^a in Viscosities Calculated from Equation 6 with Predicted <i>b</i>						
<i>b</i> from <i>M</i> (eq 7), %	8.6	2.0	13.7	2.5	9.9	7.3
<i>b</i> from <i>T_b</i> (eq 8), %	13.4	1.1	9.6	5.7	6.5	7.3
<i>b</i> from <i>T_c</i> (eq 9), %	6.9	3.2	14.7	9.3	8.9	8.6
<i>b</i> from ω (eq 10), %	2.2	5.3	3.8	0.9	4.6	3.5

$$^a \text{dev} = |\mu_{\text{exp}} - \mu_{\text{cal}}| / \mu_{\text{exp}}$$

dagger) are the arithmetic mean of those estimated from vapor pressure at $T_r = 0.7$ and the Lee-Kesler correlations (Reid et al., 1986). The variation of parameter *b* with ω was represented by the following equation.

$$b = B_0^w + B_1^w \omega + B_2^w \omega^2 \quad (10)$$

The values of B_0^w , B_1^w , B_2^w , and $|r|$ are given in Table VI. A third-order term (i.e. $B_3^w \omega^3$) for paraffins and 1-olefins was introduced to improve the match for the "heavier" members.

Comparison of Predicted Viscosities. Of the two viscosity equations considered here, Walther's two-parameter correlation, eq 5, tends to give a somewhat better representation of the viscosity-temperature data for hydrocarbons on an individual basis. However, the resulting parameter values (b_1 or b_2) do not yield a definite or consistent trend with any of the four properties for all hydrocarbon families; as was illustrated, for example, in Figure 3 for b_2 versus *M*. On the other hand, as indicated by the impressive $|r|$ values in Tables III-VI, the values of parameter *b* in the generalized equation, eq 6, follow consistent trends for every hydrocarbon family. This perhaps is the most desirable characteristic of the generalized one-parameter equation.

Finally, sample calculations were made by using eq 5, eq 6, and eq 6 combined with parameter *b* predicted from eqs 7-10 to compare the viscosities of five arbitrarily selected hydrocarbons at 323.15 K (50 °C). The five hydrocarbons, all with $M \approx 150$ -160 g/mol, were chosen as being representative of each of the five families. The calculation results are summarized in Table VII. The viscosities calculated from eqs 5 and 6, with empirically determined parameters in Table I, are within average deviations of 2-4%. Average deviations for the viscosities calculated from eq 6, with parameter *b* predicted from eqs 7-10, are within 5-15%. Between the four correlations for parameter *b*, the best predictions in these illustrative calculations at one temperature are by use of eq 10, the *b*- ω correlation.

Conclusions

The effect of temperature on the liquid-phase viscosity of 89 light and medium hydrocarbons were represented very well by the following two-parameter Walther's correlation ($\text{AADs} < 4$ -5%): $\log(\mu + 0.8) = 10^{b_1 T^{b_2}}$. A linear cross correlation between parameters b_1 and b_2 for all database hydrocarbons was observed. Subsequently, the following one-parameter generalized viscosity equation, proposed recently for pure heavy hydrocarbons, was va-

lidated for the database compounds: $\log(\mu + 0.08) = 100(0.01 T)^b$. The calculated viscosities from this one-parameter equation were within 5-15% of the data for most compounds. Parameter *b* in the above equation was expressed in terms of the hydrocarbon molar mass, normal boiling point, critical temperature, and acentric factor. This resulted in a predictive method for the viscosity of paraffins, 1-olefins, (*n*-alkyl)cyclopentanes, (*n*-alkyl)cyclohexanes, and alkylbenzenes or aromatics.

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Nomenclature

AAD = average absolute deviation, %
 AVR = average viscosity ratio
 A, B, C = empirical parameters in eqs 1-4
 b_1, b_2 = empirical parameters in eq 5
b = single parameter in eq 6
 B_0^m, B_1^m, B_2^m = regression constants in eq 7
 B_0^t, B_1^t, B_2^t = regression constants in eq 8
 B_0^c, B_1^c, B_2^c = regression constants in eq 9
 B_0^w, B_1^w, B_2^w = regression constants in eq 10
M = molar mass, g/mol
n = number of compounds
N = number of viscosity data points
 $|r|$ = correlation coefficient
T = absolute temperature, K
T_b = normal boiling point, K
T_c = critical temperature, K
T_r = reduced temperature

Greek Symbols

μ = dynamic viscosity, mPa·s
 ω = acentric factor

Subscripts

cal = calculated, predicted
 exp = experimental

Literature Cited

- API. *Properties of Hydrocarbons of High Molecular Weights*; API Research Project 42; American Petroleum Institute: Washington, DC, 1966.
 ASTM. *Annual Book of ASTM Standards*; American Society for Testing and Material: Philadelphia, PA, 1981; Part 23, p 205.
 Ely, J. F.; Hanley, H. J. M. *A Computer Program for the Prediction of Viscosity and Thermal Conductivity in Hydrocarbon Mix-*

- tures; NBS Technical Note 1039; National Bureau of Standards: Washington, DC, 1981.
- Mehrotra, A. K. A Generalized Viscosity Equation for Pure Heavy Hydrocarbons. *Ind. Eng. Chem. Res.* 1991, 30, 420.
- Monnery, W. D.; Mehrotra, A. K.; Svrcek, W. Y. Modified Shape Factors for Improved Viscosity Predictions Using Corresponding States. *Can. J. Chem. Eng.* 1991, in press.
- Pedersen, K. S.; Fredensland, A.; Christensen, P. L.; Thomassen, P. Viscosity of Crude Oils. *Chem. Eng. Sci.* 1984, 39, 1011.
- Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's Chemical Engineers' Handbook*, 6th ed.; McGraw-Hill: New York, 1984; Chapter 3.
- Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; Chapter 9.
- Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1986; Chapter 9.
- Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, PA, 1953.
- Teja, A. S.; Rice, P. Generalized Corresponding States Method for the Viscosities of Liquid Mixtures. *Ind. Eng. Chem. Fundam.* 1981, 20, 77.
- TRC. TRC Thermodynamic Tables—Hydrocarbons. *Thermodynamic Research Center Handbook*; Texas A&M University: College Station, TX, 1986; Section C.
- van Velzen, D.; Cardozo, R. L.; Langenkamp, H. A Liquid Viscosity-Temperature-Chemical Constitution Relation for Organic Compounds. *Ind. Eng. Chem. Fundam.* 1972, 11, 20.
- Vargaftik, N. B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed.; Wiley: New York, 1975.
- Walther, C. The Evaluation of Viscosity Data. *Erdöl Teer* 1931, 7, 382.

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Estimation of the Porosity of Particle Mixtures by a Linear-Mixture Packing Model

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The geometrical/analytical interpretation of the random packing structure of particles is discussed. On the basis of this analysis, a general framework for the development of a mathematical model, which relates the porosity to the particle size distribution of particulate materials, is derived. As a result, a linear-mixture packing model, which is actually the combination of the linear and mixture packing models proposed earlier, has been developed so as to coincide with the analytical packing theory. The comparisons of the theoretical results with the previously reported theoretical and experimental results indicate that this new model is superior to the linear or mixture packing model.

Introduction

Porosity, i.e., fractional voidage, is one of the most basic properties of an assemblage of particulate materials. Over the years, many studies have been done on the packing of particles, as recently summarized by Cumberland and Crawford (1987) and German (1989), respectively. Ever since the work done by Fuller and Thompson (1907), it has been well established that the porosity of a particulate mixture is strongly affected by the particle size distribution involved. Therefore, various attempts have been made to develop a mathematical model that relates the porosity to the size distribution of particulate materials. There are a number of models available in the literature for this purpose, as recently reviewed by Ouchiya and Tanaka (1989) and Yu (1989), respectively. These models may be classified into two groups: the geometrical models and the analytical models.

Since porosity is one of the structural properties of an assemblage of particles, it is more promising to develop a packing model from the viewpoint of the microstructure of particles. However, it is very difficult, if not impossible, to characterize mathematically the packing structure and hence predict the structural properties of a particle mixture. Therefore, a geometrical model is usually developed from the analysis of defined or notional simple geometrical units. Perhaps the most realistic approach to the random packing of particles is based on the statistical geometrical analysis of tetrahedral configurations. Along this line, Dodds (1980), after extending the theory of idealized gapless packing (Wise, 1952; Hogendijk, 1963), proposed

a simple statistical geometrical model. On the other hand, Ouchiya and Tanaka (1981, 1986, 1988, 1989), beginning with the analysis of the contact condition of a particle with other particles, developed a mathematical model for the porosity estimation, which they named as the simplified packing model. A similar in geometry but analytically different approach was proposed by Suzuki et al. (Suzuki and Oshima, 1985; Suzuki et al., 1985). These geometrical models, though the validity of a simple geometric unit in accurately representing the real random arrangements of particles is questionable, can also be used to predict other structural properties, e.g. the contact points of a packing of spheres.

However, a mathematical model for the porosity estimation can also be developed analytically. The most popular analytical model is the linear packing model. This model, as an algorithm, was in fact first proposed by Westman and Hugill (1930). This algorithm was adopted by Lee (1970) for the porosity estimation of multicomponent mixtures. Lee's algorithm was later extended to the packing of continuous size distributions by Bierwagen and Sanders (1974) and modified by Itoh et al. (1986). However, as pointed out by Yu and Standish (1987), the assumption made in Lee's algorithm that packing density (one minus porosity) rather than specific volume (reciprocal of packing density) is proportional to fractional solid volumes is not correct. This remark may be supported by the theoretical/experimental work described by Yerazunis et al. (1962, 1965). Recently, Stovall et al. (1986) developed the linear packing model in a more logical way, while Yu