

A Liquid Viscosity-Temperature-Chemical Constitution Relation for Organic Compounds

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A new empirical relation between liquid dynamic viscosity, temperature, and chemical constitution of organic compounds is proposed. The method is based on the De Guzman-Andrade equation and the introduction of a new property, the equivalent chain length of a compound, defined as the chain length (in carbon atoms) of the hypothetical *n*-alkane having a viscosity equal to 1 cP at the same temperature as the compound in question. Cumulative constitutional correction factors for the equivalent chain length and the slope of the log viscosity-temperature curve are proposed. With the aid of these data, the viscosity between boiling and melting points of many compounds can be predicted. The method proves to be more accurate than the existing ones and it does not make use of any other physical property.

The literature dealing with liquid viscosity is very extensive and many attempts have been made to correlate the viscosity of liquids to temperature and chemical constitution, both theoretically and empirically. Truly theoretical efforts have met with little success; at present there is no theory which allows liquid viscosities to be calculated by simple equations. Therefore empirical estimation techniques must be used.

Effect of Temperature

The best known relation to correlate liquid viscosity and temperature is

$$\eta_L = Ae^{B/T} \quad (1)$$

where *A* and *B* are positive. Equation 1 was originally proposed by De Guzman (1913) and has since become known as the Andrade equation because Andrade (1930) suggested this form as a result of an analysis of the mechanism of liquid viscosity. The equation represents the viscosity-temperature relation fairly well within the temperature range which extends from the normal boiling point to the freezing point.

For associated liquids and hydrocarbon mixtures of higher viscosity the relationship between $\log \eta_L$ and $1/T$ becomes slightly curved. Consequently, in these cases the De Guzman-Andrade relation fails. To overcome this difficulty, a large number of modifications of the original equation have been proposed, generally introducing, in one way or another, a third constant to correct the equation for the observed curvature. If many data points are available for a single compound, these can be more accurately fitted by such equations, but for general purposes the De Guzman-Andrade relation is still considered the best simple function.

Effect of Chemical Constitution

Various attempts have been made to predict viscosities as a function of chemical constitution: none is reliable; all are empirical. Hitherto all of them involve some other physical property and no relation has been developed by which the

viscosity can be estimated from the chemical constitution alone.

Reid and Sherwood (1966) judge the methods of Souders (1938), Thomas (1946), and Stiel and Thodos (1961, 1964) as the three best estimations available. These three methods will be used as a basis of comparison for the relation proposed by the authors. Reid and Sherwood (1966) tested the three methods for 40 different compounds at various temperatures. The error distribution is given in Table I and Figure 1.

It is concluded that the best approximate method available is the Thomas relation. A serious drawback is the rather poor accuracy (15% of the values are predicted with an error larger than 50%) and the fact that the critical temperature and the density of the compound must be known.

Proposed Relation for the Homologous Series of the Alkanes

The aim of the development of another viscosity-temperature-chemical constitution relation was to establish a relation in which no other physical property occurs. The basis of the relation is the De Guzman-Andrade equation, written as

$$\log \eta_L = A + B/T \quad (1a)$$

When $\eta_L = 1$ cP, $\log \eta_L = 0$ and it follows that $T = T_0 = -B/A$ at $\eta_L = 1$, from which a modification of the original equation can be derived

$$\log \eta_L = B \left[\frac{1}{T} - \frac{1}{T_0} \right] \quad (2)$$

This equation contains two unknown factors, T_0 , which is the intercept of the log viscosity-temperature line with the abscissa, and *B*, the slope of this line. For the homologous series of the *n*-alkanes *B* as well as T_0 appear to be functions of *N*, the number of carbon atoms. By regression analysis it is found that for $N \leq 20$

$$T_0 = 28.86 + 37.439N - 1.3547N^2 + 0.02076N^3 \quad (3)$$

and for $N > 20$

$$T_0 = 8.164N + 238.59 \quad (4)$$

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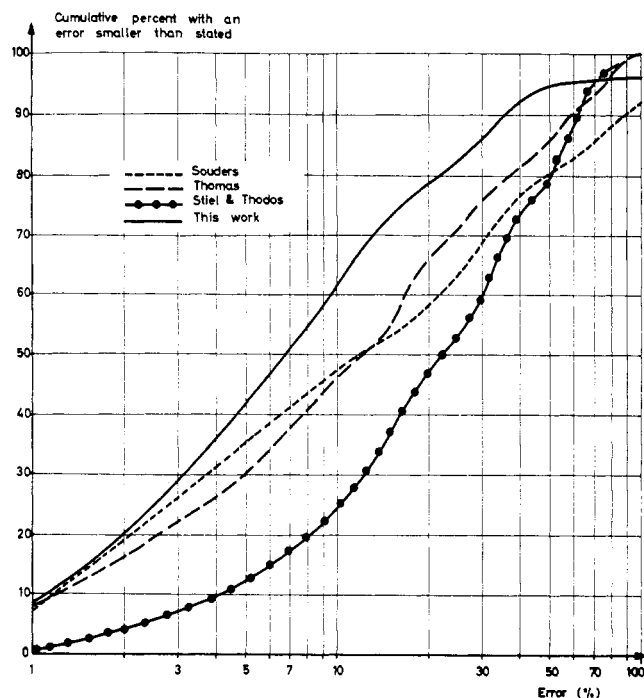


Figure 1. Error distribution of various methods. Examples from Reid and Sherwood (1966)

for $N \leq 20$

$$B = 24.79 + 66.885N - 1.3173N^2 - 0.00377N^3 \quad (5)$$

for $N > 20$

$$B = 530.59 + 13.740N \quad (6)$$

Figures 2 and 3 show the calculated lines and experimental points. The viscosity data were obtained from "Selected Values of Hydrocarbons" (1953).

With the aid of eq 3-6 the viscosities of all n -alkanes at all temperatures between the melting and the boiling points can be predicted. With the exception of methane, the calculated and experimental results agree reasonably, as appears in Table II.

As a yardstick for the reliability of the method the "mean error" for each compound has been computed. The mean error is defined as

$$E_m = \frac{\sum |E|}{n}$$

$|E|$ = absolute value of (calculated value - experimental value) and n is the number of data points available for each compound. The equations developed for the n -alkanes form the basis of the general relation for other compounds.

General Relation

The principle of the method is the introduction of the equivalent chain length (NE), which is the chain length of a hypothetical n -alkane with viscosity equal to 1 cP at the temperature at which the viscosity of the compound in question is also 1 cP. NE is calculated as the sum of the total

Table I. Cumulative Error^a Distribution of Various Methods for Calculation of Liquid Viscosity. Examples of Reid and Sherwood

Error	Percentage of the predicted values			
	Souders	Thomas	Stiel and Thodos	Proposed method
Less than 5%	36.0	30.2	12.6	41.7
Less than 10%	47.5	46.5	24.4	61.4
Less than 15%	53.3	54.3	36.2	72.4
Less than 20%	58.3	65.9	47.1	78.7
Less than 25%	63.3	70.6	53.0	82.6
Less than 30%	69.1	76.0	58.9	85.7
Less than 40%	77.0	81.4	74.0	92.8
Less than 50%	80.6	85.3	79.9	94.4
Less than 60%	82.8	90.7	88.3	94.4
Less than 70%	85.7	93.0	95.0	95.2
Less than 80%	88.6	96.9	97.5	95.2
Less than 90%	90.8	99.9	99.2	96.0
Less than 100%	92.2	99.9	99.2	96.0

$$^a \text{Error} = \left[\frac{\text{calcd} - \text{exptl}}{\text{exptl}} \right]$$

Table II. Mean Errors for Paraffinic Compounds

Compound	No. of data points	Mean error, %
Methane	4	111.8
Ethane	18	9.0
Propane	29	12.3
Butane	18	9.3
Pentane	39	4.0
Hexane	49	3.5
Heptane	54	2.7
Octane	52	1.8
Nonane	46	2.4
Decane	47	1.8
Undecane	48	1.9
Dodecane	45	1.6
Tridecane	55	2.1
Tetradecane	49	1.8
Pentadecane	53	2.2
Hexadecane	49	2.1
Heptadecane	62	2.3
Octadecane	58	2.2
Nonadecane	59	2.3
Eicosane	61	1.9
Hexacosane	1	6.4
triacontane	1	8.6

number of carbon atoms of the compound (N) and one or more structural and/or configurational factors (ΔN).

In the same way, B is calculated as

$$B = B_a + \Delta B$$

where B_a is the value of B for the hypothetical alkane with the equivalent chain length NE (calculated by eq 5 or 6, or from Figure 3) and ΔB is a correction factor depending on the chemical constitution of the compound. Generally, ΔN is not a constant, but a function of N , whereas in most cases ΔB is a function of NE .

It appears that for compounds with more than one func-

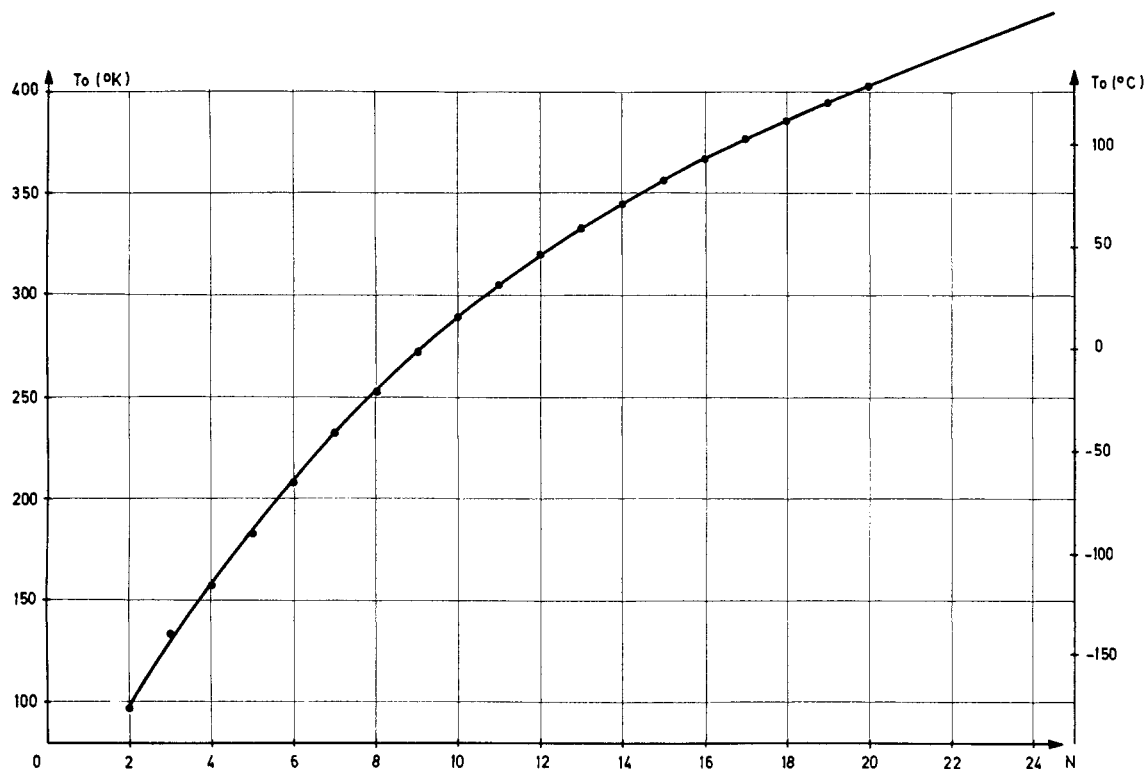


Figure 2. Dependence of T_0 on N for n -alkanes



Figure 3. Dependence of B on N for n -alkanes

tional group both ΔN and ΔB are cumulative factors. Thus, the equivalent chain length can be found from

$$NE = N + \Delta N_1 + \Delta N_2 \dots$$

Once NE is known, T_0 can be calculated from eq 3 or 4, inserting NE for N . B_a is found from eq 5 or 6, inserting B_a

and NE for B and N . Subsequently the required viscosity is calculated by eq 2, as both factors B and T_0 are now known.

Table III gives the various functions for ΔN and ΔB for a number of functional groups and structural configurations. There exists one important difference between the calculation of NE and B . If the compound contains two or more identical functional groups, the ΔN correction for this group should be

applied *twice, thrice*, etc. On the contrary, for the calculation of B , the functional correction has to be applied only *once*.

A few examples follow.

I. Pentanoic Acid (Valeric Acid). Calculation of NE from N and Table III

$$\begin{aligned} N &= 5.00 \\ \Delta N(\text{acids}): 6.795 + 5 \times 0.365 &= 8.62 \\ NE &= 13.62 \end{aligned}$$

Calculation of B from NE , eq 5, and Table III

$$\begin{aligned} B_a &= 24.79 + 66.885 \times 13.62 - 1.3173 \times 13.62^3 - \\ &\quad 0.00377 \times 13.62^3 = 681.86 \\ \Delta B(\text{acids}): -249.12 + 22.449 \times 13.62 &= 56.64 \\ B &= 738.50 \end{aligned}$$

Calculation of T_0 from NE (eq 3)

$$\begin{aligned} T_0 &= 28.86 + 37.439 \times 13.62 - 1.3547 \times 13.62^2 + \\ &\quad 0.02076 \times 13.62^3 = 339.93^\circ\text{K} \end{aligned}$$

$$\text{Thus: } \log \eta_L = 738.50 \left[\frac{1}{T} - \frac{1}{339.93} \right]$$

Table III. Functions for ΔN and ΔB

	ΔN	ΔB	No. of compounds used
Functional Groups			
<i>n</i> -Alkanes	22
Alkene	$-0.152 - 0.042N$	$-44.94 + 5.410NE$	19
Acid $3 \leq N \leq 10$	$6.795 + 0.365N$	$-249.12 + 22.449NE$	10
$N > 10$	10.71	$-249.12 + 22.449NE$	4
Ester	$4.337 - 0.230N$	$-149.13 + 18.695NE$	22
Primary alcohol	$10.606 - 0.276N$	$-589.44 + 70.519NE$	6
Secondary alcohol	$11.200 - 0.605N$	497.58	1
Tertiary alcohol	$11.200 - 0.605N$	928.83	2
Diol	Alcoholic correction	557.77	2
	+ configurational factor		
Ketone	$3.265 - 0.122N$	$-117.21 + 15.781NE$	9
Ether	$0.298 + 0.209N$	$-9.39 + 2.848NE$	5
Primary amine	$3.581 + 0.325N$	$25.39 + 8.744NE$	6
Secondary amine	$1.390 + 0.461N$	$25.39 + 8.744NE$	5
Tertiary amine	3.27	$25.39 + 8.744NE$	3
Fluoride	1.43	5.75	2
Chloride	3.21	-17.03	4
Bromide	4.39	$-101.97 + 5.954NE$	9
Iodide	5.76	-85.32	4
Aromatic and 1-nitro	$7.812 - 0.236N$	$-213.14 + 18.330NE$	4
2-Nitro	5.84	$-213.14 + 18.330NE$	6
3-Nitro	5.56	$-338.01 + 25.086NE$	9
4-, 5-Nitro	5.36	$-338.01 + 25.086NE$	6
Configurational Factors			
Correction for Aromatic Nucleus			
Alkyl-, halogen-, nitrobenzenes, secondary and tertiary amines $8 \leq N \leq 15$	0.60	$-140.04 + 13.869NE$	9,4,4,5,3
$N > 15$	$3.055 - 0.161N$	$-140.04 + 13.869NE$	7
Acids	4.81	$-188.40 + 9.558NE$	3
Esters	$-1.174 + 0.376N$	$-140.04 + 13.869NE$	3
Alcohols: OH attached to nucleus: take for all phenolic compounds		213.68	8
$NE = 16.17^a$			
Alcohols: OH in side chain	-0.16	213.68	2
Ketones	2.70	$-760.65 + 50.478NE$	2
Ethers: take for all aromatic ethers			
$NE = 11.50^a$		$-140.04 + 13.869NE$	9
Primary amines: NH_2 attached to nucleus: take for all anilinic compounds			
$NE = 15.04^a$			7
Primary amines: NH_2 in side chain	-0.16		1
Various			
Polyphenyls	$-5.340 + 0.815N$	$-188.40 + 9.558NE$	4
Ortho configuration: OH group present	0.51	-571.94	2
without OH		54.84	5
Meta configuration	0.11	27.25	6
Para configuration	-0.04	-17.57	6
Cyclopentane $7 \leq N \leq 15$	$0.205 + 0.069N$	$-45.96 + 2.224NE$	9
$N > 15$	$3.971 - 0.172N$	$-339.67 + 23.135NE$	6
Cyclohexane $8 \leq N \leq 16$	1.48	$-272.85 + 25.041NE$	9
$N > 16$	$6.517 - 0.311N$	$-272.85 + 25.041NE$	6

(Continued on next page)

(Table III. Continued)

	ΔN	ΔB	No. of compounds used
Iso Configuration			
Alkanes	1.389 - 0.238N	15.51	4
Double iso in alkanes (extra correction)	0.93	...	3
Alkenes	1.389 - 0.238N	8.93	3
Alcohols	0.24	94.23	5
Esters, alkylbenzenes, halogenides, ketones	-0.24	8.93	5,1,5,1
Acids	-0.24	...	2
Ethers, amines	-0.50	8.93	4,2
Various			
C(Cl) _x configuration	1.91 - 1.495X	-26.38	4
-CCl-CCl-	0.96	...	2
-C(Br) _x -	0.50	81.34 - 86.850X	2
-CBr-CBr-	1.60	-57.73	3
CF ₃ - (in alcohols)	-3.93	341.68	2
(other compounds)	-3.93	25.55	6
Diols	-2.50 + N	See alcohols	2

^a Other substituents, such as Cl, CH₃, NO₂, are neglected for the determination of NE. For the calculation of B, they have to be taken into account.

Table IV. Viscosity Data

Temp °C	Viscosity, cP	
	Calcd	Exptl
Pentanoic Acid		
16.5	2.38	2.41
20	2.22	2.30
25	2.015	2.050
50	1.296	1.315
70	0.954	0.986
90	0.726	0.753
Chloroform		
0	0.774	0.700
10	0.680	0.625
20	0.602	0.563
30	0.538	0.502
40	0.483	0.465
50	0.438	0.425
60	0.399	0.389
Benzophenone		
25	12.4	13.6
55	5.11	4.67
95	1.96	1.74

Table V. Error Distribution

	No. of compounds	Percentage
0-5%	177	56.4
5-10%	68	21.7
10-15%	27	8.6
15-20%	13	4.1
20-25%	8	2.5
25-30%	5	1.6
30-40%	8	2.5
40-50%	3	1.0
50-60%	2	0.6
60-70%
70-80%
80-90%	1	0.3
90-100%
>100%	2	0.6

II. Trichloromethane (Chloroform). Calculation of NE

$$\begin{aligned}
 N &= 1.00 \\
 \Delta N_1: 3 \times (\text{chlorine}) &= 3 \times 3.21 &= 9.63 \\
 \Delta N_2: (\text{C}(\text{Cl})_3 \text{ configuration}) &= 1.91 - 3 \times 1.459 &= -2.47 \\
 NE &= 8.16
 \end{aligned}$$

Calculation of B

$$\begin{aligned}
 B_a: 24.79 + 66.885 \times 8.16 - 1.3173 \times 8.16^2 - 0.00377 \times 8.16^3 &= 480.81 \\
 \Delta B_1: (\text{chlorine}) &= -17.03 \\
 \Delta B_2: (\text{C}(\text{Cl})_3 \text{ configuration}) &= -26.38 \\
 B &= 437.40
 \end{aligned}$$

From eq 3 it follows that $T_0 = 255.44^\circ\text{K}$ and

$$\log \eta_L = 437.40 \left[\frac{1}{T} - \frac{1}{255.44} \right]$$

III. Benzophenone (Diphenyl Ketone). Calculation of NE

$$\begin{aligned}
 N &= 13.00 \\
 \Delta N_1: (\text{ketones}) &3.265 - 13 \times 0.122 &= 1.68 \\
 \Delta N_2: 2 \times (\text{aromatic (ketones)}) &= 2 \times 2.70 &= 5.40 \\
 NE &= 20.08
 \end{aligned}$$

Calculation of B (eq 6)

$$\begin{aligned}
 B_a: 530.59 + 13.74 \times 20.08 &= 806.49 \\
 \Delta B_1: (\text{ketones}) - 117.21 + 15.781 \times 20.08 &= 199.67 \\
 \Delta B_2: (\text{aromatic (ketones)}) - 760.65 + 50.418 \times 20.08 &= 252.95 \\
 B &= 1259.11
 \end{aligned}$$

From eq 4 it follows that $T_0 = 402.50^\circ\text{K}$ and

$$\log \eta_L = 1259.11 \left[\frac{1}{T} - \frac{1}{402.50} \right]$$

A comparison of the viscosity data and the calculated values for these examples is given in Table IV.

The viscosity data for pentanoic acid and benzophenone were obtained from the "International Critical Tables" (1930); the chloroform data, from Landolt-Börnstein (1955).

Discussion

The relationships given in Table III have been developed and tested by consideration of a large number of data, cover-

ing 314 different compounds with nearly 4500 data points. A survey of these compounds with all viscosity data and calculated values will be issued as a separate report (van Velzen and Langenkamp, 1971). It appears that the agreement between the calculated and experimental values is generally satisfactory. The error distribution is shown in Table V.

The very large errors are usually found in the first numbers of a homologous series, *e.g.*

methane	111.8%	methanol	172.0%
ethene	45.2%	ethanol	84.7%
propene	25.4%	benzene	30.7%
methanoic acid	58.0%	cyclohexane	33.4%
ethanoic acid	26.3%	cyclopentane	33.1%

This may partially be due to the fact that, in a number of cases, the applied relation is not necessarily the right one for these compounds. For instance, benzene has been calculated as an alkylbenzene with $N = 6$, *i.e.*, as an alkylbenzene without an alkyl group, no better relation being available.

The above error distribution compares very favorable with the error distribution given in Table I for the Thomas, Souders, and Stiel and Thodos methods. However, a direct comparison would be misleading because the data from Table I are based on other compounds (less numerous) than the present work. For this reason the example of Reid and Sherwood for the three methods has been extended by the new method. The results are found in Table I, last column. It appears that in this case the errors are greater than for the total data, which is caused by the fact that the 40 compounds chosen by Reid and Sherwood comprise eight of the ten "anomalous" compounds mentioned above (methane, ethene, ethanoic acid, methanol, ethanol, benzene, cyclohexane, and cyclopentane). In comparison with the other methods the reliability of the new method is quite good: only 14% of the values showed an error above 30% as opposed to 24% for the Thomas, 31% for the Souders, and 41% for the Stiel and Thodos method.

Two final remarks have to be made. (1) A number of the relations given in Table III are based on a limited number

of data points. This implies that extrapolation beyond the range for which it has been developed may yield erroneous results. The relationships given in Table III must therefore not be considered as definitive; if more data become available, in certain cases other relationships will have to be inserted to match all experimental data as well as possible. (2) The proposed relation is based on the De Guzman-Andrade equation, although the modified forms of this equation generally yield a better fit of experimental and calculated points for single compounds. In the course of the present study the authors have made many attempts to base the relation on the formula of Gutmann and Simmons (1952) and Girifalco (1955). These attempts were not successful, as the introduction of a third constant (C) severely influences the value of B . No simple and cumulative relations could be developed for B and C . Generally NE is not seriously affected by the use of modified forms of the De Guzman-Andrade equation.

The final conclusion is that the aim to develop a relation in which no other physical properties occur and which is reasonably accurate has adequately been reached.

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