R & D NOTES

Viscosity of Liquids: An Equation with Parameters Correlating with Structural Groups

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INTRODUCTION

The viscosity of liquids depends strongly on temperature. In the absence of a general and rigorous theory, the optimal analytical representation of the viscosity-temperature function is not obvious. Numerous different equations have been proposed, ranging from simple two-parameter forms for a narrow temperature range to rather sophisticated functions based on some model for momentum transport in liquids. The objective of this work is to develop an equation that can adequately describe the large amount of available experimental viscosity data. This implies a function that works over the whole temperature range of the liquid. It is particularly aimed at a type of equation with parameters that correlate with structural groups of molecules like the $(CH)_x$ groups for hydrocarbons. In this way, the parameters of the equation obtain physical significance, which is desirable for establishing a group contribution estimation method.

DERIVATION OF THE EQUATION

The simple activation energy type of expression (Andrade, 1930)

$$\eta = A\, e^{B/T} \tag{1}$$

can be modified to read (van Velzen et al., 1972):

$$\log \eta = B\,[1/T - 1/T_o]\,, \tag{2}$$

If T_o is the temperature at which $\eta = 1$ cp (1 mPa · s). Analogously, the simple free-volume type of expression (Batschinski, 1913)

$$\eta = \frac{D}{V - V_o} \tag{3}$$

can be modified to give

$$\eta = \frac{V_{\text{ref}} - V_o}{V - V_o}\,, \tag{4}$$

if V_{ref} is the volume at which $\eta = 1$ cp. Although the differences from the traditional equations are trivial, the new forms—Eqs. 2 and 4—are much more effective in yielding sensible parameters, since these parameters are now dimensional physical quantities. This is demonstrated in Figures 1 and 2, where the parameters of Eq. 2, fitted in the temperature region $0.4 \leq T/T_c \leq 0.60$, and the parameters of Eq. 4, fitted in the temperature region $0.55 \leq T/T_c \leq 0.97$, are plotted against the number of carbon atoms for the alkanes. The obvious regularity is rather encouraging. The final equation for the whole temperature range reads:

$$\eta = x_{TV}\,\eta_T + (1 - x_{TV})\,\eta_V \tag{5}$$

where

$$\log \eta_T = B\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{6}$$

$$\eta_V = \left(\frac{V_{\text{ref}} - V_o}{V - V_o}\right)^{1.15} \tag{7}$$

and

$$x_{TV} = \frac{10^3 \exp\left[-0.5\, T_c \left(\frac{T}{T_c} - 0.55\right)\right]}{1 + 10^3 \exp\left[-0.5\, T_c \left(\frac{T}{T_c} - 0.55\right)\right]} \tag{8}$$

Here Eq. 8 represents a switching function that effectively damps the activation energy term for $T/T_c > 0.55$ and the free-volume term for $T/T_c < 0.55$. Thus the new equation reduces to the activation energy equation at low temperatures and to the free-volume equation at high temperatures. This is physically incorrect, but using the free-volume term at low temperatures in a viscosity correlation is practically undesirable, since it then becomes dramatically dependent on the accuracy with which the volume, i.e., the density, is known or can be calculated. In Eq. 7 the density is generally eliminated in favor of temperature by the method of Gunn and Yamada (1971),

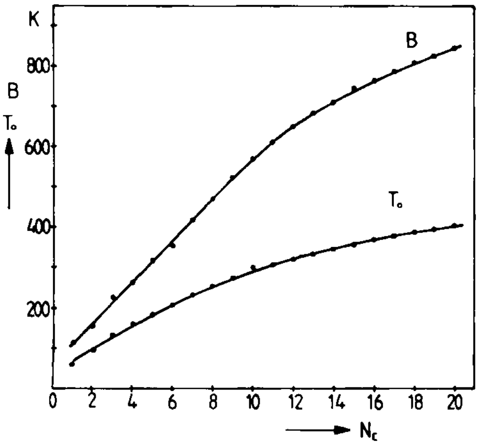

Figure 1. Parameters of Eq. 2 vs. number of carbon atoms for the alkanes.

thus eliminating any ambiguity of the density determination. For particularly low temperatures, i.e., $0.30 \le T/T_c \le 0.4$, we propose to use

$$\eta = \eta_T \left(\frac{0.4}{T/T_c} \right)^n \tag{9}$$

with the additional parameter n. Although a total of five adjustable parameters is used for the full temperature range, it is essential to note that these are not all fitted simultaneously, but instead only two parameters are fitted in the range $0.4 \le T/T_c \le 0.6$ and another two parameters are fitted in the range $0.55 \le T/T_c \le 0.97$. The parameter n is only occasionally needed.

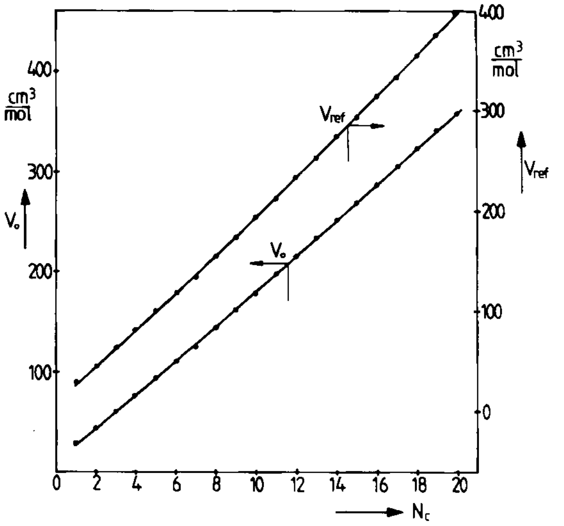

Figure 2. Parameters of Eq. 4 vs. number of carbon atoms for the alkanes.

VERIFICATION

The new viscosity equation was tested against more than 300 organic substances with about 5,300 data points. It was found to be capable of correlating the viscosity data available in the literature essentially within their estimated uncertainties over the whole temperature range. Table 1 shows a selection of the typical results obtained. Occasionally, highly accurate viscosity data are available over a limited temperature range. It is not

TABLE 1. CORRELATION RESULTS FOR SOME ORGANIC LIQUIDS

Liquid		Err. 1*	Err. 2**	Sta.†	B	T_o	V_o	V_{ref}	Range
Formula	Name	%	%	%	K	K	cm³/mol	cm³/mol	°C
CH_4	Methane	1.47	0.79	±1.87	114.09	58.50	29.22	30.49	−180 to −98
$C_2H_4O_2$	Acetic acid	0.75	0.05	±1.06	593.11	306.62	53.14	58.16	15 to 113
C_2H_6O	Ethanol	2.77	−0.26	±3.70	677.14	303.46	55.48	59.53	−98 to 200
C_3H_60	Acetone	0.88	0.09	±1.30	367.97	210.78	61.62	66.09	−80 to 60
$C_4H_8O_2$	Propylformate	1.90	−0.14	±2.42	446.74	246.83	85.06	91.71	0 to 220
$C_4H_{10}O$	Diethyl ether	0.59	0.04	±0.85	342.92	190.54	82.84	88.85	−80 to 100
C_5H_{12}	Pentane	2.30	0.13	±2.96	317.12	183.71	92.62	99.03	−125 to 150
$C_6H_5NO_2$	Nitrobenzene	1.90	0.25	±2.37	634.45	343.02	96.50	106.42	3 to 208
$C_6H_{15}N$	Triethyl amine	1.42	0.09	±1.51	421.07	225.26	119.63	127.70	10 to 80
$C_7H_{11}F_3$	Trifluoromethylcyclohexane	0.27	0.00	±0.33	531.34	289.78			20 to 60
C_8H_{10}	Ethylbenzene	0.51	0.07	±0.75	473.30	265.37	110.72	118.93	−25 to 130
C_9H_{18}	Butylcyclopentane	0.63	0.19	±0.70	516.01	285.10	146.00	158.79	−20 to 110
$C_{10}H_{22}$	Decane	1.17	0.24	±1.69	569.44	289.21	179.02	193.61	−25 to 175
$C_{13}H_{26}$	1-tridecene	1.52	0.16	±1.86	658.28	324.56	226.21	245.58	0 to 115
$C_{18}H_{14}$	M-terphenyl	1.42	0.15	±1.71	983.09	463.86	158.83	173.13	150 to 450

* $\text{Err. } 1 = \frac{1}{N} \sum_{i=1}^{N} \frac{(|\eta_{calc,i} - \eta_{exp,i}|)\,100}{\eta_{exp,i}}$

** $\text{Err. } 2 = \frac{1}{N} \sum_{i}^{N} \frac{(\eta_{calc,i} - \eta_{exp,i})\,100}{\eta_{exp,i}}$

† $\text{Sta.} = \sqrt{\frac{\sum_{i=1}^{N} (\Delta\eta_i - \text{Err. } 2)^{2'}}{N-1}}$

$\Delta\eta_i = \frac{(\eta_{calc,i} - \eta_{exp,i})\,100}{\eta_{exp,i}}$

claimed that the present equation is equally satisfactory for such rare data sets. It has been developed to correlate the bulk of the available data in an adequate way.

The fact that the parameters are regular within homologous series indicates physical significance. Also, due to the linearity of the equation, it appears plausible to assume that they may permit the extrapolation into temperature regions not used to determine their values. We have checked this in the following way. We determined the parameters of η_T and η_V by using the full data set in one calculation and a limited, rather narrow data set in a second calculation, i.e., $0.50 \leq T_r \leq 0.60$ for η_T, and $0.55 \leq T_r \leq 0.65$ for η_V. The calculated viscosities were in both cases rather close and we conclude that extrapolation of a given data set to low as well as to high temperatures is possible. It is believed, therefore, that the new form of equation for the temperature dependence of liquid viscosity may prove to be a useful tool for correlation and extrapolation as well as a basis for a predictive method based on the structural group concept.

NOTATION

A = constant in Eq. 1
B = constant in Eqs. 1 and 2
D = constant in Eq. 3
n = exponent in Eq. 9
N_C = number of carbon atoms
T = temperature
T_o = temperature parameter in Eqs. 2 and 6
V = volume
V_o = volume parameter in Eqs. 3, 4, and 7
V_{ref} = volume parameter in Eqs. 4 and 7
η = dynamic viscosity

Subscript

c = critical

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