PREDICTION OF LIQUID VISCOSITY FOR N-ALKANES, N-ALCOHOLS, AND N-ALKANONES

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PREFACE

This study is concerned with the development of a new liquid viscosity prediction method. The proposed method is capable of predicting liquid viscosity over a wide range of temperatures and a wide range of chain lengths. The Cox equation for viscosity is used as a liquid viscosity-temperature working equation. A new type of group-contribution technique, which is essential to the success of this method, is also developed. This prediction method has been tested for three homologous series, and the results indicate that the present method is better than any other currently existing method. Several extensions of the present method appear to be promising; I sincerely hope that the continuations of this study will be successful.

I wish to express my deepest appreciation to my major adviser, Dr. Robert N. Maddox, for his intelligent guidance and invaluable assistance throughout this study. I am also very grateful to the other committee members, Dr. John H. Erbar, Dr. Robert L. Robinson, Jr., and Dr. Gilbert J. Mains for their assistance and advisement in the course of this work.

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NOMENCLATURE

A	constant in Equations (1-1), (1-2), (1-10), (2-3)
A_i	constants in Equation (1-11)
A'	constant in Equation (2-1)
a_0, a_1, a_2	parameters in the Cox equation for viscosity, Equations (1-17), (2-3), (2-4)
a_0', a_1', a_2'	parameters in Equation (2-1)
a_0^*, a_1^*, a_2^*	constants in Equation (2-2)
a	parameter in Equations (2-5), (2-6); predictive constant in n-alkane series
a_f	parameter in Equations (2-7), (2-10)
Δa	predictive constant corresponding to a functional group
AAPE	average absolute percent error
$AAPE_m$	the average of AAPE's defined by Equation (3-3)
B	constant in Equations (1-1), (1-2), (1-3)
ΔB_i	correction term in Equation (1-9)
B_i	constant in Equation (1-12)
B_a	parameter defined by Equations (1-7), (1-8)
b	parameter in Equations (2-5), (2-6)
b_f	parameter in Equations (2-7), (2-10)
Δb	predictive constant corresponding to a functional group
C	constant in Equation (1-2)
calc.	calculated liquid viscosity
d	liquid density at 20° C, g/cm^3

E	percent error defined by Equation (3-1)
$\lvert E \rvert$	the absolute value of percent error
exp.	experimental liquid viscosity
EXPD	AAPE for a compound outside the range of regression
err_1	percent error caused by each additional carbon atom beyond m
err_2	AAPE for compounds inside the range of fitting
F_n	fitted value for a certain parameter, a function of n
M	molecular weight
m	number of carbon atoms of a compound member up to which the regression is performed
MC	number of carbon atoms in the carbon chain
n, N	number of carbon atoms in a compound
$\underline{n}$	used in $\underline{n}$th methylene (or methyl) group
N^*	equivalent chain length defined by Equation (1-4)
ΔN_i	structural or functional group correction in Equation (1-4)
n_1, n_2	upper and lower bound of the n range
NCPD	number of compounds in a certain sample
NPT	number of data points for a certain compound
P	vapor pressure in Equations (2-1), (2-2), atm
P_c	critical pressure
P_f	position where the functional group occurs
r	decay ratio
r_f	parameter in Equation (2-7)
T	temperature, K
T_R	relative temperature defined in Equation (1-17)

T^*	parameter in Equation (1-3), defined by Equation (1-5), (1-6)
T_c	critical temperature, K
T_{MPE}	temperature where maximum percent error occurs
T_r	reduced temperature
T_b	normal boiling point, K
T_0	reference temperature, K
η_L	liquid viscosity, cP
λ	predictive constant for functional group position effect
μ_0	reference viscosity, mPa s
μ	liquid viscosity, mPa s
ξ	parameter defined by Equation (1-13)
ξ_f	relative position of a functional group
$(\mu\xi)^{(0)}$	a quantity defined by Equation (1-15)
$(\mu\xi)^{(1)}$	a quantity defined by Equation (1-16)
ω	acentric factor
$\Delta \ln\mu$	difference of natural logarithmic liquid viscosity between two neighboring members of the n-alkane series

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

A new method for predicting liquid dynamic (absolute) viscosity of normal alkanes, normal alcohols, and normal alkanones over a wide range of temperatures and a wide range of carbon chain lengths has been developed. Also a new type of group-contribution technique which involves the use of the geometric series is proposed to generate the predictive parameters in the working equation. No other physical properties are required in this prediction method. The only information needed is the structure of that compound. The new method can predict (also correlate) liquid viscosity more accurately than any other existing method for all three compound series.

Historical Background

While the mechanism or theory of gas viscosity has met with some success by the application of the kinetic theory of gases, the development of the theoretical foundation of liquid viscosity is still in the primitive stage. So far there is no theory which can reduce to a simple function form and allow liquid viscosities to be estimated adequately with resonable effort. Therefore, empirical methods are used in all practical situations. These methods allow parameters or certain theoretical constants to be approximated from structure or other physical properties through study of experimental data.

The best known correlation for showing the effect of temperature on liquid viscosity is the De Guzman-Andrade equation

$$\mu = A \exp(B/T) \tag{1-1}$$

where A and B are positive constants. This equation was proposed by De Guzman (1913) and then suggested by Andrade (1930) from an analysis of the theory of liquid viscosity. It holds fairly well over a temperature range from somewhat above the normal boiling point to near the freezing point. Because of its simplicity, this equation has been the basis of many empirical prediction methods. However, it often fails at low temperatures as the freezing point is approached; also, it is not suitable for reduced temperatures above 0.75. One variation of equation (1-1), which resembles the Antoine equation, was proposed by Gutman and Simmons (1952)

$$\ln \mu = A + B/(T + C) \tag{1-2}$$

where A, B, C are constants. Although this modification has been shown to be quite accurate at low temperatures, it is not particularly good for the high temperature region (Reid et al., 1977).

Above the normal boiling point, the correlations commonly used are no longer liquid viscosity-temperature equations. The correlations of Letsou and Stiel (1973), for example, are of a corresponding-states type. The prediction methods for low temperatures based on the viscosity-temperature equation are mainly structural in nature, whereas the prediction methods for high temperatures are not. Because of this difference in approaches, one can hardly expect good matches from these two different types of estimation methods in the connection region (around reduced temperature $T_r = .75$). A single liquid viscosity prediction method which can be applied over a wide range of temperatures is highly desirable.

Prediction Methods in the Literature

There are a number of prediction methods existing in the literature: the methods of Soulders (1938), Thomas (1946), Jossi et al. (1962), Stiel and Thodos (1964), Morris (1964), van Velzen et al. (1972), Orrick and Erbar (1973), and Letsou and Stiel (1973). Among them, the three favorably recommended by Reid et al. (1977) are chosen as a basis of comparison for the proposed method: van Velzen, Cardozo, and Langenkamp (1972) method; Orrick and Erbar (1973) method; and Letsou and Stiel (1973) method.

Van Velzen et al. (1972) proposed a modification of the De Guzman-Andrade equation, written as

$$\log \eta_L = B(1/T - 1/T^*) \tag{1-3}$$

where η_L = liquid viscosity, cP

T = temperature, K

B, T^* = constants related to structure.

The equivalent chain length N^* is defined by

$$N^* = N + \sum_i \Delta N_i \tag{1-4}$$

where N is the actual number of carbon atoms in the molecule, and ΔN_i represents the structural or functional group contributions. The value of N^* is used to determine the parameters B and T^* in (1-3). That is,

$$T^* = 28.86 + 37.439N^* - 1.3547N^{*2} + 0.02076N^{*3} \qquad N^* \leq 20 \tag{1-5}$$

$$= 238.59 + 8.164N^* \qquad N^* > 20 \tag{1-6}$$

$$B_a = 24.79 + 66.885N^* - 1.3173N^{*2} - 0.00377N^{*3} \qquad N^* \leq 20 \tag{1-7}$$

$$= 530.59 + 13.740N^* \qquad N^* > 20 \tag{1-8}$$

$$B = B_a + \sum \Delta B_i \tag{1-9}$$

where ΔB_i is a correction term depending on the chemical constitution of the compound. Generally, ΔN_i is a function of N, whereas ΔB_i is a function of N^*. For n-alkanes, both ΔN_i and ΔB_i are zero; for n-alcohols, $\Delta N_i = 10.606 - 0.276N$, $\Delta B_i = -589.44 + 70.519N^*$; for n-alkanones, $\Delta N_i = 3.265 - 0.122N$, $\Delta B_i = -117.21 + 15.781N^*$.

This method, which does not make use of any other physical property, was recommended by Reid et al. (1977) as the best prediction method for low temperature liquid viscosity. However, like other methods based on the De Guzman-Andrade equation, it can not be applied over a wide temperature range since the linear relationship between log η_L and 1/T holds only for a rather limited temperature range.

The Orrick and Erbar (1973) group-contribution technique for liquid viscosity prediction employs the following equation

$$\ln(\mu/Md) = A + B/T \tag{1-10}$$

where μ = liquid viscosity, cP

d = liquid density at 20° C, g/cm^3

M = molecular weight

T = temperature, K

A, B = constants to be calculated from group contributions.

If the liquid has a normal boiling point below 20° C, the density at the normal boiling point is used; if the liquid has a freezing point above 20° C, the density at the freezing point should be employed. A and B can be obtained from:

$$A = -6.95 + \sum_i A_i \tag{1-11}$$

$$B = 275 + \sum_i B_i \tag{1-12}$$

For methylene (or methyl) group, $A_i = -0.21$, $B_i = 99$;

for hydroxyl group, $A_i = -3.0$, $B_i = 1600$;

for carbonyl group, $A_i = -0.5$, $B_i = 350$.

The method of Orrick and Erbar has a range of applicability similar to the method of van Velzen et al. However, this method requires the liquid density at 20° C as input data.

For saturated liquid viscosity at high temperatures, Letsou and Stiel (1973) developed a corresponding-states approach which employs the acentric factor ω,

$$\xi = T_c^{1/6} / M^{1/2} P_c^{2/3} \qquad (1\text{-}13)$$

$$\mu\xi = (\mu\xi)^{(0)} + \omega(\mu\xi)^{(1)} \qquad (1\text{-}14)$$

where T_c = critical temperature, K

P_c = critical pressure, atm

M = molecular weight

μ = saturated liquid viscosity, cP

$(\mu\xi)^{(0)}$, $(\mu\xi)^{(1)}$ = functions of reduced temperature T_r.

Although Letsou and Stiel (1973) tabulate these two functions for T_r between 0.76 and 1.00, analytic forms are available from Reid et al. (1977) from $T_r = 0.76$ to $T_r = 0.98$:

$$(\mu\xi)^{(0)} = 0.015174 - 0.02135T_r + 0.0075T_r^2 \qquad (1\text{-}15)$$

$$(\mu\xi)^{(1)} = 0.042552 - 0.07674T_r + 0.0340T_r^2 \qquad (1\text{-}16)$$

Equations (1-13)-(1-16) are recommended by Reid et al. (1977) as the best method for predicting saturated liquid viscosities at $T_r = 0.76$ and higher. It has been tested only for non-polar compounds. And, as mentioned before, this approach is applicable only for the high temperature region. Also, critical properties and acentric factor are needed.

None of the three methods described above is suitable for long chain compounds (e.g. $n > 30$ for n-alkanes).

Proposed Prediction Method

In this work the Cox (1936) equation, a vapor-pressure correlation, is slightly modified to represent the temperature dependence of liquid viscosity. The Cox equation for viscosity is capable of correlating liquid viscosity versus temperature over a wide temperature range (from the melting point to the critical point). It takes a general form similar to corresponding-states type correlation:

$$\ln(\mu/\mu_0) = \exp(a_0 + a_1 T_R + a_2 T_R^2)(1/T_R - 1) \qquad (1\text{-}17)$$

where $T_R = T/T_0$

T_0 = reference temperature

μ_0 = reference viscosity

a_0, a_1, a_2 = constants.

A new group-contribution technique, which is structural in nature, is subsequently used to generate the parameters in Equation (1-17). In this context the present work combines the aforementioned two approaches (structural and corresponding-states) into one.

In the proposed group-contribution technique, each methylene (or methyl) group contribution differs from the preceding one by a constant ratio r. So the total n methylene (or methyl) group contributions amount to the partial sum of the first n terms of the geometric series. Furthermore, the functional group (e.g. hydroxyl group) contribution is not a constant; rather, it is a function of the number of carbon atoms. Another distinct feature of this work is that a parameter (ξ_f) is introduced to help to account for the effect of the functional group position along the carbon chain. This improved group-contribution technique covers a wide range of carbon atoms (e.g. from ethane to n-tetrahexacontane in the n-alkane series).

The theoretical developments of this work will appear in Chapter II, which include the Cox vapor-pressure equation, the Cox equation for viscosity, the new group-contribution approach, and the effect of functional group position. Chapter III will give a description of the regression procedure, a summary of the computed results, an analysis of extrapolation tests, and comparisons with other methods. Chapter IV will present the conclusions drawn from this study and the recommendations for future investigation.

CHAPTER II

THEORETICAL DEVELOPMENTS

The Cox Vapor-Pressure Equation

One of the objectives in this work is to develop a liquid viscosity prediction method capable of covering a wide temperature range. To achieve this goal, a qualified liquid viscosity-temperature correlation is a must. Unfortunately, no suitable one could be found in the literature. However, based on the knowledge that a good function form for vapor pressure is usually equally good for liquid viscosity, the Cox (1936) vapor-pressure equation, which can represent vapor pressure very well over the entire liquid range, is tested and proved to be, after a slight modification, an excellent correlation for liquid viscosity.

Cox (1936) found that the following equation is generally valid for vapor pressures of a variety of compounds:

$$\log P = A' \left(1 - T_b/T\right) \tag{2-1}$$

in which

$$\log A' = a_0' + a_1' T_r + a_2' T_r^2, \qquad T_r = T/T_c$$

where P = vapor pressure, atm

T = temperature, K

T_b = normal boiling point, K

T_c = critical temperature, K

a_0', a_1', a_2' = constants.

If the reference point is changed from the normal boiling point to the critical point and natural logarithms are adopted, then Equation (2-1) can be rewritten as

$$\ln (P/P_c) = A^* (1 - T_c/T) \tag{2-2}$$

in which

$$\ln A^* = a_0^* + a_1^* T_r + a_2^* T_r^2, \qquad T_r = T/T_c$$

where P = vapor pressure, atm

P_c = critical pressure, atm

T = temperature, K

T_c = critical temperature, K

a_0^*, a_1^*, a_2^* = constants.

Note that Equation (2-2) takes the function form of a corresponding-states type relation.

The Cox Equation for Viscosity

Equation (2-2) needs to be slightly modified to suit liquid viscosity use. If a general reference point is employed, then

$$\ln (\mu / \mu_0) = A (T_0/T - 1) \tag{2-3}$$

in which

$$\ln A = a_0 + a_1 T_R + a_2 T_R^2, \qquad T_R = T/T_0$$

where T = temperature, K

T_0 = reference temperature, K

μ = liquid viscosity, mPa s

μ_0 = reference viscosity, mPa s

a_0, a_1, a_2 = constants.

Equation (2-3) can be expressed in an alternative form:

$$\ln \mu = \exp\left(a_0+a_1T_R+a_2T_R^{\,2}\right)\left(1/T_R-1\right) + \ln \mu_0 \qquad (2\text{-}4)$$

where $T_R = T/T_0$.

Equation (2-4), with five parameters a_0, a_1, a_2, $\ln \mu_0$, and T_0, is the working equation in this study. T_0 is chosen by fitting experimental critical temperature data (or estimations when experimental ones are not available) into a smoothed curve. Because T_0 can be generated easily from an analytic equation, the reference temperature T_0, rather than the actual critical temperature T_c, will be used hereafter in the prediction method. μ_0 is supposed to be the liquid viscosity at temperature T_0, but since $\ln \mu_0$ is actually determined through regression, $\ln \mu_0$ is better interpreted as an empirical constant.

New Group-Contribution Technique

The task remaining is to generate the parameters in Equation (2-4). The five parameters a_0, a_1, a_2, $\ln \mu_0$, T_0 are now considered to be group dependent. In an effort to obtain the group-contribution values for these parameters, the group contribution of each methylene group is found not to be constant in the n-alkane series for any of the five parameters in Equation (2-4). As a matter of fact, the contribution of each additional methylene group is, in general, decreasing. This situation is similar to that of the methylene (or methyl) group contribution to the natural logarithm of liquid viscosity in n-alkanes at constant reduced temperature as shown in Figure 1 (Note that no distinguishment is made between methylene and methyl group). From this observation, a certain model which can represent this specific trend must be employed.

The one chosen in this work is the geometric series model in which each methylene (or methyl) group contribution differs from the preceding

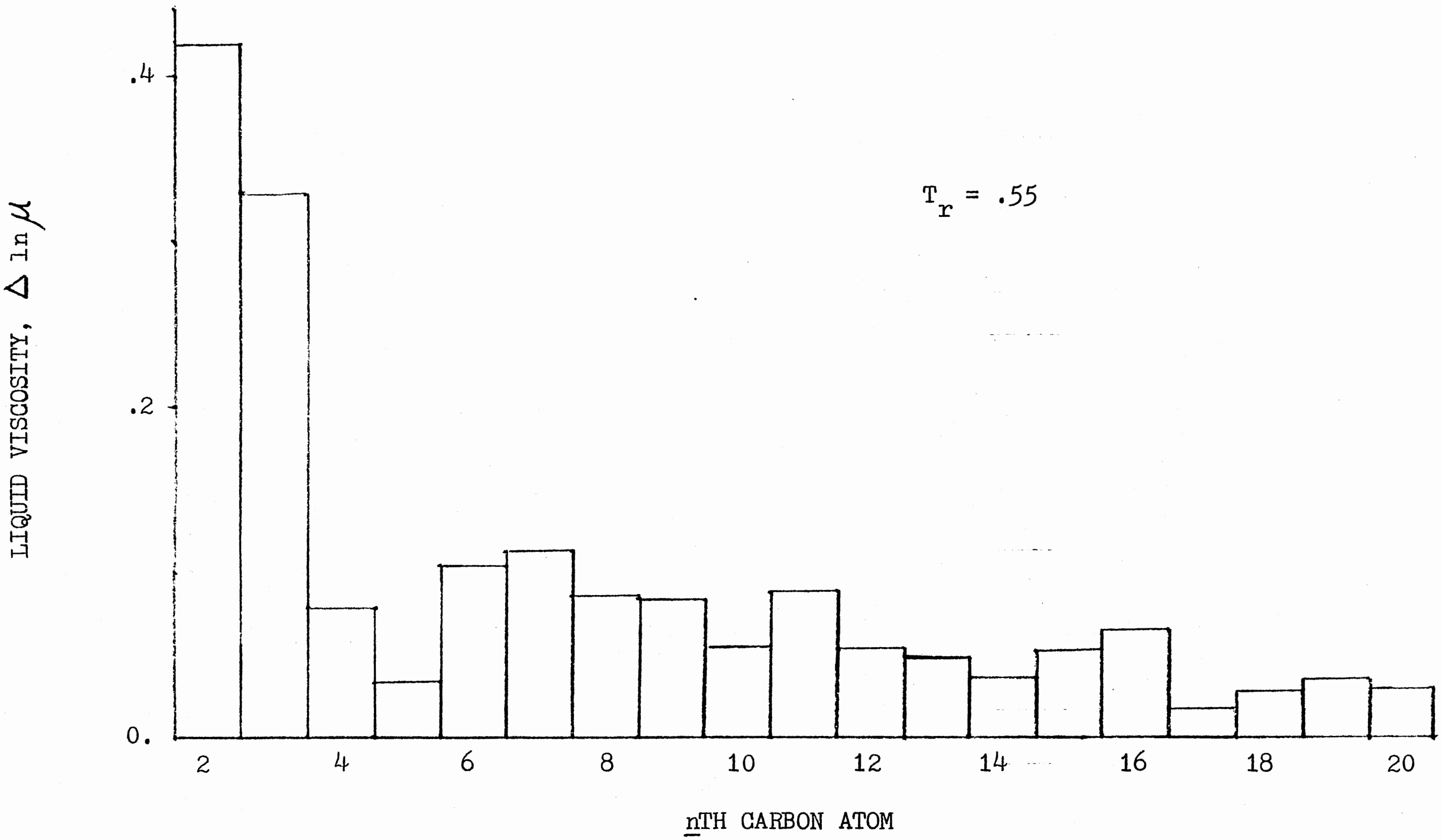

Figure 1. Contribution of nth Methylene (or Methyl) Group to Natural Logarithm of Liquid Viscosity at $T_r = .55$ for n-Alkanes

one by a constant ratio r so that the total n methylene (or methyl) group contributions amount to the partial sum of the first n terms of the geometric series. That is, a general form as follows is used to generate the parameters in Equation (2-4) for a homologous series:

$$F_n = a + b\,(1 - r^n) / (1 - r) \qquad \text{for} \quad r \neq 1 \tag{2-5}$$

$$= a + bn \qquad \text{for} \quad r = 1 \tag{2-6}$$

where F_n is the fitted value for one of the five parameters in Equation (2-4), n is the number of carbon atoms in that particular compound, and a, b, r are adjustable constants. Equations (2-5), (2-6) present a generalization of classical group-contribution concepts. As we can see from these two equations, the group contribution of each methylene group in the n-alkane series can remain constant (with $r = 1$), or decrease (with $r < 1$), or even increase (with $r > 1$). However, r is actually restricted between 0.8 and 0.99 ($0.8 \leqslant r \leqslant 0.99$) in all of our work because most of the fitted r values (including those in other homologous series) fall in this region and the fitted parameters appear to be more systematic with this restriction. Since in this study r is always less than one, it will be called the "decay ratio" hereafter. The dependence of F_n on the number of carbon atoms in the n-alkane series is shown in Figure 2. The methylene (or methyl) group contributions are b, br, br^2, . . . and so forth.

For a homologous series with a functional group such as the n-alcohol series, Equation (2-5) can be rewritten as

$$F_n = a_f + b_f\,(1 - r_f^{\,n}) / (1 - r_f) \tag{2-7}$$

in which

$$a_f = a + \Delta a$$

$$b_f = b + \Delta b$$

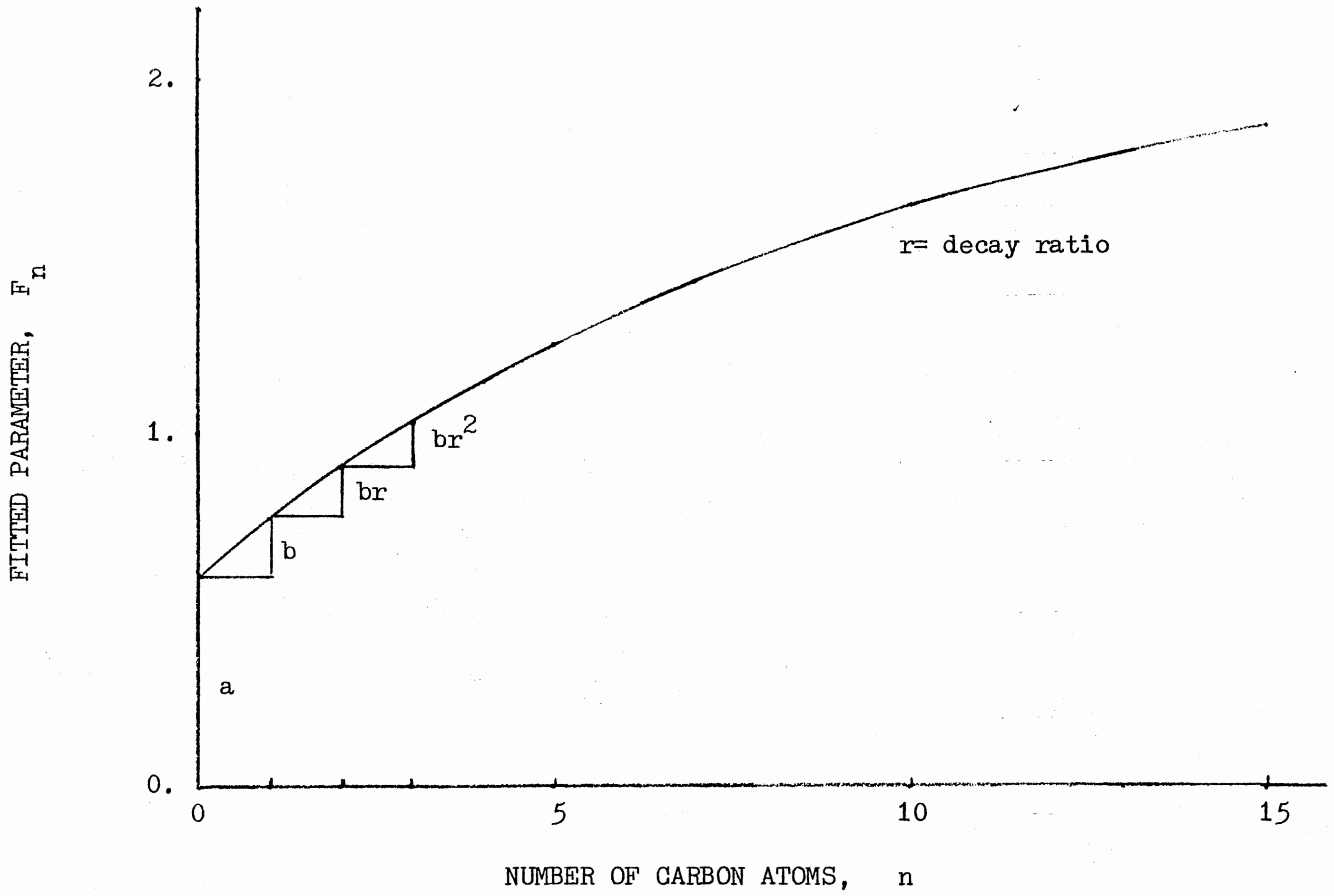

Figure 2. Dependence of F_n on the Number of Carbon Atoms in n-Alkanes

$$r_f = r + \Delta r$$

where a, b, r are the same constants derived from n-alkanes, Δa, Δb, Δr are characteristic of that particular functional group (e.g. hydroxyl group), n is the number of carbon atoms in that compound. Equation (2-7) is used to generate each of the five parameters in Equation (2-4). Therefore, there are 15 constants (three constants for each parameter) required to predict the liquid viscosities of the entire n-alkane series, and another 15 constants are necessary to be added to the 15 n-alkane constants to predict the n-alcohol series liquid viscosities.

The functional group contribution can vary with respect to the carbon chain length as shown in Figure 3.

Effect of the Functional Group Position

For n-alkanones we need to take into account the effect of the carbonyl group position along the carbon chain. This is done by adding an additional term to a_f in Equation (2-7). First, a new parameter ξ_f is introduced to represent the relative position of a functional group along the carbon chain. ξ_f is defined as follows:

$$\xi_f = (P_f-2)/((MC-1)/2-1) \qquad \text{if } P_f \leq (MC+1)/2 \qquad (2\text{-}8)$$

$$= ((MC-1)-P_f)/((MC-1)/2-1) \text{ if } P_f > (MC+1)/2 \qquad (2\text{-}9)$$

where MC is the number of carbon atoms in the carbon chain, P_f is the position where the functional group occurs. ξ_f is designed to vary from 0 to 1 for all possible functional group positions. For instance, if the carbonyl group position is 2 (e.g. 2-heptanone), then $\xi_f = 0$; if the carbonyl group occurs at the central position of the carbon chain (e.g. 4-heptanone), then $\xi_f = 1$; for 3-heptanone, $P_f = 3$, $\xi_f = 0.5$.

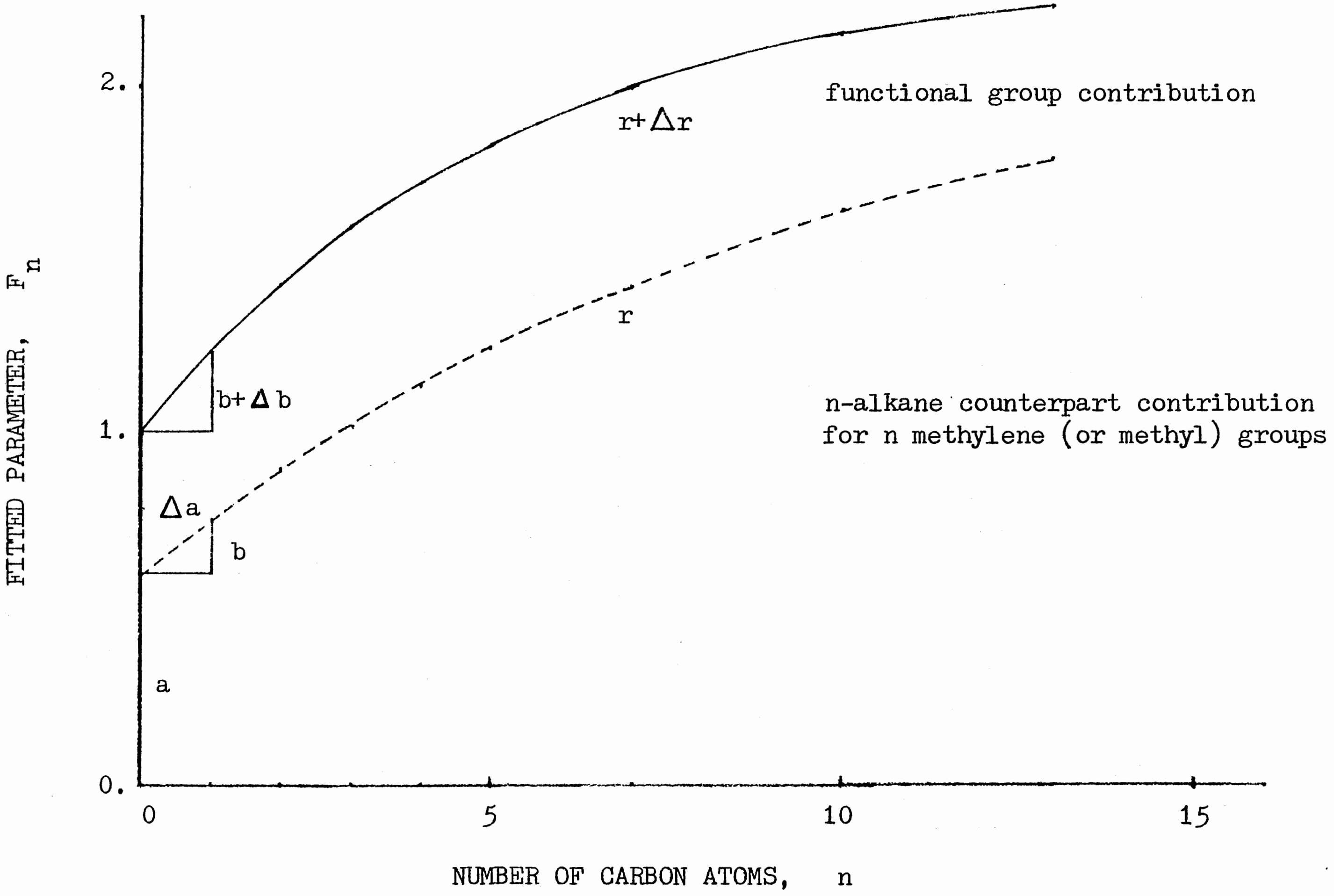

Figure 3. Illustration of the Functional Group Contribution As a Function of the Number of Carbon Atoms

The effect of the functional group position along the carbon chain is assumed to be proportional to ξ_f and is felt only through the a_f term as mentioned before. That is,

$$F_n = a_f + b_f (1 - r_f^n) / (1 - r_f) \tag{2-10}$$

in which
$$a_f = a + \Delta a + \lambda \xi_f$$
$$b_f = b + \Delta b$$
$$r_f = r + \Delta r$$

where λ, Δa, Δb, Δr are characteristic of that particular functional group for which the functional group position can vary along a carbon chain; a, b, r are the same as in n-alkanes.

A Special Case

A special case of the proposed group-contribution technique is worth mentioning here. If Δr is set equal to zero in Equation (2-7) and Equation (2-10), then $r_f = r$, and these two equations reduce to

$$F_n = (a+\Delta a)+(b+\Delta b)(1-r^n)/(1-r) \tag{2-11}$$

$$F_n = (a+\Delta a+\lambda \xi_f)+(b+\Delta b)(1-r^n)/(1-r) \tag{2-12}$$

respectively. Because of its simplicity, this approach is attractive and might be useful for further developments. However, all the work done so far has been based on the general approach (i.e. Equations (2-7), (2-10)). An illustration of Equation (2-12) is shown in Figure 4. As can be seen, the contribution of a functional group is still a function of n, the number of carbon atoms.

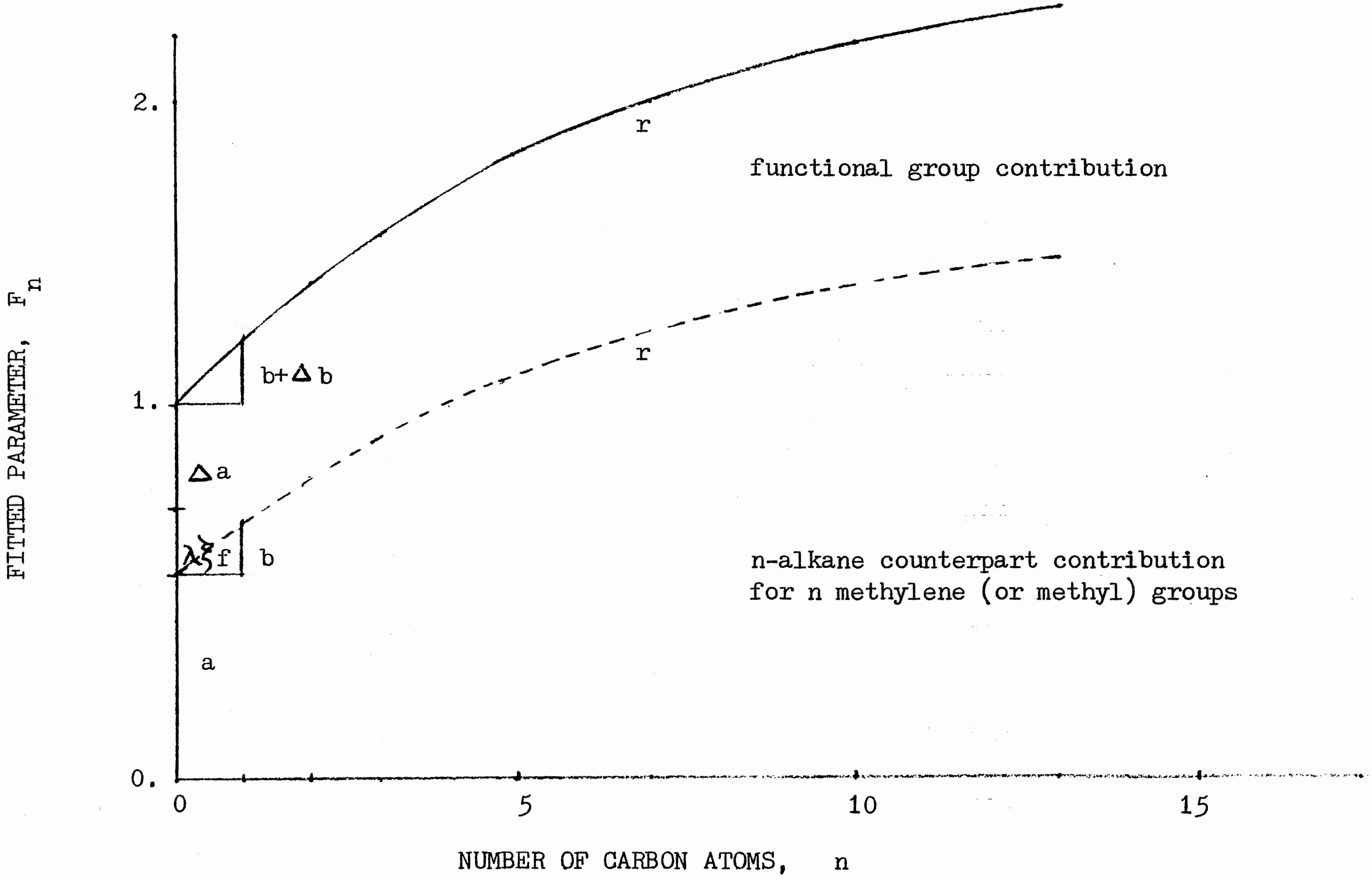

Figure 4. Illustration of the Functional Group Contribution with Functional Group Position Effect and Constant Decay Ratio

CHAPTER III

RESULTS AND COMPARISONS WITH OTHER METHODS

Regression Procedure

A nonlinear least-squares fitting subroutine MARQ written by Chandler (1979) was used to find the optimal constants in this prediction method. First, the predictive constants related to T_0 were obtained by fitting the experimental critical temperature data (or Lydersen's (1955) estimations of critical temperature) with the proposed model represented by Equations (2-5), (2-7), (2-10). Second, with a_0, a_1, a_2, $\ln \mu_0$ in terms of predictive constants, the remaining constants were obtained simultaneously by fitting experimental liquid viscosity data of a homologous series. That is, 3 constants (4 in n-alkanones) are determined first; then 12 constants (16 in n-alkanones) are fixed subsequently for a certain series.

Summary of the Computed Results

The proposed method has been applied to 23 n-alkanes, 12 n-alcohols, and 9 n-alkanones. The deviations between the computed results and the experimental data are summarized in Tables I, II, and III. The number of data points, temperature range, maximum percent error, temperature where maximum percent error occurs, and average absolute percent error are presented. Compounds which were not included in the regression are indicated by asterisks. Obviously the results are equally good for those compounds

TABLE I

RESULTS OF N-ALKANE LIQUID VISCOSITY CORRELATION AND PREDICTION

Compound	No. of Data Points	Temp. Range (deg. K)	T_{MPE}^{**} (deg. K)	Max. % Error	Avg. Abs. % Error
Ethane	11	98 -- 293	293	19.60	12.63
Propane	14	93 -- 353	213	-12.02	6.65
n-Butane	11	183 -- 373	233	- 9.07	5.94
n-Pentane	19	143 -- 453	396	-12.07	4.34
n-Hexane	13	178 -- 426	426	-11.22	2.72
n-Heptane	13	183 -- 424	183	- 7.93	1.57
n-Octane	12	213 -- 447	373	5.73	3.04
n-Nonane	12	218 -- 423	218	- 5.41	1.34
n-Decane	17	243 -- 511	478	7.54	2.06
n-Undecane	13	248 -- 468	468	4.22	1.25
n-Tetradecane	14	278 -- 528	528	5.41	2.64
n-Octadecane	16	303 -- 588	303	8.69	3.97
n-Tetracosane	6	329 -- 578	329	10.23	5.51
n-Octacosane	6	335 -- 574	335	9.53	4.78
n-Hexatriacontane	5	373 -- 574	474	- 5.17	3.34
n-Tritetracontane	6	363 -- 579	579	9.94	3.03
n-Tetrahexacontane	5	383 -- 574	574	16.75	8.30
*n-Tridecane	6	268 -- 473	373	- 2.57	1.66
*n-Hexadecane	7	293 -- 558	293	8.30	4.01
*n-Heptadecane	7	295 -- 573	295	8.02	4.09
*n-Eicosane	9	308 -- 613	613	9.92	4.60
*n-Hexacosane	5	333 -- 373	333	11.12	5.92
*n-Pentatriacontane	6	353 -- 579	353	7.10	3.52

* not included in regression

** temperature where maximum % error occurs

TABLE II

RESULTS OF N-ALCOHOL LIQUID VISCOSITY CORRELATION AND PREDICTION

Compound	No. of Data Points	Temp. Range (deg. K)	T_{MPE}^{**} (deg. K)	Max. % Error	Avg. Abs. % Error
Methanol	10	173 -- 463	173	-25.16	9.24
Ethanol	10	173 -- 423	173	31.07	8.70
n-Propanol	10	193 -- 373	193	-21.91	13.86
n-Butanol	10	222 -- 393	222	21.25	5.13
n-Pentanol	11	273 -- 505	450	30.03	15.62
n-Heptanol	9	288 -- 514	514	-11.10	5.54
n-Octanol	8	288 -- 551	393	-19.59	8.20
n-Decanol	5	293 -- 363	363	-14.96	6.06
n-Hexadecanol	4	323 -- 373	323	-10.43	5.39
n-Octadecanol	4	343 -- 423	398	7.64	5.74
*n-Hexanol	7	278 -- 428	278	8.51	2.52
*n-Undecanol	5	293 -- 358	293	9.36	4.89

* not included in the regression

** temperature where maximum % error occurs

TABLE III

RESULTS OF N-ALKANONE LIQUID VISCOSITY CORRELATION AND PREDICTION

Compound	No. of Data Points	Temp. Range (deg. K)	T^{**}_{MPE} (deg. K)	Max. % Error	Avg. Abs. % Error
Acetone	16	181 -- 521	521	-6.22	1.77
2-Butanone	8	273 -- 504	356	-3.56	1.77
2-Pentanone	6	273 -- 373	273	6.07	3.18
3-Pentanone	9	273 -- 507	491	7.82	3.49
2-Heptanone	6	288 -- 393	393	6.27	3.24
3-Heptanone	6	306 -- 502	502	-7.45	5.87
2-Undecanone	8	300 -- 512	327	-6.05	2.27
6-Undecanone	2	288 -- 303	303	5.34	4.78
*4-Heptanone	1	293	293	-1.32	1.32

* not included in the regression

** temperature where maximum % error occurs

which are excluded from the fitting. This shows the predictive power of the present method (interpolatively). The percent error E is defined as

$$E = [(\text{calc.} - \text{exp.}) / \text{exp.}] \times 100. \tag{3-1}$$

where calc. is the calculated value, exp. is the experimental value. The average absolute percent error (AAPE) is defined as

$$\text{AAPE} = \sum |E| / \text{NPT} \tag{3-2}$$

where $|E|$ is the absolute value of percent error, NPT is the number of data points for each compound. The maximum percent error is defined as the percent error E whose absolute value $|E|$ is the largest among NPT E's. The average value of AAPE's for NCPD different compounds is defined as

$$\text{AAPE}_m = \sum \text{AAPE} / \text{NCPD} \tag{3-3}$$

where AAPE_m is the average value of AAPE's.

The predictive constants for the n-alkane series are presented in Table IV. These constants should be used in Equations (2-4), (2-5). Because many of the experimental data used in the regressions of n-alcohols and n-alkanones are proprietary and have not been released yet, the predictive constants for these two series can not be included as part of this dissertation. A prediction program which utilizes the predictive constants obtained through the procedures outlined in the previous section is available in the Physical Properties Laboratory, Oklahoma State University.

Extrapolation Tests

An extensive survey of the extrapolation properties of this prediction method has been conducted. The purpose of this survey is to find out the trend of prediction errors when predictive constants are used to predict liquid viscosities for those compounds beyond the region of

TABLE IV

PREDICTIVE CONSTANTS FOR THE N-ALKANE SERIES

	a_0	a_1	a_2	$\ln \mu_0$	T_0
a	-.35304	1.93583	-.59080	-3.47767	195.205
b	.27694	-.70202	.83549	.06272	63.423
r	.88879	.88707	.80000	.98863	.90424

fitting, so a reasonable estimation can be made of how far the prediction method can be extrapolated with a certain level of prediction errors.

After a regression based on compounds up to a member of m carbon atoms in a certain homologous series is performed, the extrapolated prediction results indicate that the following equation can approximate EXPD (average absolute percent errors for a compound outside the range of this regression) very well. That is,

$$\mathrm{EXPD} = \mathrm{err}_1 \times (n - m) + \mathrm{err}_2 \qquad (3\text{-}4)$$

where err_1 is the percent error caused by each additional carbon atom beyond m, err_2 is the average value of AAPE's (AAPE_m) inside the fitting range, n is the number of carbon atoms for a compound beyond the range of this fitting.

For all three compound series, various regressions (up to different m's) have been made, and the results are summarized in terms of parameters of Equation (3-4) as shown in Table V. Note that the n range is expressed as $n_1 \leqslant n \leqslant n_2$ in this table.

One observation from our extrapolation tests is that a well-established regression can be extrapolated beyond its fitting region without much error and that a regression with $m \geqslant 18$ (based on members up to 18 carbon atoms or higher) is considered a well-established regression. Another observation is that there is no significant difference between the extrapolation properties of different compound series. For example, regressions covering members up to 5 carbon atoms give similar extrapolation properties, i.e., err_1's are almost the same for different series as long as the n range is the same (see Table V).

In this study the predictive constants are obtained through regressions with m = 64 for n-alkanes, m = 18 for n-alcohols, and m = 11 for

TABLE V

SUMMARY OF EXTRAPOLATED PREDICTIONS

Compound Series	m	n_1	n_2	err_1	err_2
n-Alkane	5	6	11	12.04	2.62
n-Alkane	5	6	18	7.93	2.62
n-Alkane	5	6	64	3.92	2.26
n-Alkane	11	12	64	1.86	3.81
n-Alkane	18	19	64	0.56	4.10
n-Alkane	36	37	64	0.70	4.07
n-Alkane	43	44	64	0.50	4.09
n-Alcohol	5	6	11	9.11	7.55
n-Alcohol	5	6	18	6.63	7.55
n-Alcohol	10	11	18	0.00	8.85
n-Alcohol	16	17	18	3.36	7.73
n-Alkanone	5	6	11	8.24	1.50
n-Alkanone	7	8	11	2.77	2.80

n-alkanones. Based on the aforementioned two observations, err_1 at m = 11 is estimated from the average of m = 10, 11, 16; err_1 at m = 18, 64 is estimated from the average of m = 18, 36, 43. With err_2's determined by each corresponding regression, the following conclusion concerning extrapolation is drawn:

for n-alkane series

$$EXPD\% = 0.59\% \times (n - 64) + 4.30\% \qquad (3\text{-}5)$$

for n-alcohol series

$$EXPD\% = 0.59\% \times (n - 18) + 8.35\% \qquad (3\text{-}6)$$

for n-alkanone series

$$EXPD\% = 1.74\% \times (n - 11) + 3.30\% \qquad (3\text{-}7)$$

are the expected AAPE's in extrapolated prediction. Equations (3-5)-(3-7) indicate that the present method is capable of, and suitable for, predicting extrapolatively.

Comparisons with Other Methods

Comparisons of the proposed method with the method of van Velzen et. al., the method of Orrick and Erbar, and the method of Letsou and Stiel are presented in Tables VI, VII, and VIII. Table VI is a full temperature range comparison with all three methods. Since the methods of van Velzen et. al. and Orrick and Erbar are recommended for low-temperature range prediction and since the method of Letsou and Stiel is recommended for high-temperature range prediction, comparisons of the present method with these methods at their recommended temperature ranges can be interesting and informative. Table VII is a low-temperature range comparison with the method of van Velzen et. al. and the method of Orrick and Erbar. Table VIII is a high-temperature range comparison with the

TABLE VI

FULL TEMPERATURE RANGE COMPARISON OF ALL METHODS

Compound	T_r Range	V-C-L	O-E	L-S	This Work
Ethane	.32 -- .96	32.29	15.61	18.90	12.63
n-Pentane	.30 -- .97	14.20	11.43	22.69	4.34
n-Decane	.34 -- .83	2.53	3.48	31.56	2.06
n-Octadecane	.41 -- .79	2.56	16.03	45.69	3.97
n-Pentatriacontane	.36 -- .59	27.47	39.51	50.86	3.52
n-Tetrahexacontane	.35 -- .53	263.09	75.87	53.71	8.30
Ethanol	.34 -- .82	117.93	71.70	58.25	8.70
n-Hexanol	.46 -- .70	10.42	5.92	62.56	2.52
n-Heptanol	.46 -- .81	20.01	8.53	58.64	5.54
n-Undecanol	.44 -- .54	8.32	13.70	86.83	4.89
n-Octadecanol	.46 -- .57	47.04	28.85	72.99	5.74
Acetone	.36 --1.03	6.91	11.91	30.28	1.77
3-Heptanone	.51 -- .84	18.22	10.95	27.56	5.87
2-Undecanone	.44 -- .76	26.23	7.63	42.50	2.27
$AAPE_m$ =		42.66	22.94	47.35	5.15

1. Value listed here are AAPE's (average absolute percent errors).
2. V-C-L is the van Velzen, Cardozo, and Langenkamp method; O-E is the Orrick and Erbar method; and L-S is the Letsou-Stiel method.
3. $AAPE_m$ is the average value of average absolute percent errors for NCPD (=14) compounds.

TABLE VII

LOW-TEMPERATURE RANGE COMPARISON

Compound	T_r Range	V-C-L	O-E	This Work
Ethane	.32 -- .70	11.33	16.76	12.70
n-Pentane	.30 -- .71	3.72	5.63	3.05
n-Decane	.39 -- .73	2.30	3.29	1.38
n-Octadecane	.41 -- .74	2.78	14.22	3.61
n-Pentatriacontane	.36 -- .59	27.47	39.51	3.52
n-Tetrahexacontane	.35 -- .53	263.09	75.87	8.30
Ethanol	.34 -- .70	141.62	87.39	10.38
n-Hexanol	.46 -- .70	10.42	5.92	2.52
n-Heptanol	.46 -- .69	12.66	6.69	4.33
n-Undecanol	.44 -- .54	8.32	13.70	4.89
n-Octadecanol	.46 -- .57	47.04	28.85	5.74
Acetone	.36 -- .74	5.22	12.94	1.44
3-Heptanone	.51 -- .68	11.87	14.49	5.16
2-Undecanone	.44 -- .72	24.10	6.80	2.37
$AAPE_m$ =		40.86	23.71	4.96

1. Values listed under each method are AAPE's (average absolute percent errors).

2. V-C-L is the method of van Velzen et al.; O-E is the Orrick and Erbar method.

3. $AAPE_m$ is the average of AAPE's for these compounds.

TABLE VIII

HIGH-TEMPERATURE RANGE COMPARISON

Compound	T_r Range	L-S	This Work
Ethane	.76 -- .96	6.22	12.51
n-Pentane	.75 -- .97	3.65	6.10
n-Decane	.77 -- .83	11.72	7.14
n-Octadecane	.77 -- .79	24.06	6.52
Ethanol	.76 -- .82	7.18	1.96
n-Heptanol	.75 -- .81	21.98	9.78
Acetone	.76 --1.03	32.88	2.49
3-Heptanone	.77 -- .84	28.79	7.30
2-Undecanone	.76	28.88	1.57
$AAPE_m$ =		18.37	6.15

1. Values listed here are AAPE's (average absolute percent errors).
2. L-S is the Letsou-Stiel method.
3. $AAPE_m$ is the average of AAPE's for 9 compounds.

Letsou and Stiel method. Fourteen selected compounds are included in these comparisons. T_r (reduced temperature) is defined as T/T_c where T_c is the experimental (or estimated) critical temperature.

As we can see from these tables, the proposed method performs significantly better than other liquid viscosity prediction methods. Even in the limited temperature range comparisons, this method predicts (or correlates) more accurately. In addition, none of the other methods can cover a wide range of carbon atoms; all of them fail badly in long chain compounds.

The Orrick and Erbar method and the Letsou and Stiel method require other physical property data to predict viscosity. Some of these data may not be readily available (e.g. room temperature liquid density); some data are virtually unavailable (e.g. critical properties and acentric factors of long chain compounds)--and have to be estimated. For the Letsou and Stiel method, the critical properties are calculated by the method of Lydersen (1955) and the acentric factors are calculated by the method of Edmister (1958). For very long carbon chains, these methods are very risky because even the normal boiling points have to be estimated. As shown in Table VIII, the Letsou and Stiel method is, in general, not suitable for polar compound liquid viscosity predictions.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions can be drawn from the results of this work:

1. The Cox equation, which is originally a vapor pressure correlation, becomes an excellent liquid viscosity correlation with slight modification.
2. A prediction method, which is the first of its kind, capable of covering a wide range of temperatures (from the melting point to the critical point) and a wide range of carbon chain lengths has been developed.
3. A new group-contribution technique for predicting viscosity employing the geometric series model is proposed. This technique is a generalization of the classical group-contribution concepts.
4. A new parameter is introduced for the relative position of a functional group along the carbon chain. This parameter helps to account for the position effect of a functional group through a linear model.
5. The proposed method is superior to any other currently existing method: it is applicable to and more accurate for a wide range of temperatures, and it is applicable to both short and long chain compounds.

6. The proposed method has been tested for both nonpolar (n-alkanes) and polar (n-alcohols and n-alkanones) compounds. The same procedure is equally applicable to other (uni-functional group) homologous series.

Recommendations

The following recommendations are made for further investigation:

1. Apply the current method to other uni-functional group compound series.
2. Extend the present work to multi-functional group compounds.
3. Develop structural corrections for branched compounds and cyclic compounds.
4. Apply the same approach to treat other pure compound physical properties.

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