Estimation of the Liquid Viscosity of Hydrocarbons from Their Normal Boiling Points

由碳氫化合物之正常沸點推測其液態黏度

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ABSTRACT

Herein a generalized approach is presented for predicting the viscosity (η) of liquid hydrocarbons using only their normal boiling temperatures (T_b) as a single characterizing parameter. Published experimental data were used to determine the proposed model, $\ln(\eta) = A+B(T_b/T)$, in which the two correlation parameters, A and B, were generalized by a polynomial expansion of the carbon number in normal alkanes. The model so derived accurately gives the viscosity of a liquid hydrocarbon as a function of temperatures over a wide range of temperatures. By applying the concept of the effective carbon number, the model has been successfully extended to estimate the viscosity of other hydrocarbons including isomeric alkanes, alkenes and aromatics with acceptable reliability. The proposed approach is simple to use, requiring only the normal boiling points as input data.

Keywords: Correlation, Prediction, Liquid viscosity, Hydrocarbon, Normal boiling point.

摘要

本文提出一種僅使用正常沸點(T_b)作為唯一特性參數，推測液態烴類黏度(η)的一般性方法。利用收集已發表之實驗數據，確定出所提出之模式，$\ln(\eta) = A+B\left(\frac{T_b}{T}\right)$，其中 A、B 兩個共聯參數，係由正常烷烴中有效碳數的多項式展開予以一般化。依此導出之模式，在廣大溫度範圍內，能準確推算出作為溫度函數的液態烴類黏度。經由應用有效碳數概念，本文模式已經順利延伸到包含異構化烷烴、烯烴、及芳香烴的中意可靠度估算。本文模式使用簡單，只需正常沸點作為輸入數據。

INTRODUCTION

An experimentally determined liquid viscosity is always preferred to an estimated value. However, a simple mathematical expression for experimental data is frequently needed to assist the recording and to provide a way for prediction and design purposes. A number of models have been proposed for correlation and/or prediction of the liquid viscosity of hydrocarbons (van Velzen *et al.,* 1972; Allan and Teja, 1991; Mehrotra, 1991a, 1991b, 1994; Orbey and Sandler, 1993). Among those, the approach of van Velzen *et al.* (1972), based on the use of the functional group contributions to emphasize the effect of chemical structure on liquid viscosity, is considerably superior to any of the other correlations for prediction of the viscosity of a hydrocarbon. They proposed a modification of the Andrade equation (Andrade，1930) for predicting liquid viscosity of organic compounds，

$$\ln(\eta) = C\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad (1)$$

where C and T_o are specific parameters related to the molecular structure of each compound. Since it requires these two parameters to be calculated from the equivalent chain length for each compound, it is complicated to apply this structural basis approach in simulation programs. The aim of the present study is to generalize the two specific

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parameters of the Andrade equation for predicting the liquid viscosity of hydrocarbons using a single characterizing parameter normal boiling temperature, T_b.

The effective carbon number N^* is a non-integer number assigned to branched and unsaturated members of a specific family (Ambrose and Sprake, 1970; Chase, 1984). This is based on the simple relationship that exists between the normal boiling point and the number of carbon atoms N of the straight-chain members in a homologous series. Kudchadker and Zwolinski(1966), for example, demonstrated that the following equation gave a good relationship between T_b and N for normal alkanes (heptane to octadecane),

$$\ln(1078 - T_b) = 3.032 - 4.999\times10^{-2}N^{2/3} \quad (2)$$

As there is a good correlation between chemical structure of organic compounds and their physical and thermodynamic properties in a specific homologous series, the effective carbon number can be used for the prediction of physical properties with a minimum amount of information(Chase,1984).

A number of approaches for predicting thermodynamic properties have been developed using the effective carbon number as a single characterization parameter. Willman and Teja (1985), for example, demonstrated that a correlation, based on the known properties of normal alkanes, could be extended to predict vapour pressures of other members including isomeric alkanes, alkenes, alkynes,cycloalkanes, alkadienes, aromatics and sulfur-containing compounds. A similar approach has been used to predict other physical properties, such as the heat of vaporization which was predicted for a wide variety of families including aliphatic hydrocarbons, alcohols, aliphatic acids and acetates (Dickson and Daubert, 1988)

In the present study, a large amount of existing experimental data for normal alkanes were used to determine a generalized correlation, using the normal boiling temperature as a single parameter. Attempts were also made to extend this proposed model to predict the viscosity of other hydrocarbons including isomeric alkanes, alkenes, aromatics and cycloalkanes.

NORMAL ALKANE CORRELATION

Based on the Andrade equation(Andrade, 1930), a functional form has been chosen to represent liquid viscosity η and temperature T for normal alkanes

$$\ln(\eta) = A + B\left(\frac{T_b}{T}\right) \quad (3)$$

where A and B = correlation parameters, T_b = normal boiling temperature. Equation(3) was used to correlate liquid viscosity and temperature over a wide range of temperatures ($T_{r.} \leqq 0.8$) for 20 normal alkanes from methane to eicosane, and a linear relationship resulted for all the substances.

The vast majority (93%) of experimental viscosity data used to develop the above model was taken from the API Research Project 44 (1978) in which the data have been critically reviewed and selected from the best experimental data available in the literature; the estimated experimental error was detemined to be 0.003 to 0.030 mPa·s. The remaining 7% of the data was collected from the International Critical Tables (ICT,1930) , Landolt-Bornstein(1955) and the CRC Handbook of Chemistry and Physics (Weast and Astle, 1980).

For alkanes with $N \leqq 15$, both the intercept A and slope B are strongly dependent on the carbon numbers with the exception of methane which deviates systematically from the curve that represents the other normal alkanes, while for those with N greater than 15 the values of A and B become approximately constant. The properties of the first member, e.g. methane, often differ considerably from those of the other members in a specific homologous series (Reid et al., 1987).

For alkanes with $N \leqq 15$, the following relationships can be used to represent the values of A and B, with regression coefficients of 0.999,

$$A = -3.346 - 1.556\times10^{-1}N + 4.566\times10^{-3}N^2 \quad (4)$$

and

$$B = 1.608 + 1.919\times10^{-1}N - 6.440\times10^{-3}N^2 \quad (5)$$

respectively.

For alkanes with $N>15$, equation (3) becomes

$$\ln(\eta) = -4.634 + 3.032\left(\frac{T_b}{T}\right) \quad (6)$$

Thus, equation (3) (for $N \leq 15$) in conjunction with equations (2), (4) and (5), or equation (6), (for $N>15$) allows complete prediction of the viscosity of normal alkanes, and only requires T_b values to be known. In a test with 896 experimental data points, covering 20 normal alkanes from methane to eicosane, the calculated results give an overall average absolute deviation (AAD) of 2.9% from experimental data; the corresponding value for the approach of van Velzen et al. (1972) is 3.4%. The AAD value for each compound is given in Table 1, together with the published normal boiling temperature (Daubert et al., 1989), the effective carbon number calculated by equation (2), the number of data points, and the temperature range (ΔT) used. The agreement between the predicted and experimental values is good with the exception of methane which gave a relatively large deviation. Note that the accuracy of the proposed approach could be improved if the carbon numbers present in normal alkanes were used directly for N in equations (4) and (5).

VISCOSITY ESTIMATES FOR OTHER HYDROCARBONS

By assuming that the simple relationship that exists between T_b and N for the straight-chain members is still valid for the branched and unsaturated members in a specific homologous series (Ambrose and Sprake, 1970), the above equations can be used to estimate the viscosity of other hydrocarbons including isomeric alkanes, alkenes, aromatics and cycloalkanes. The effective carbon numbers N^* for branched and unsaturated members were calculated from equation (2). Having calculated the valued of N^*, the values of A and B can then be determined from equations (4) and (5), respectively, for compounds with $N^* \leqq 15$, inserting N^* for N. For substances with $N^*>15$, equation (6) was used directly.

Using present approach, the overall AAD value is 7.4% for 4 isomeric alkanes, 8.6% for 20 alkenes and 8.9% for 20 aromatics; the corresponding value for the approach of van Velzen et al. (1972) in accordance with equation (1) is 3.9% for 4 isomeric alkanes, 5.2% for 20 alkenes and 6.7% for 20 aromatics. The individual AAD value for each compound is given in Table 2. Good agreement between the experimental and predicted values was generally found for isomeric alkanes, alkenes and aromatics, with the exception of isobutene and benzene, for which the AAD values are unacceptably high.

Table 3 summarizes the overall deviations from experimental data for 4 groups of hydrocarbons for both the proposed method and the approach of van Velzen et al. (1972). From 2020 experimental viscosity data points, covering 64 substances, the overall deviation for 4 groups of hydrocarbons is 6.1% for this proposal and 4.3% for the approach of van Velzen et al. (1972). Although the approach of van Velzen et al. (1972) gives a slightly better estimation of viscosity, it suffers disadvantages in that this structural based approach is rather complicated to use in simulation programs, and requires more input data. The proposed model is more friendly to use, requiring only the normal boiling points to be known.

The viscosity prediction for cycloalkanes was rather poor when using present model; the overall AAD value is 16.5% for 13 cyclopentanes and 28.7% for 7 cyclohexanes. This shows that care must be taken when extending present approach to other families of a specific homologous series. Cyclohexanes, for example, are rigid molecular structures compared to normal alkanes which are more flexible, and this difference may account for the poor prediction of the liquid viscosity of cycloalkanes using present model.

CONCLUSION

The proposed approach described above accurately gives the liquid viscosity of normal alkanes as a function of temperatures over a wide range of temperatures. The normal boiling point is the only characterizing parameter for this proposed model. The generalized correlation determined using experimental data of normal alkanes is capable of being extended to predict the viscosity of other hydrocarbons including isomeric alkanes, alkenes and aromatics with acceptable reliability. The proposed model could readily be extended to predict the viscosity of other homologous series.

NOMENCLATURE

A，B	parameters defined in equation　(3)
C	parameter defined in equation (1)
N	the carbon number
N*	the effective carbon number
T	the absolute temperature, K
ΔT	the range of temperatures studied
Tb	normal boiling point, K
To	parameter defined in equation (1)
η	liquid viscosity, mPa·s

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Table 1. Prediction of the viscosity of normal alkanes

Substance	No. of data point	$T_b^{(a)}$,K	N*	Ref.	ΔT,K	AAD(1),%	
						This work	van Velzen *et al* (1972).
Methane	4	111.7	0.91	(b)	93.2~108.2	45.18	111.6
Ethane	18	184.6	2.06	(b)	98.2~183.2	11.56	9.07
Propane	29	231.1	3.01	(b)	88.2~228.2	10.36	12.29
Butane	18	272.7	4	(b)	183.2~268.2	6.77	9.32
Pentane	39	309.2	5	(b),(d),(e)	148.2~308.2	3.68	4.02
Hexane	49	341.9	6	(b),(c),(e)	178.2~338.2	2.86	3.53
Heptane	55	371.6	7	(b),(c),(e)	183.2~368.2	2.71	2.73
Octane	52	398.8	8	(b),(c),(e)	218.2~395.3	2.16	1.79
Nonane	46	424	9.01	(b),(d),(e)	223.2~423.2	1.98	2.41
Decane	47	447.3	10.01	(b),(e)	248.2~448.2	1.77	1.76
Undecane	48	469.1	11.01	(b),(e)	248.2~468.2	2.1	1.92
Dodecane	45	489.5	12.01	(b)	268.2~488.2	1.7	1.63
Tridecane	55	508.6	13.02	(b),(c),(e)	268.2~508.2	2.01	2.05
Tetradecane	49	526.7	14.02	(b)	283.2~523.2	1.73	1.82
Pentadecane	53	543.8	15.02	(b)	283.2~543.2	2.43	2.16
Hexadecane	49	560	16.02	(b)	293.2~533.2	1.77	2.1
Heptadecane	62	575.3	17.02	(b),(d)	298.2~573.2	1.74	2.26
Octadecane	58	589.9	18.01	(b)	303.2~588.2	1.89	2.23
Nonadecane	59	603.1	18.95	(b)	308.2~598.2	2.07	2.26
Eicosane	61	616.9	19.99	(b)	313.2~613.2	2.05	1.93
Overall	896					2.9	3.4

(a)Daubert et al., (b) APIRP44, 1978; (c)ICT, 1930; (d) Landolt-Bornstein, 1955;(e) Weast and Astle, 1980; (1) Σ|(exptl. value-calcd. value)/exptl. value|(100/no. of data points).

Table 2. Prediction of the viscosity of isomeric alkanes, alkenes and aromatics

Substance	No. of data ponits	$T_b^{(a)}$,K	N*	Ref.	ΔT,K	AAD(1),%	
						This Work	van Velzen *et al* (1972).
Isobutane	14	261.4	3.72	(b)	193.2~258.2	25.77	5.18
Isopentane	24	301.0	4.77	(b),(d),(e)	223.2~298.2	8.22	1.54
Isohexane	26	333.4	5.73	(b),(d),(e)	273.2~333.2	3.94	4.74
Isoheptane	34	363.2	6.71	(b),(d),(e)	273.2~363.2	1.82	4.41
Ethene	13	169.5	1.79	(b)	108.2~168.2	6.01	45.21
Propene	19	225.4	2.88	(b)	88.2~178.2	17.30	25.39
1-Butene	17	266.9	3.86	(b)	158.2~238.2	3.55	3.62
1-pentene	19	303.1	4.83	(b)	183.2~273.3	9.65	4.43
1-Hexene	24	336.6	5.83	(b)	218.2~333.2	12.65	6.39
1-Heptene	19	366.8	6.83	(b)	273.2~362.2	10.00	2.88
1-Octene	24	394.4	7.84	(b)	273.2~388.2	8.67	1.85
1-Nonene	24	420.0	8.84	(b)	273.2~388.2	9.28	2.23
1-Decene	24	443.8	9.85	(b)	273.2~388.2	9.99	2.68
1-Undecene	24	465.8	10.86	(b)	273.2~388.2	10.65	2.68
1-Dodecene	24	486.5	11.86	(b)	273.2~388.2	11.19	2.43
1-Tridecene	24	505.9	12.87	(b)	273.2~388.2	10.68	2.24
1-Tetradecene	24	524.3	13.88	(b)	273.2~388.2	9.17	2.05
1-Pentadecene	24	541.6	14.89	(b)	273.2~388.2	6.87	2.10
1-Hexadecene	23	558.0	15.89	(b)	278.2~388.2	4.11	1.89
1-Heptadecene	21	573.5	16.89	(b)	288.2~388.2	6.58	1.62
1-Octadecene	20	588.0	17.88	(b)	293.2~388.2	5.77	1.87
1-Nonadecene	19	602.2	18.89	(b)	298.2~388.2	5.49	2.45
1-Eicosene	17	615.5	19.89	(b)	308.2~388.2	5.21	2.51

Table 2. *Continued*

Substance	No.of data points	$T_b^{(a)}$,K	N*	Ref.	ΔT,K	AAD$^{(1)}$,%	
						This work	van Velzen et al (1972).
Isoprene	16	307.2	4.94	(c),(d)	273.2~303.2	4.73	6.36
Benzene	29	353.2	6.37	(c),(d),(e)	273.2~348.2	42.47	30.80
Toluene	44	383.8	7.44	(b),(d),(e)	248.2~378.2	18.77	10.80
Ethylbenzene	44	409.4	8.41	(b),(c),(e)	248.2~403.2	8.80	3.30
Propylbenzene	36	432.4	9.36	(b)	248.2~423.2	7.50	3.49
Butylbenzene	36	456.5	10.42	(b)	248.2~423.2	2.28	3.00
Pentylbenzene	35	478.6	11.47	(b)	253.2~423.2	3.42	4.35
Hexylbenzene	35	499.3	12.52	(b)	253.2~423.2	3.49	4.82
Heptylbenzene	35	519.3	13.60	(b)	253.2~423.2	3.79	4.87
Octylbenzene	30	537.6	14.65	(b)	253.2~393.2	4.83	4.83
Nonylbenzene	30	555.2	15.72	(b)	253.2~398.2	6.37	5.41
Decylbenzene	34	571.0	16.73	(b)	258.2~423.2	6.32	4.79
Undecylbenzene	33	586.4	17.77	(b)	263.2~423.2	6.79	4.23
Dodecylbenzene	31	600.8	18.79	(b)	273.2~423.2	6.52	3.28
Tridecylbenzene	30	614.4	19.80	(b)	278.2~423.2	7.03	2.94
o-xylene	34	417.6	8.74	(b)	268.2~413.2	15.33	14.69
m-xylene	32	412.3	8.53	(b)	273.2~408.2	3.41	4.73
p-xylene	28	411.5	8.50	(b)	293.2~408.2	2.99	4.13
p-ethylbenzene	15	435.2	9.48	(b)	283.2~353.2	13.64	16.15
2-propylbenzene	13	425.6	9.07	(b)	273.2~333.2	5.54	0.60
1,2,4-trimethyl-enzene	3	442.5	9.80	(b)	298.2~308.2	13.24	8.69

(a)Daubert et al., 1989;(b)APIRP44, 1978; (c)ICT, 1930; (d)Landolt-Bornstein, 1955;(e)Weast and Astle, 1980;(1) Σ|(exptl. value-calcd. value)/exptl. value|(100/no. of data points).

Table 3. Summary of the liquid viscosity predictions for each class of hydrocarbon**s**

The class of family	No. of data points	Overall AAD(1), %	
		This work	The method of van Velzen et al (1972).
Normal Alkanes	896	2.9	3.4
Isomeric Alkanes	98	7.4	3.9
Alkenes	419	8.6	5.2
Aromatics	607	8.9	6.7
Average	2020	6.1	4.3

(1) Σ|(exptl. value-calcd. value)/exptl. value|(100/no. of data points).