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Viscosity estimation at low temperatures ($T_r < 0.75$) for organic liquids from group contributions

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Abstract

A group-contribution method has been developed for calculating the viscosity of organic liquids at temperature $T_r < 0.75$ and atmospheric pressure. Group-contribution parameters of 91 functional groups were obtained and the various groups are presented as a four-constant equation. The proposed method is easy to be used and only requires the critical pressure of each compound. When compared with 4627 experimental data for 482 organic liquids, this method produces a standard deviation of 0.18 mPa s and an average absolute percentage deviation of 4.14%. The comparison for this method was made with the methods of van Velzen et al. [Ind. Eng. Chem. Fundam. 11 (1972) 20], Orrick and Erbar [Estimation of viscosity for organic liquids, Proposition Report, Oklahoma State University, Stillwater, OK, 1973], and Przezdziecki and Sridhar [AIChE J. 31 (1985) 333].

Keywords: Viscosity; Estimation; Group contributions; Organic liquids

1. Introduction

An accurate knowledge of the viscosity of organic liquids is important for the design of chemical process equipments. Although the experimental data can be very accurate, it is difficult to provide all the data needed for every single compound. For this reason, a reliable estimation method is usually required. Several methods have been proposed in the past for the estimation of liquid viscosity. Reid et al. [1] have reviewed many of these and critically examined the utility and reliability of more practical approaches. The methods proposed by van Velzen et al. [2], Orrick and Erbar [3], and Przezdziecki and Sridhar [4] have been recommended for the estimation of the liquid viscosity at the reduced temperature (T_r) of 0.75 or below.

The method of van Velzen et al. assumes a linear relationship between the logarithm of viscosity and the reciprocal of temperature and adopts a statistical analysis to include the effect of structure on liquid viscosity. However, such a linear relationship is found to be applicable only over a limited temperature range for many liquids. Its calculation is quite complicated and inconvenient to be applied. The method of Orrick and Erbar is slightly modified to include the linear liquid density relation and employs a group-contribution technique to estimate liquid viscosities. While the method of Przezdziecki and Sridhar employs the Hildebrand equation [5], which necessitates knowledge of melting point, liquid volumes, critical properties, and acentric factor. All three methods are not reliable for nitriles, sulfur-containing compounds, the compounds with highly branched structures, and many heterocyclics.

In this work, an attempt is made to develop an estimation method that is free from many of these shortcomings. Six correlation equations are examined for their abilities to express the temperature dependence of the viscosity of organic liquid. A four-constant equation with an additional term of critical pressure is used to relate the chemical structure of organic compounds. Based on this approach, a group-contribution method is developed to permit the liquid viscosity to be estimated reliably and extensively at temperature $T_r < 0.75$.

2. Fundamentals

2.1. Correlation equations for viscosity

Six relations for correlating the temperature dependence of absolute viscosity (η, mPa s) were tested as follows:

$$\ln\eta = A + BT \tag{1}$$

$$\ln\eta = A + \frac{B}{T} \tag{2}$$

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Nomenclature

a_i, b_i, c_i, d_i	group constants used in Eq. (8) and Tables 2–4
A, B, C, D	equation constants used in Eqs. (1)–(7)
AAD%	average absolute percentage deviation
d%	deviation defined as [calc − expt] × 100
F_{obj}	objective function defined in Eq. (9)
M	number of data points
N_i	number of group i
P_{c}	critical pressure (bar)
Q	index used to number the molecular groups in Tables 2–4
T	temperature (K)

Greek letters

ε	average absolute error for viscosity (mPa s)
η	absolute viscosity (mPa s)
σ	standard deviation for viscosity (mPa s)

Superscripts

calc	calculated value
expt	experimental value

Subscripts

A	in the aromatic ring
AC	on the aromatic ring
c	critical property
i	molecular group i
n, m	group with n or m halogen atoms attached to the same carbon atom
obj	objective function
r	reduced property
R	in the nonaromatic ring
RC	on the nonaromatic ring

$$\ln \eta = A + \frac{B}{T} + CT \tag{3}$$

$$\ln \eta = A + \frac{B}{T} + \frac{C}{T^2} \tag{4}$$

$$\ln \eta = A + BT + \frac{C}{T^2} \tag{5}$$

$$\ln \eta = A + BT + \frac{C}{T^2} + D \ln T \tag{6}$$

where A, B, C, and D are parameters and T is the absolute temperature (K). Table 1 shows the correlation results for 519 organic liquids with 5432 data points by Eqs. (1)–(6). Among three-constant relations, Eq. (5) gave the best result with an average deviation of 0.62%. Whereas the best result for two-constant relations was 2.04% and a large deviation (4.46%) was obtained for alcohols. Although the four-constant relation gave a better correlating result (0.36%) than Eq. (5), one more parameter would be required for the calculation of viscosity. Therefore, Eq. (5) was chosen as the basic relation for developing the group-contribution method.

2.2. *Development of the group-contribution method*

The group-contribution method based solely on the relation of Eq. (5) failed to provide reasonable result for the viscosity of organic liquids. Attempts were then made to include a critical property in the group-contribution correlation. It was found that the correlation for liquid viscosity would be more successful by having critical pressure (P_{c}, bar) in the model. Thus, an equation of the following form is used for this work:

$$\ln \eta = A + BT + \frac{C}{T^2} + D \ln P_{\mathrm{c}} \tag{7}$$

Based on the classical group-contribution concepts, the viscosity of a compound is considered as the sum of all the contributions made by the group present in a molecule. Further, the contribution of a given group in a molecule is the same in another molecule. Thus, the group-contribution model used for the calculation of liquid viscosity at temperature $T_{\mathrm{r}} < 0.75$ and atmospheric pressure in this study is then

$$\ln \eta = \sum_i N_i \left\{ a_i + b_i(T) + \frac{c_i}{T^2} + d_i \ln P_{\mathrm{c}} \right\} \tag{8}$$

where a_i, b_i, c_i, and d_i are the predictive constants of group i. The values of the optimum constants, a_i, b_i, c_i, and d_i for the 91 molecular groups are shown in Tables 2–4. The critical pressure required for each compound was obtained from the data of two compilations [6,7], but otherwise from the group-contribution method proposed by Joback and Reid [8].

Estimation of the optimum group constants, a_i, b_i, c_i, and d_i, in Eq. (8) was based on minimization of the objective function, F_{obj}, in terms of the calculated and experimental $\ln \eta$ values by a multiple regression analysis based on the least-squares method [9]. The function F_{obj} can be given as

$$F_{\mathrm{obj}} = \sum_{i=1}^{M} \left(\frac{\ln \eta_i^{\mathrm{calc}} - \ln \eta_i^{\mathrm{expt}}}{\ln \eta_i^{\mathrm{expt}}} \right)^2 \tag{9}$$

where M is the number of data points used, η^{expt} the experimental viscosity, and η^{calc} is the calculated viscosity. The final correlation involves the viscosity data from three compilations [10–12] and the original sources [13–23].

2.3. *Use of the method*

The proposed method may be used to find the liquid viscosity of any compound for which necessary groups are available at temperature $T_{\mathrm{r}} < 0.75$ and atmospheric pressure. Two examples of viscosity calculation by using the proposed method are given below.

Table 1
Correlation equations and their correlation results for the viscosities of organic liquids

Compound series	Data points (compounds)	AAD%					
		Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)
Alkane	390 (24)	4.61	1.76	1.10	0.96	0.84	0.59
Alkene	171 (14)	4.05	2.09	1.29	1.11	0.92	0.76
Alkyne	59 (7)	3.19	0.43	0.55	0.56	0.67	0.16
Cyclane	129 (13)	5.30	2.43	0.89	0.62	0.55	0.43
Aromatics	374 (30)	3.62	1.40	0.51	0.45	0.50	0.29
Alcohol	750 (67)	6.49	4.46	1.60	1.56	1.18	0.37
Aldehyde	52 (6)	1.29	0.56	0.29	0.27	0.26	0.23
Ether	327 (33)	4.64	1.83	0.94	0.73	0.66	0.33
Ketone	201 (20)	3.12	1.58	0.71	0.64	0.58	0.58
Acid	171 (19)	2.29	1.15	0.56	0.54	0.46	0.37
Ester	422 (47)	2.32	1.80	0.70	0.67	0.64	0.34
Nitrogen-containing	1027 (100)	4.49	2.56	0.70	0.55	0.52	0.38
Halogen-containing	1093 (103)	2.14	0.90	0.37	0.34	0.32	0.24
Sulfur-containing	223 (34)	1.88	1.10	0.42	0.36	0.35	0.18
Overall	5432 (519)	3.81	2.04	0.78	0.71	0.62	0.36

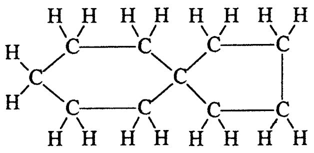
Table 2
The molecular groups and their contribution constants to liquid viscosity for carbon–carbon bonds and carbon–hydrogen bonds

Q	Groups[a]	a_i	$b_i \times 10^2$	$c_i \times 10^{-4}$	d_i
1	CH_4	−1.7296	−1.0563	0.8928	−0.0019
2	$-CH_3$	0.0570	−0.2383	0.7556	−0.1765
3	$-CH_2-$	−0.1497	0.0060	1.4157	0.0751
4	$>CH-$	−2.2942	0.4028	4.5094	0.6679
5	$>C<$	1.0031	−0.3677	−6.0316	1.1972
6	$=CH_2$	0.9256	−0.2656	0.9860	−0.4417
7	$=CH-$	1.3365	0.1612	1.9408	0.2507
8	$=C<$	−3.5020	0.4305	3.1287	1.0465
9	$\equiv CH-$	87.6040	−0.1106	4.4245	−24.1836
10	$\equiv C-$	−91.6154	−0.0111	0.3265	25.0542
11	$(-CH_2-)_R$	6.0416	−0.1778	0.8437	−1.5184
12	$(>CH-)_R$	−33.8745	0.7637	7.2433	8.5951
13	$(=CH)_R$ (cycloalkene)	1.2028	−0.0120	2.0143	−0.3677
14	$(>C<)_R$ (spirocyclane)	−56.2158	1.7694	19.0452	13.3885
15	$(=CH-)_A$	−0.8570	−0.0098	2.4376	0.1311
16	$(=C<)_A$	0.7896	−0.0231	−0.9222	0.1928
17	$(=C<)_A$ (bi/terphenyl)	2.0973	0.0444	8.1690	−0.4351
18	$(=C<)_A$ (naphthalene)	0.4392	0.0683	8.8426	−0.1685
19	$(=C<)_A$ (turpentine)	27.3350	1.2165	34.2857	−11.6500
20	$(=C<)_A$ (tetralin)	14.2586	−0.8665	−14.7474	−2.7574

[a] R: in the nonaromatic ring; A: in the aromatic ring.

2.3.1. Example 1: Estimation of the viscosity of spiro[4.5]decane

The experimental viscosity is 1.619 mPa s at 310.95 K [12] and P_c is calculated from the method of Joback and Reid [8] is 33.0 bar. The molecular structure and group information are



Q	Groups	No.	a_i	$b_i \times 10^2$	$c_i \times 10^4$	d_i
11	$(-CH_2-)_R$	9	6.0416	−0.1778	0.8437	−1.5184
14	$(>C<)_R$ (spirocyclane)	1	−56.2158	1.7694	19.0452	13.3885
Total			−1.8414	0.1692	26.6385	−0.2771

Table 3
The functional groups and their contribution constants to liquid viscosity for oxygen- and sulfur-containing organics

Q	Groups[a]	a_i	$b_i \times 10^2$	$c_i \times 10^{-4}$	d_i
21	–OH (primary) ($C \leq 2$)[b]	5.7852	−0.5310	9.5499	−1.0300
22	–OH (primary) ($C > 2$)	1.4351	−1.0010	13.8366	0.3418
23	–OH (secondary)	−2.6895	−0.3645	29.8404	0.4246
24	–OH (tertiary)	−18.5630	2.4275	78.5417	0.9650
25	(–OH)$_{\mathrm{RC}}$	16.7808	0.8509	77.1759	−6.9285
26	–OH (polyhydric)	−0.0125	−0.3634	23.2329	−0.0172
27	(–OH)$_{\mathrm{AC}}$	−2.0856	0.6362	50.0840	−1.0539
28	–OH (alkoxyalcohol)	−2.6991	−0.4377	17.2243	0.7139
29	–O–	−0.7185	0.0985	2.9405	0.1149
30	(–O–)$_{\mathrm{R}}$	−29.8045	−0.2847	−4.3145	8.3131
31	(–O–)$_{\mathrm{AC}}$	−2.3454	0.0872	6.4296	0.5389
32	–CHO	−0.8288	−0.2612	3.7241	0.2386
33	>CO	−2.6622	0.1142	6.7008	0.7348
34	(>CO)$_{\mathrm{R}}$	45.9143	−0.2405	3.8828	−12.4994
35	HCOOH	−2.7291	0.0413	27.4079	0.0002
36	–COOH ($C \leq 6$)	−4.0451	−0.1841	12.6878	1.1139
37	–COOH ($C > 6$)	−0.6721	−0.1693	20.0309	0.0279
38	HCOO–	−3.3731	−0.0113	9.4694	0.6071
39	–COO– ($C \leq 7$)	−0.0635	−0.2162	1.9325	0.4686
40	–COO– ($C > 7$)	−2.5390	0.0006	5.4231	0.8717
41	>CHO–	−5.4872	1.5834	34.5474	−0.4244
42	–(CO)–O–(CO)– (anhydride)	−11.8236	0.0111	7.2831	3.6587
43	–O–(CO)–O– (carbonate)	−8.0314	0.2848	9.3746	2.1486
44	(>NO)$_{\mathrm{R}}$	−16.9531	1.0614	49.1049	2.8583
45	–NO$_2$	−13.0333	0.1801	12.9392	2.8987
46	=CHNO$_2$	−1.9653	0.1322	15.8672	−0.0701
47	(–NO$_2$)$_{\mathrm{AC}}$	−1.2954	0.0427	12.1837	−0.0948
48	–S–	−3.2767	0.0779	4.4123	0.9549
49	–SH (primary)	−2.1030	−0.0965	6.0066	0.3464
50	–SH (secondary)	−0.2481	−0.3285	1.9387	0.1148
51	–SH (tertiary)	−12.3498	1.2621	23.1473	1.3950
52	–CSO– ($C \leq 12$)	−15.2678	0.5248	14.2694	3.7646
53	–CSO– ($C > 12$)	3.7475	−1.2592	−23.9353	0.8329
54	>SO	−32.8607	0.6232	27.5184	7.7525

[a] RC: on the nonaromatic ring; AC: on the aromatic ring; R: in the nonaromatic ring.

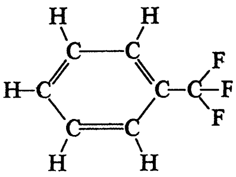
[b] $C \leq 2$: for number of carbon atoms less than 3.

$$\ln \eta = \sum_i N_i \left\{ a_i + b_i(T) + \frac{c_i}{T^2} + d_i \ln P_{\mathrm{c}} \right\}$$
$$= -1.8414 + 0.1692 \times 10^{-2} T + \frac{26.6385 \times 10^4}{T^2} - 0.2771 \ln 33.0$$

At $T = 310.95$ K, $\eta^{\mathrm{expt}} = 1.619$ mPa s, $\eta^{\mathrm{calc}} = 1.601$ mPa s and %error $= [(1.601 - 1.619)/1.619] \times 100 = -1.11$.

2.3.2. Example 2: Estimation of the viscosity of benzotrifluoride

The experimental viscosity is 0.4624 mPa s at 313.15 K [12] and the experimental P_{c} is 35.59 bar [6]. The molecular structure and group information are



Q	Groups	No.	a_i	$b_i \times 10^2$	$c_i \times 10^4$	d_i
5	>C<	1	1.0031	−0.3677	−6.0316	1.1972
15	(=CH–)$_{\mathrm{A}}$	5	−0.8570	−0.0098	2.4376	0.1311
16	(=C<)$_{\mathrm{A}}$	1	0.7896	−0.0231	−0.9222	0.1928
80	(–F)$_3$	1	1.5394	0.8465	17.8121	−2.9915
Total			−0.9529	0.4067	23.0465	−0.9460

Table 4
The functional groups and their contribution constants to liquid viscosity for nitrogen- and halogen-containing organics

Q	Groups[a]	a_i	$b_i \times 10^2$	$c_i \times 10^{-4}$	d_i
55	$\mathrm{-NH_2}$	−1.1345	−0.2126	7.0544	0.1336
56	–NH–	−6.9489	−0.1723	5.7804	1.6467
57	$\mathrm{-N}{<}$	−2.1403	0.4842	6.1893	0.4718
58	$(\mathrm{-NH_2})_{\mathrm{AC}}$	−6.3646	−0.0180	23.2752	1.0653
59	$(\mathrm{-NH-})_{\mathrm{AC}}$	−1.7592	0.2208	14.9707	0.1171
60	$(\mathrm{-N}{<})_{\mathrm{AC}}$	−1.2982	0.5975	14.0415	−0.0031
61	$\mathrm{HCONH_2}$	−1.5435	−0.2774	31.8007	0.0001
62	HCONH–	−8.1097	0.0432	20.9135	1.8795
63	$\mathrm{HCON}{<}$	−122.3280	26.4615	394.1670	0.3530
64	$\mathrm{-CONH_2}$	−6.7363	0.1316	45.5193	1.2172
65	–CONH–	8.9977	1.5664	60.8742	−4.6399
66	$\mathrm{-COONH_2}$	17.8400	−4.5188	−62.0987	1.2353
67	–COONH–	−10.1316	0.6712	37.9465	1.9199
68	$({>}\mathrm{NH})_{\mathrm{R}}$	−0.1589	0.1910	12.0578	−0.0276
69	$(\mathrm{=N-})_{\mathrm{R}}$	−4.7601	0.1120	6.98437	0.9719
70	–C≡N	−2.7194	−0.1324	7.7955	0.6293
71	$(\mathrm{-C{\equiv}N})_{\mathrm{AC}}$	0.9435	−0.0086	8.6310	−0.6443
72	–Cl (primary)	−1.7997	−0.3851	3.0118	0.5524
73	=CHCl	1.5851	−0.1934	3.7798	−0.4748
74	$(\mathrm{-Cl})_2$[b]	−3.0561	−1.0770	0.1882	1.2223
75	$(\mathrm{-Cl})_3$	−1.3357	−0.3220	8.8683	0.1702
76	$(\mathrm{-Cl})_4$	4.2070	−0.4130	13.3194	−1.1972
77	$(\mathrm{-Cl})_{\mathrm{AC}}$	−0.3083	−0.0623	4.1382	−0.2644
78	–F (primary)	−9.4982	0.2607	11.3406	1.8461
79	$(\mathrm{-F})_2$	−10.3980	−1.1189	1.3134	2.6681
80	$(\mathrm{-F})_3$	1.5394	0.8465	17.8121	−2.9915
81	$(\mathrm{-F})_{\mathrm{AC}}$	0.4079	−0.2352	−0.1505	−0.2893
82	(–F)(–Cl)[c]	−0.8565	−0.3682	4.6451	−0.0751
83	$(\mathrm{-F})(\mathrm{-Cl})_2$	−3.4552	−0.5629	3.6831	0.3613
84	$(\mathrm{-F})_2(\mathrm{-Cl})$	54.2824	0.0109	5.9474	−14.5771
85	$(\mathrm{-F})_2(\mathrm{-Cl})_2$	−2.1710	0.1403	10.3743	−1.1972
86	–Br (primary)	−0.7586	−0.6623	−2.4228	0.7385
87	–Br (secondary)	−279.0030	−0.3420	1.4253	73.6293
88	$(\mathrm{-Br})_{\mathrm{AC}}$	−8.1919	−0.1635	3.0150	0.0621
89	–I (primary)	−1.4672	−0.2787	4.3362	0.5635
90	$(\mathrm{-I})_{\mathrm{AC}}$	70.9918	−0.0245	7.2061	−18.9106
91	–(CO)–Cl	−2.3300	−0.0470	8.2815	0.4485

[a] AC: on the aromatic ring; R: in the nonaromatic ring.

[b] $(\mathrm{-Cl})_n$: groups with n chlorine atoms attached to the same carbon atom (e.g. one $(\mathrm{-Cl})_3$ group for $\mathrm{CHCl_3}$).

[c] $(\mathrm{-F})_n(\mathrm{-Cl})_m$: group with n fluorine atoms and m chlorine atoms attached to the same carbon atom (e.g. one $(\mathrm{-F})_2(\mathrm{-Cl})_2$ group for $\mathrm{CF_2Cl_2}$).

$$\begin{aligned}\ln \eta &= \sum_i N_i \left\{a_i + b_i(T) + \frac{c_i}{T^2} + d_i \ln P_{\mathrm{c}}\right\}\\ &= -0.9529 + 0.4067 \times 10^{-2}T + \frac{23.0465 \times 10^4}{T^2}\\ &\quad -0.9460 \ln 35.59\end{aligned}$$

At $T = 313.15\,\mathrm{K}$, $\eta^{\mathrm{expt}} = 0.4624\,\mathrm{mPa\,s}$, $\eta^{\mathrm{calc}} = 0.4925\,\mathrm{mPa\,s}$ and $\%\mathrm{error} = [(0.4925 - 0.4624)/0.4624] \times 100 = 6.51$.

3. Results and discussion

Based on the 482 organic compounds with 4627 experimental data points, the proposed method has been examined for the estimation of the viscosity of organic liquids by using the group constants in Tables 2–4. Table 2 lists the molecular groups for carbon–carbon bonds and carbon–hydrogen bonds, which form the basic structure of organics. The functional groups for oxygen-, sulfur-, nitrogen-, and halogen-containing organics are included in Tables 3 and 4. Table 5 shows the detailed analysis, including compound series, number of data points, average absolute deviation (ε), standard deviation (σ), average absolute percentage deviation (AAD%), the temperature range and the viscosity range of application. As can be seen from Table 5, the proposed method gave an ε of 0.08 mPa s, an σ of 0.18 mPa s, and an AAD% of 4.14. Larger deviations were observed for aromatics (6.45%), alcohols (6.43%), and ketones (5.33%) in this method.

Comparison of this method with the methods of van Velzen et al. [2], Orrick and Erbar [3], and Przezdziecki and Sridhar [4] in the estimation of liquid viscosities for 35 organic compounds with 117 data points was shown in

Table 5
Average deviation in the estimation of the viscosities of organic liquids

Compound series	Data points (compounds)	ε (mPa s)	σ (mPa s)	AAD%	Temperature range (K)	Viscosity range (mPa s)
Alkane	414 (35)	0.04	0.10	3.37	85.5–573	0.07–11.1
Alkene	191 (17)	0.03	0.08	4.26	88.0–413	0.07–15.3
Alkyne	59 (7)	0.03	0.10	3.09	163–443	0.20–6.76
Cyclane	171 (17)	0.07	0.16	2.57	243–453	0.31–15.8
Aromatics	334 (31)	0.11	0.29	6.45	273–513	0.12–112.
Alcohol	587 (52)	0.33	0.66	6.43	173–513	0.43–96.0
Ether	199 (21)	0.04	0.20	4.64	163–518	0.20–4.25
Aldehyde	52 (5)	0.07	0.08	1.17	273–423	0.25–0.91
Ketone	229 (22)	0.04	0.08	5.33	153–518	0.14–7.58
Acid	159 (18)	0.16	0.29	4.10	293–433	0.82–10.9
Ester	349 (46)	0.06	0.13	3.74	183–373	0.23–4.07
Nitrogen-containing	757 (94)	0.03	0.07	2.96	203–473	0.14–17.0
Halogen-containing	914 (81)	0.03	0.06	3.43	208–463	0.20–3.68
Sulfur-containing	212 (36)	0.06	0.10	3.29	278–495	0.26–10.8
Overall	4627 (482)	0.08	0.18	4.14	85.5–676	0.07–112

Table 6
Comparison of this method with other three methods for estimating liquid viscosities[a]

Compound	T (K)	η (cP) (experimental)	d%			
			This work	[3]	[2]	[4]
Acetone	183	2.075	1.7	−25	−20	−11
	213	0.892	7.2	−6.7	−0.1	−4.6
	273	0.389	2.5	−8.3	0.1	−2.3
	303	0.292	5.0	−9.4	−0.2	−1.2
	333	0.226	5.2	−8.3	1.6	0.2
Acetic acid	283	1.450	7.0	−22	−34	8.6
	213	0.901	3.9	−15	−28	0
	353	0.561	1.8	−9.5	−24	−1.3
	383	0.416	0.4	−5.3	−21	0.3
Aniline	263	13.40	9.3	–[b]	−52	–
	293	4.380	2.3	–	−23	–
	333	1.520	15	–	−2.8	−49
	393	0.658	4.2	–	−11	−33
Benzene	278	0.826	−15	−45	−42	1.1
	313	0.492	6.3	−35	−30	7.3
	353	0.318	3.0	−26	−20	12
	393	0.219	16	−46	−8.5	18
n-Butane	183	0.630	−1.5	−14	−7.2	−9.0
	213	0.403	4.6	−20	−9.8	−8.9
	273	0.210	4.7	−23	8.8	−5.8
1-Butene	163	0.790	−2.2	−22	−6.1	−13
	193	0.450	6.4	−20	0	−9.6
	233	0.260	7.9	−18	8.7	−3.3
n-Butyl alcohol	273	5.140	−8.1	−2.1	5.6	–
	313	1.770	−5.1	−1.6	0	–
	353	0.762	0.7	0.5	−2.3	–
	393	0.394	12	−1.4	−5.3	–
Carbon tetrachloride	273	1.369	−0.9	20	−10	−24
	303	0.856	−0.2	22	−6.1	−15
	343	0.534	0.2	20	−4.3	−6.7
	373	0.404	0.6	19	−4.0	−2.8

Table 6 (*Continued*)

Compound	T (K)	η (cP) (experimental)	d%			
			This work	[3]	[2]	[4]
Chlorobenzene	273	1.054	−7.5	1.4	15	−8.3
	313	0.639	−1.9	−0.6	7.0	−7.0
	353	0.441	−1.6	−0.9	0.2	−5.2
	393	0.326	−4.3	−5.1	−5.0	−3.8
Chloroform	273	0.700	−0.8	40	11	−11
	303	0.502	0.4	34	7.0	−8.9
	333	0.390	0.6	27	2.1	−7.9
Cyclohexane	278	1.300	8.5	−51	−51	−38
	333	0.528	−2.7	−38	−27	−22
Cyclopentane	293	0.439	−0.1	−32	−32	−33
	323	0.323	4.5	−28	−26	−29
2,2-Dimethylpropane	258	0.431	8.2	−3.5	7.2	20
	283	0.281	−9.2	−0.8	20	30
Ethane	98	0.985	13	30	2.6	−24
	153	0.257	−1.7	−12	8.2	−14
	188	0.162	−9.7	−22	12	−13
Ethylene chloride	273	1.123	−11	−43	−4.0	–
	313	0.644	−8.7	−35	−4.0	–
	353	0.417	−0.1	−27	−3.5	–
Ethyl alcohol	273	1.770	4.7	27	69	–
	311	0.826	−6.5	3.5	38	–
	348	0.465	−12	−5.4	27	–
Ethyl acetate	293	0.458	6.8	−4.2	3.1	−16
	353	0.246	3.6	0.4	7.2	−5.3
	413	0.153	7.6	7.4	14	−1.8
	463	0.100	5.4	27	34	−4.8
Ethylbenzene	253	1.240	−22	−2.9	−3.8	−33
	313	0.535	−14	−1.2	−3.3	−23
	373	0.308	−10	−1.7	−4.7	−16
	413	0.231	−8.7	−1.2	−4.6	−13
Ethyl bromide	293	0.395	−4.8	27	2.9	−23
	333	0.269	−6.5	32	10	−17
	373	0.199	−3.6	36	16	−16
Ethylene	103	0.700	−5.8	−25	4.0	−25
	133	0.310	3.2	−27	40	−17
	173	0.150	−2.6	−22	–	−6.4
Ethyl ether	273	0.289	0.1	0	−4.7	0
	293	0.236	0.1	0	−3.9	2.2
	333	0.167	−0.7	2.0	−1.2	4.0
	373	0.118	−7.7	11	8.8	7.4
Ethyl formate	273	0.570	−5.4	−18	−3.3	−16
	303	0.362	3.2	−17	−1.8	−11
	328	0.288	1.3	−16	−1.2	−9.6
n-Heptane	183	3.77	−13	−21	−18	−1.7
	233	0.965	−1.7	−0.5	−0.8	−27
	293	0.418	0.4	−1.9	−1.8	−21
	373	0.209	4.3	−3.3	−4.4	−17
n-Hexane	213	0.888	−7.4	2.9	4.2	−8.3
	273	0.380	−3.1	−2.4	−0.9	−8.2
	343	0.205	2.2	−4.9	−3.8	−7.1

Table 6 (*Continued*)

Compound	T (K)	η (cP) (experimental)	d%			
			This work	[3]	[2]	[4]
Isobutane	193	0.628	−5.8	−23	−3.5	−37
	233	0.343	3.5	−25	−6.4	−29
	263	0.239	3.5	−24	−5.4	−23
Isopropyl alcohol	283	3.319	−2.4	−24	−2.8	–
	303	1.811	2.9	−15	−3.4	–
	323	1.062	1.8	−10	−3.6	–
Methane	88	0.226	2.6	60	–	−11
	113	0.115	6.2	23	–	−43
2-Methylbutane	223	0.550	−4.2	−13	−4.0	−30
	253	0.353	−2.5	−12	−2.7	−21
	303	0.205	−2.8	−10	−1.1	−12
n-Pentane	153	2.350	−13	−1.0	−1.7	11
	193	0.791	−12	3.8	5.5	−7.0
	233	0.428	−5.8	−3.3	0.6	−6.0
	273	0.279	−1.2	−8.2	−3.6	−4.7
	303	0.216	1.5	−11	−5.2	−4.9
Phenol	323	3.020	−18	0	22	−50
	373	0.783	−38	37	11	−5.4
Propane	133	0.984	3.3	−1.5	−8.4	−23
	193	0.327	7.9	−22	−12	−19
	233	0.205	4.9	−25	−9.7	−16
n-Propyl alcohol	283	2.897	−7.7	−9.1	4.1	–
	313	1.400	−3.7	−9.8	1.4	–
	373	0.443	7.3	−6.5	2.0	–
Toluene	253	1.070	3.9	−19	−19	−33
	293	0.587	−1.4	−13	−29	−24
	333	0.380	−0.6	−10	−8.7	−16
	383	0.249	3.9	−6.8	−4.6	−10
o-Xylene	273	1.108	8.9	3.1	−9.7	−5.5
	313	0.625	4.6	5.0	−13	−4.8
	373	0.345	7.2	3.7	−1.1	−0.3
	413	0.254	11	3.6	−21	1.9
m-Xylene	273	0.808	−21	1.1	9.9	1.9
	313	0.492	−18	1.4	3.9	1.8
	353	0.340	−11	0.3	−1.9	2.9
	413	0.218	−0.6	1.4	−5.8	4.6

[a] Experimental and calculated data of the three methods compared were obtained from Tables 9–11 of [1].

[b] Not available.

Table 6 . The experimental data of these 1117 data points and the calculated results for the three methods compared were obtained from Reid et al. [1]. Of these methods, the proposed method gave the estimation with 5.9% in average deviation, followed by the method of van Velzen et al. (11.0%), the method of Przezdziecki and Sridhar (14.4%), and the method of Orrick and Erbar (14.9%). In calculating liquid viscosity, the Orrick and Erbar method needs one liquid density and the method of van Velzen et al. requires a complicated analysis of the molecular structure. While the Przezdziecki and Sridhar method must have values of critical temperature, critical pressure, critical volume, melting point, acentric factor, volume at melting point in addition to the volume at the temperature of interest.

The proposed method requires the value of P_c and the knowledge of molecular structure. If the experimental P_c of a compound is not available, the calculated P_c from the group-contribution method proposed by Joback and Reid [8] can be used. The present method should not be expected to be accurate: (i) for the temperatures with $T_r > 0.75$ or pressures above 1 bar; (ii) for the compounds with highly branched structures or multifunctional groups.

4. Conclusions

Six relations with two, three, and four constants have been studied for the correlation of viscosity of organic liquids. A three-constant relation that can adequately express the temperature dependence of the viscosity is used with an additional term of critical pressure to develop the proposed group-contribution method. The proposed group-contribution method, which is a generalization of classical group-contribution concept, is fairly easy to be used. The proposed method can calculate the viscosities of 482 organic liquids with an average deviation of 4.14%. Based on a sample of 35 compounds, the proposed method has a smaller average error than those of van Velzen et al. [2], Orrick and Erbar [3], and Przezdziecki and Sridhar [4]. The proposed method based on molecular structure requires only the critical pressure for each compound and can be applied reliably to the estimation of the viscosity of organic liquids up to 112 mPa s at temperature $T_r < 0.75$ and atmospheric pressure.

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