Journal of the Indian Institute of Science
Vol. 53, No. 2, April 1971

A NEW CORRELATION TO PREDICT CRITICAL VOLUME

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[Received: October 27, 1970]

ABSTRACT

A new correlation employing parachor as the only input datum for predicting critical volume has been developed and tested. In the case of 159 organic compounds the average absolute deviation is 1.31 %.

A knowledge of critical constants of substances is essential for the use of various generalized correlations for liquids and gases The experimental determination of these constants is not simple and for this reason any method for predicting the constants should be of great value. Among the many available correlations, the method due to Lydersen[4] predicts the critical volume with an average error of 2 3% and that due to Das *et al*[1] predicts with an average error of 1.7% according to the authors themselves. The former method employs additive group technique, originally suggested by Schuster[6] and the latter method employs molecular weight as the input datum. Critical volume can also be estimated by critical compressibility method In this method the values of Z_c, T_c and P_c must be either known or estimated. This method predicts critical volume with an average error of 3.6%.

The proposed method employs parachor as the input datum. Parachor can be estimated by group contribution technique employing the values listed by Reid and Sherwood[5]. The present correlation employs the following expressions for predicting critical volume.

$$V_c = 1.4\,[P] + C \qquad [1]$$

1. HOW THIS CORRELATION WAS DEVELOPED

Approximate relation to predict hard sphere volume, from critical volume for spherical non-polar molecules obeying the Lennard-Jones (6-12) potential is

$$b_0 = 0.75\ V_c \qquad [2]$$

The hard sphere volume is also related to the intermolecular distance by the following expression

$$b_0 = 1.2615\ \sigma^3 \qquad [3]$$

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[*] Deceased.

From Equations [2] and [3] we have

$$V_c = \frac{1.2615}{0.75} \sigma^3 \qquad [4]$$

According to cell-theory, the collision diameter is related parachor (3) as,

$$[P] = 7.1 \times 10^{23} \epsilon^{0.25} \sigma^{5/2} \qquad [5]$$

Since a gm. mole contains 6.023×10^{23} molecules, we have

$$[P] = \frac{7.1 \times 10^{23} \epsilon^{0.25}}{6.023 \times 10^{23}} \sigma^{5/2}$$

$$= 1.1788 \epsilon^{0.25} \sigma^{5/2} \qquad [6]$$

From Equation [6] we have

$$\sigma^3 = \frac{[P]^{1.2}}{1.217 \epsilon^{0.3}} \qquad [7]$$

From Equations [4] and [7], we have

$$V_c = 1.382 \frac{[P]^{1.2}}{\epsilon^{0.3}} \qquad [8]$$

Equation [8], shows the critical volume, is directly related to parachor.

A linear relation is obtained when critical volume was plotted against parachor, for different homologous series. The slopes fot all the lines was found to be 1.4 which is in close agreement with the value 1.38 of Equation [8]. The intercepts for different homologous series are given in Table 4.

As the slope is constant for different homologous series, one experimental data is sufficient to calculate the constant C in Equation [1], for a particular series.

Group contribution method:

Based on the data obtained above a group contribution technique has been developed. The Equation [1] can be written as

$$V_c = A + C \qquad [9]$$

A and C are calculated by employing the values in Table 2.

Example : Benzene

A is calculated as follows :

6 Carbon atoms $= 6 \times 12.6 = 75.6$
6 Hydrogen atoms $= 6 \times 21.7 = 130.2$
3 Double bonds $= 3 \times 26.74 = 80.22$
6 membered ring closure $= 1.12$

287.14

C is calculated as follows :

$C_6H_6 = (CH_3)_6 - 12H + 3$ double bonds + ring closure
6 CH_3 groups $= 6 \times -8 = -48$
12 Hydrogen atoms $= 0 \times 12 = 0.0$
3 Double bonds $= 3 \times 11 = +33.0$
6 membered closure $= -15$
$V_c = A + C$ -30

Substituting the values of *A* and *C*, we have

$V_c = 257.14$ c.c./g. mole, whereas the experimental value is 260.33 c.c./g. mole,

Table 1 groups all the 159 compounds considered and shows the critical volume obtained from literature (2.5) and compares with the calculated values. Table 2 gives different atomic contributions and group contributions to evaluate constants *A* and *C* respectively. The values given in Table 2 to evaluate constant C, are applicable only to first member of each homologous series. The constant *C* is evaluated for the first member of homologous series and it remains the same for that series. In calculation of V_c it is only the value of *A* that changes from member to member in homologous series. Table 3 compares the present method with Lydersen and Das *et al* methods. The methods due to Lydersen[4] and Das *et al.*[1] are claimed by authors to give an average error of 2.3 and 1.7% respectively. A comparison made in the present study considering the same number of compounds for which experimental data is available, however, gives average errors as shown in Table 3. From the table it is seen that the error involved in the present method is of the same order as Lydersen's method and the present method is better than Das *et al* method. However, in the case of the 159 substances considered the present method gives an average absolute error of 1.31%.

TABLE I

Experimental and calculated values of critical volume

	V_c, c.c./g mole		% Error
	Exptl.	Calcd.	
1 *Paraffins*			
Methane	99.5	84.4	−15.20*
Ethane	148.0	147.4	−0.40
Propane	200.0	203.4	1.70
n-Butane	255.0	259.4	1.72
n-Pentane	311.0	315.4	1.41
2-Methyl butane	308.0	311.2	1.03
Neopentane	303.0	311.2	2.70
n-Hexane	368.0	371.4	0.92
2-Methyl pentane	367.0	367.2	0.05
3-Methyl pentane	367.0	367.2	0.05
2,2-Dimethyl butane	359.0	363.0	1.11
2,3-Dimethyl butane	358.0	363.0	1.39
n-Heptane	426.0	427.4	0.32
2-Methyl hexane	428.0	423.2	−1.21
3-Methyl hexane	418.0	423.2	1.24
3-Ethyl pentane	416.0	423.2	1.73
2,4-Dimethyl pentane	420.0	419.0	−0.23
n-Octane	486.0	483.4	0.58
3-Methyl heptane	478.0	479.2	0.25
4-Metyl heptane	476.0	479.2	0.73
2,2-Dimetyl hexane	466.0	475.0	2.36
2,5-Dimethyl hexane	478.0	475.0	−0.62
n-Nonane	543.0	539.5	−0.64
n-Decane	602.0	595.5	−1.09
n-Undecane	660.0	651.4	−1.45
n-Dodecane	718.0	712.44	−0.77
n-Tridecane	780.0	768.86	−1.42
n-Tetradecane	830.0	825.28	−0.56
n-Pentadecane	890.0	881.7	−0.93

TABLE I – (*contd.*)

Experimental and calculated values of critical volume.

		V_c c.c./g. mole		
		Exptl.	Calcd.	% Error
	n-Hexadecane	950.0	938.1	−1.25
	n-Heptadecane	1000.0	994.6	0.54
	n-Octadecane	1100.0	1050.9	4.45
	n-Nonadecane	1100.0	1107.38	0.67
	n-Eicosane	1200.0	1171.8	2.35
			Average:	1.14
2.	*Mono-Olefins*			
	Ethene	133.5	133.7	0.17
	Propene	181.0	189.7	4.82
	n-Butene	241.0	245.7	1.95
	n-Pentene	309.2^c	301.7	−2.41
	n-Hexene	365.4^c	357.7	−2.09
	n-Heptene	416.9^c	413.7	−0.77
	n-Octene	468.2^c	469.7	0.32
	n-Nonene	504.9^c	515.7	2.16
	n-Decene	576.4^c	581.7	0.91
			Average:	1.73
3.	*Alkynes*			
	Acetylene	113.0	110.4	−2.26
	Propyne	167.0^d	166.4	−0.33
	Ethyl acetylene	222.0^d	222.4	0.19
	Dimethyl acetylene	222.0^d	222.4	0.19
	Propyl acetylene	277.0^d	278.4	0.51
			Average	0.69
4.	*Cyclopentanes*			
	Cyclopentane	259.4	259.0	0.19
	Methyl cyclopentane	318.9	315.0	−1.05
	Ethyl cyclopentane	374.7	371.0	−1.01
	n-Propyl cyclopentane	417.4^c	427.2	2.34
	n-Butyl cyclopentane	467.1^c	483.2	3.44
			Average	1.60

TABLE I—(*contd.*)

Experimental and calculated values of critical volume.

	V_c c.c./g. mole		% Error
	Exptl.	Calcd.	
5. *Cyclohexanes*			
Cyclohexane	309.6	319.1	3.06
n-Propyl cyclohexane	481.3[c]	487.1	1.20
n-Butyl cyclohexane	541.4[c]	543.1	0.31
n-Pentyl cyclohexane	600.63[c]	599.1	−0.25
n-Hexyl cyclohexane	659.7[c]	655.1	−0.70
n-Heptyl cyclohexane	720.2[c]	716.5	−0.54
n-Octyl cyclohexane	779.9[c]	783.5	0.89
n-Nonyl cyclohexane	839.4[c]	829.4	−1.19
		Average	1.01
6. *Alcohols*			
Methyl alcohol	118.0	109.4	6.42*
Ethyl alcohol	167.0	165.4	−0.94
n-Propyl alcohol	218.2	221.4	1.47
Iso-propyl alcohol	220.4	217.2	1.53
Allyl alcohol	203.0[d]	204.6	0.79
n-Butyl alcohol	274.6	277.4	1.03
Isobutyl alcohol	272.2	273.2	0.37
Amyl alcohol	333.0[d]	333.4	0.12
n-Heptyl alcohol	443.0[d]	445.4	0.54
n-Octyl alcohol	498.0[d]	501.4	0.68
2-Octyl alcohol	494.0[d]	497.2	0.65
		Average	0.81
7. *Ketones*			
Acetone	211.0	210.9	0.0
Ethyl methyl ketone	267.0	263.7	−1.22
Diethyl ketone	336.0	317.6	−5.47
Methyl n-propyl ketone	302.0	317.6	−5.17
Methyl iso-propyl ketone	310.0	313.4	1.10
Methyl iso-butyl ketone	371.0[d]	367.7	−0.87
		Average	2.30

TABLE 1 – (*contd.*)

Experimental and calculated values of critical volume.

	V_c c.c./g. mole Exptl.	V_c c.c./g. mole Calcd.	% Error
8. *Acids*			
Acetic acid	171.0	171.6	0.36
Propionic acid	230.0	227.6	−1.03
n-Butyric acid	290 0	283.6	−2.20
Iso-butric acid	292.0	279.4	−4.30
n-Valeric acid	340.0[d]	339.6	−0.11
Iso-valeric acid	336.0[d]	335.4	0 17
		Average	1.36
9 *Ethers*			
Dimethyl ether	178.0	165.1	−9.95*
Ethyl methyl ether	221.0	221.1	0.05
Diethyl ether	274.0	277.1	1.13
Ethyl propyl ether	339.0	333.1	—1.73
Iso-propyl ether	382 0[d]	384.9	0.76
Vinyl ethyl ether	260.0[d]	260.4	0.17
		Average	0.76
10. *Esters*			
Methyl formate	172.0	170.7	−0 76
Ethyl formate	229.0	226.6	−1.05
Propyl formate	225.0	283.0	−0.93
Amyl formate	381.0[d]	395 0	3.68
Iso-amyl formate	391.0[d]	390.0	−0 33
Methyl acetate	228 0	226.6	−0 62
Ethyl acetate	286 0	283.0	−1 05
n-Propyl acetate	345.0	339.0	– 1.80
n-Butyl acetate	395 0	395.0	0.00
Iso-amyl acetate	446.0[d]	446.5	0.11
Methyl propionate	282 0	283 0	0 36
Ethyl propionate	345.0	338 8	−1.80

TABLE I – (*contd.*)

Experimental and calculated values of critical volume.

	V_c c.c /g. mole		% Error
	Exptl.	Calcd.	
Propyl propionate	395.0^d	395.0	0.00
Iso-butyl propionate	446.0^d	446.5	0.11
Iso-amyl propionate	501.0^d	502.0	0.20
Methyl butyrate	340.0	338.6	–0.35
n-Propyl butyrate	450.0^d	450.5	0.11
Iso-butyl butyrate	501.0^d	502.0	0.20
Iso-amyl n-butyrate	556.0^d	558.0	0.36
Methyl iso-butyrate	339.0	334.0	–1.48
n-Propyl iso-butyrate	446.0^d	446.5	0.11
Iso-butyl iso-butyrate	497.0^d	498.0	0.21
Ethyl iso-valerate	446.0^d	446.5	0.11
n-Propyl iso-valerate	501.0^d	502.0	0.20
Iso-butyl iso-valerate	552.0^d	555.0	0.55
Ethyl n-caprylate	615.0^d	618.0	0.49
		Average	0.65
II. *Halogenated Hydrocarbons*			
Methyl chloride	143.0	144.9	1.38
Methyl bromide	165.0^d	162.9	–1.27
Methyl iodide	190.0^d	194.1	2.16
Methylene Chloride	193.0^d	200.5	3.97
Fluoroform	145.0^d	147.9	2.01
Carbon tetrafluoride	153.0^d	148.7	2.80
Ethyl fluoride	168.0^d	160.2	4.61
Ethyl chloride	199.0	200.9	0.95
Ethyl bromide	215.0	218.9	1.81
Propyl chloride	254.0	256.9	1.17
Dibromo ethane	235.0	236.4	0.59
1,1-Dichloro ethane	244.0^d	256.6	5.14
Allyl chloride	234.0^d	240.3	2.70
Bromo-trifluoromethane	205.0^d	207.4	1.18
Dichloro-difluoromethane	218.0	230.2	5.61
		Average	2.42

TABLE 1 – (*contd.*)

Experimental and calculated values of critical volume.

	V_c c.c./g. mole		% Error
	Exptl.	Calcd.	
12. *Halobenzenes*			
Chlorebenzene	308.0	307.6	–0.12
Bromobenzene	324.0	325.5	0.46
Fluorobenzene	271.0	266.8	–1.52
Iodobenzene	351.0	357.8	1.95
Dichlorobenzene	360.0	363.2	0.88
		Average	0.98
13. *Aromatics*			
Benzene	260.3	257.1	–1.22
Toluene	319.9^c	313.1	–2.14
Ethyl benzene	366.0	369.1	0.85
n-Propyl benzene	439.8	425.1	–3.36
n-Butyl benzene	498.0	481.1	–3.37
n-Pentyl benxene	521.5^c	537.1	3.00
n-Hexyl benzene	582.5^c	593.1	1.83
n-Heptyl benzene	642.9^c	649.1	0.97
n-Octyl benzene	702.0^c	705.1	0.43
n-Nonyl benzene	759.4^c	765.7	0.76
n-Undecyl benzene	878.0^c	878.0	0.00
n-Dodecyl benzene	935.8^c	935.4	–0.04
n-Tridecyl benzene	994.9^c	991.8	–0.30
n-Tetradecyl benzene	1052.4^c	1048.2	–0.35
n-Pentadecyl benzene	1109.6^c	1104.7	–0.44
n-Hexadecyl benzene	1168.0^c	1161.1	–0.60
		Average	1.22
14. *Sulphur Compounds*			
Methyl mercaptan	149.0	148.1	0.57
Ethyl mercaptan	207.0	204.1	1.38
Dimethyl sulfide	201.0	204.1	1.56
Methyl ethyl sulfide	260.0	260.1	0.00
Diethyl isulfide	323.0	316.1	2.12
Diethyl disulfide	370.0^d	384.8	4.02
Allyl sulfide	385.0^d	394.8	2.55
		Average	1.74

$$\% \text{ Error} = \frac{\text{Exptl.} - \text{Calcd.}}{\text{Exptl.}} \times 100$$

c – Dreisbach (2)
d – Lydersen's (4)
* – Values not used to find average errors.

TABLE 2

Group contribution to evaluate constants in Equation 9

Atomic contribution to evaluate C		Group contribution to evaluate C	
CH_2 in $(CH_2)_n$			
$n \leq 12$	56 00	Base group CH_3	−8
$n > 12$	56.42	Addition or subtraction of H	0
C	12.60		
H	21.70	Double bond	11
H in OH	14.00	Triple bond	1
O	27.72	OH group in alcohols	−12
O_2 in esters	76.12	CO group in ketones	0
N	24.50	COOH group in acids	−15
S	68.74	O in ethers	−2
P	56.70	COO group in esters	−10
F	36.54	Halogen addition replacing H in aliphatic compounds	−2
Cl	77.28		
Br	95.20	Addition of S	−12
I	126.42	Halogen addition replacing H in aromatic compounds	−4
Double bond	26.74		
Triple bond	56 84		
Carbonyl bond in Ketones:		Aromatic ring closure	−15
Total number of Carbon atoms:		Aliphatic ring closure (5 membered)	15
		Aliphatic ring closure (6 membered)	30
3	31.22		
4	28 00		
5	25 90		
6	24 22		
7	24 22		
8	21.14		
9	19.74		
10	18.20		
Ring closure:			
3 membered ring	17.50		
4 membered ring	8 40		
5 membered ring	4.20		
6 membered ring	1.12		
7 membered ring	5 60		
Chain branching per branch	−4.2		

TABLE 3

Values of constant in Equation 1 and comparison of present method with other methods.

Sl. No.	Series	Number considered	Constant C	% average error	Number of compounds compared	% Average Error in V_c calculated by the method due to		
						Authors	Lydersen	Das *et al.*
1.	Paraffins	34	−8	1.14	33	1.14	1.68	1.0 (19)
2.	Mono-olefins	9	−5	1.73	3	2.31	3.5 (2)	4.2
3.	Alkynes	5	−15	0.69	1	2.26	0.9	...
4.	Cyclopentanes	5	−25	1.60	3	0.75	0.43	1.96
5.	Cyclohexanes	8	−18	1.01	1	3.06	0.3	2.90
6.	Alcohols	11	−10	0.81	3	1.31	0.67	2.10
7.	Ketones	6	−16	2.30	6	2.30	4.4 (2)	3.20
8.	Acids	6	−15	1.36	4	1.97	1.95	0.75
9.	Ethers	6	−18	0.76	4	0.76	1.97	2.37
10.	Esters	26	−18	0.65	9	0.91	0.93	0.75
11.	Halogenated hydrocarbons	15	−10	2.42	2	1.58	1.50	----
12.	Halobenzenes	5	−34	0.98	4	1.01	1.80	...
13.	Aromatics	16	−30	1.22	5	2.24	1.64	6.48
14.	Sulphur compounds	7	−20	1.74	5	1.32	1.20	......
		159	Av Abs. deviation	1.31	83	1.63	1.63	2.57

The number in bracket indicates the number of compounds considered if different from present comparison.

NOMENCLATURE

A = Constant in Equation [9].

bo = Hard sphere volume, c.c./g. mole.

C = Constant in Equation [1].

$[P]$ = Parachor.

V_c = Critical volume, c.c./g. mole.

σ = Intermolecular distance, Å.

ϵ = Minimum potential energy, ergs.

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