A NEW CORRELATION TO PREDICT CRITICAL TEMPERATURE

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Abstract

A new correlation employing parachor and molar refraction as input data for predicting critical temperature has been developed and tested. In the case of 135 organic compounds the average absolute deviation is 0.93%. The method has been extended to multicomponent mixtures and the method predicts data on 17 binary systems with an average absolute deviation of 0.69% and three ternary, two quaternary and two quinary systems with an average error of 0.88%.

Information on critical temperature is essential in the use of number of important approximate methods for predicting, pressure-volume temperature relations for liquids and gases, heats of vaporization, surface tension, etc. Methods of predicting critical temperature are given elsewhere[1,2]. Among the many availabe correlations, the methods due to Lydersen[3], Eduljee quoted by Gambill[4] and Forman-Thodos[5] predict the critical temperatures with an average error of less than 2%. The former two methods employ normal boiling temperatures and group contribution constants. Forman-Thodos method does not require normal boiling temperatures, but uses a relationship between van der Waals' constants and structure, and the group contribution technique.

The proposed method employs parachor and molar refraction as the input data. These values can be computed from atomic and structural values[2]. These two properties are extensive and constitutive. They are xtensive because they depend upon the number and type of atoms present in he compound, and are constitutive in that they depend at least to some extent n arrangement of the atoms.

Lewis[7] was the first to propose relations involving the parachor and the oiling temperature, while Wan[16] introduced relation involving the molar efraction. Later Herzog[6], Meissner[8], and Pilcher and Ward[17] have improved hese relations. But none of these relations have wide applicability because f their limited use. The present correlation employs the following xpression for predicting critical temperature

$$T_c\,[P] = A\,R_D^{1.5} + B \qquad [1]$$

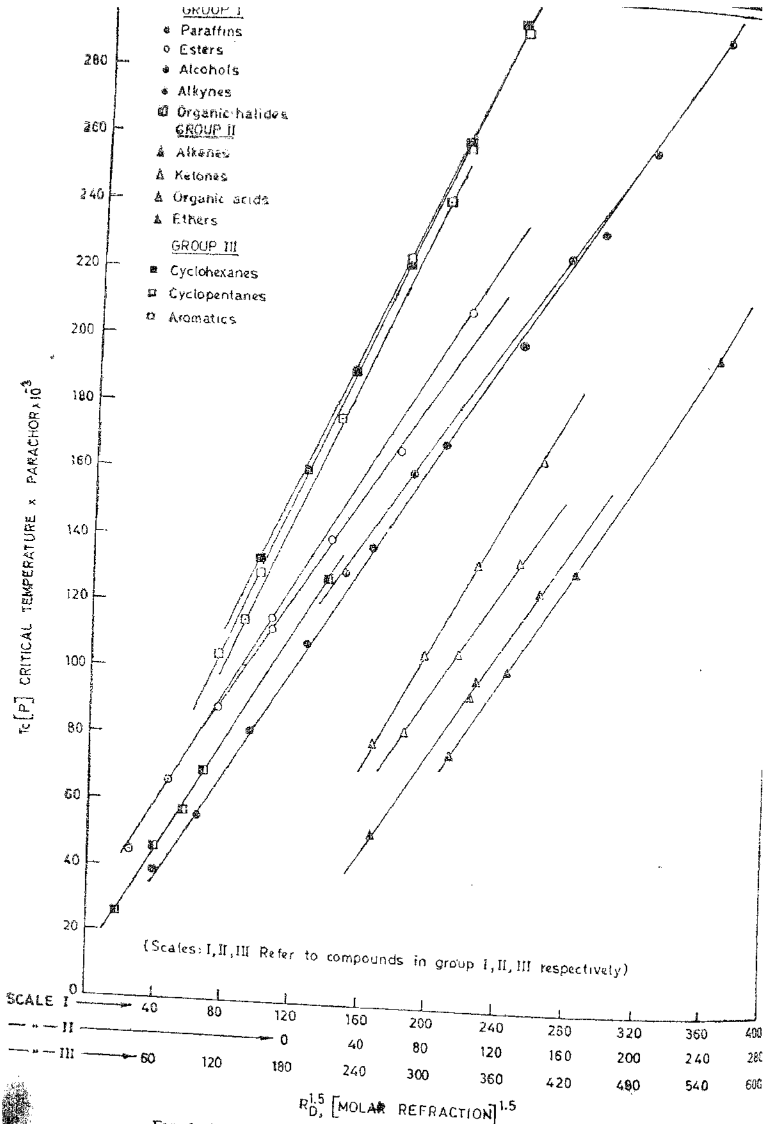

FIG. 1 Molar Refraction-Parachor-Critical Temperature Correlation

A linear relation was obtained when the product of critical temperature and parachor, was plotted against molar refraction raised to the power of 1.5, for different homologous series. In the case of paraffins a distinct break in the slope of the straight line was observed for compounds containing more than 10 carbon atoms. Hence for this group two different sets of equations are obtained. Figure 1 shows Equation [1] in graphical form. It can be seen from the figure that there is an excellent agreement between $T_c\,[P]$ and $R_D^{1.5}$.

Table 1 groups all the 135 compounds considered and shows the critical temperatures obtained from literature[2, 3] and compares with the calculated values. It can be seen from this table that the accuracy of the method is good for all compounds except methane, ethylene, ethyne, propyne, nonyl cyclopentane and methyl alcohol. These compounds are not included in calculating average deviations of the corresponding homologous series.

Table 2 gives values of the constants A and B, in the critical temperature equation, for different homologous series. Table 2 also compares the present method with other methods. The accuracy of the present method is the same as Eduljee's method and the present method is superior to Vowel's method The method due to Lydersen, Riedel and Thodos have not been tested as the present method.

Critical temperature of multicomponent mixtures

The same correlation has been extended to predict critical temperature of multicomponent mixtures. Table 3 gives different systems considered with references, and compares the results with that of Thodos[15]. From the table it is clear that the accuracy of the proposed correlation is good. This correlation is not valid for mixtures containing, methane, ethylene, acetylene, propylene, as the error involved in calculating pure component critical temperature of these compounds is very large.

An example ; Experimental critical temperature of pentane-benzene mixture containing 0.378 mole fraction pentane is 528.6°K[9].

	$[P]$	R_D	A	B
n-Pentane	231.0	25.29	810	4000
Benzene	204.8	26.307	770	12000
	$x\,[P]$	$x\,R_D^{1.5}$	$x\,A$	$x\,B$
	87.25	48.2	306	1512
	127.38	83.8	479	7460
	214.63	132.0	785	8972

The correlation employed for multicomponent mixtures is

$$T_{CM} = \frac{\sum_{i=1}^{n} A_i x_i \sum_{i=1}^{n} x_i R_{Di}^{1.5} + \sum_{i=1}^{n} x_i B_i}{\sum_{i=1}^{n} x_i [P_i]} \qquad [2]$$

Using the above expression we have,

$$T_{CM} = 525^\circ\mathrm{K}$$

$$\%\ \text{error} = \frac{525 - 528.6}{528.6} = -0.68$$

TABLE I

Experimental and calculated values of critical temperatures

	T_c, °K Expl.	Calc.	% Error
1. *Paraffins*			
Methane	190.7	259.0	35.9*
Ethane	305.4	318.0	4.13
Propane	369.9	371.5	0.43
n-Butane	425.2	421.0	−0.98
n-Pentane	469.5	463.0	−0.75
2-Methylbutane	460.4	470.0	2.08
n-Hexane	507.3	504.0	−0.65
2-Methylpentane	496.5	508.0	2.32
3-Methylpentane	504.7	508.0	0.65
n-Heptane	540.3	540.3	0.0
2-Methylhexane	530.3	545.0	2.77
3-Methylhexane	535.6	545.0	1.76
3-Ethylpentane	540.8	545.0	0.78
2-3 Dimethylpentane	537.8	551.0	2.45
3-3 Dimethylpentane	536.0	551.0	2.80
n-Octane	568.6	571.0	0.42
3-Methyl heptane	565.0	575.0	1.77
3-Ethyl hexane	567.0	565.0	1.41
2-3 Dimethyl hexane	566.0	581.0	2.65
3-3 Dimethyl hexane	564.0	581.0	3.02

TABLE 1—(*contd.*)

Experimental and calculated values of critical temperatures

	T_c, °K		
	Expl.	Calc.	% Error
3-4 Dimethyl hexane	571.0	581.0	1.75
3-Ethyl-2-methyl pentane	568.0	581.0	2.29
3 Ethyl-3 methyl pentane	578.0	581.0	0.57
n-Nonane	594.6	611.0	2.76
n-Decane	617.6	644.0	4.27
		Average	1.81
n-Undecane	640.0	641.0	0.15
n-Dodecane	659.0	659.0	0.00
n-Tridecane	677.0	678.0	0.14
n-Tetradecane	694.0	690.0	0.58
n-Pentadecane	710.0	710.0	0.00
n-Hexadecane	717.0	725.0	1.12
n-Heptadecane	735.0	748.0	1.77
		Average	0.54
2. *Alkenes*			
Ethylene	283.1	312.5	10.8*
Propylene	365.1	371.0	1.62
n-Butene	419.6	421.0	0.33
n-Pentene	464.8	467.5	0.58
n-Hexene	504.0	506.0	0.40
n-Octene	578.0	580.0	0.35
		Average	0.63
3. *Alkynes*			
Ethyne	309.5	497.0	60.5*
Propyne	401.0	473.0	17.9*
n-Hexyne	521.0	526.0	0.96
n-Heptyne	553.0	553.0	0.00
n-Nonyne	607.0	606.0	−0.16

TABLE 1—(*contd.*)

Experimental and calculated values of critical temperatures

	T_c, °K		
	Expl.	Calc.	°/₀ Error
n-Decyne	627.0	629.0	0.32
n-Undecyne	646.0	646.0	0.00
n-Dodecyne	664.0	669.0	0.75
n-Tridecyne	681.0	695.0	2.06
n-Tetradecyne	695.0	717.0	3.17
		Average	0.93
4. *Cyclopentanes*			
Cyclopentane	511.6	510.0	−0.32
Methyl cyclopentane	532.6	532.8	0.00
Ethyl cyclopentane	569.3	567.5	−0.32
n-Propyl cyclopentane	590.1	590.0	0.00
n-Butyl cyclopentane	616.5	619.0	0.40
n-Pentyl cyclopentane	639.0	646.0	1.08
n-Hexyl cyclopentane	660.0	669.0	1.36
n-Heptyl cyclopentane	678.8	690.0	1.65
n-Octyl cyclopentane	694.3	710.0	2.26
n-Nonyl cyclopentane	710.4	742.0	4.45*
		Average	0.82
5. *Cyclohexanes*			
Cyclohexane	554.0	554.0	0.00
Methyl cyclohexane	572.1	575.0	0.51
Ethyl cyclohexane	594.3	594.0	−0.10
n-Propyl cyclohexane	619.0	619.0	0.00
n-Butyl cyclohexane	645.5	645.0	−0.10
n-Pentyl cyclohexane	667.0	660.0	−1.05
n-Hexyl cyclohexane	685.0	681.5	−0.51
n-Heptyl cyclohexane	703.0	700.0	04.3
n-Octyl cyclohexane	722.0	727.0	0.69
n-Nonyl cyclohexane	736.0	738.0	0.27
		Average	0.37

TABLE 1—(*contd.*)

Experimental and calculated values of critical temperatures

	T_c, °K		
	Expl.	Calc.	% Error
6. *Esters*			
Methyl formate	487.2	517.0	4.06
Ethyl formate	508.5	516.0	1.47
Propyl formate	538.1	537.5	−0.11
Isobutyl formate	551.4	557.0	1.02
n-Amyl formate	575.8	572.0	−0.65
Isoamyl formate	577.8	577.5	−0.05
Methyl acetate	506.9	516.0	1.79
Ethyl acetate	523.3	531.0	1.47
n-Propyl acetate	549.4	550.0	0.11
n-Butyl acetate	579.1	572.0	−1.22
Isobutyl acetate	561.5	577.5	2.85
Isoamyl acetate	599.3	603.0	0.45
Methyl propionate	530.6	537.5	1.30
Ethyl propionate	550.0	546.1	0.71
Propyl propionate	578.0	572.0	−1.04
Isobutyl propionate	591.9	603.0	1.88
Isoamyl propionate	611.4	620.0	1.41
Methyl butyrate	554.5	550.0	−0.81
Ethyl butyrate	566.2	572.0	10.3
Propyl butyrate	599.8	597.0	−0.30
Isobutyl butyrate	611.4	620.0	1.41
Isoamyl n-butyrate	618.8	646.0	4.40
Methyl isobutyrate	540.8	557.0	3.00
Ethyl isobutyrate	553.6	577.5	4.35
n-Propyl isobutyrate	589.2	603.0	2.31
Isobutyl isobutyrate	601.9	612.0	1.81
Methyl-n-valerate	566.9	572.0	0.90
Ethyl-n-valerate	570.2	597.0	4.70
Ethyl isovalerate	588.0	603.0	2.55
n-Propyl isovalerate	609.1	620.0	1.79
Ethyl n-caprylate	658.7	666.0	1.11
Ethyl polargonate	674.0	687.0	1.93
Methyl laurate	712.0	732.0	2.81
		Average	1.72

TABLE 1—(*contd.*)

Experimental and calculated values of critical temperatures

	T_c, °K Expl.	Calc.	% Error
7. *Alcohols*			
Methyl alcohol	513.2	542.5	5.72*
Ethyl alcohol	512.5	516.3	−0.74
n-Propyl alcohol	536.7	533.5	−0.60
Allyl alcohol	545.1	556.0	2.00
n-Butyl alcohol	563.0	557.5	−0.98
Amyl alcohol	582.9	582.0	−0.15
Heptyl alcohol	638.0	638.0	0.00
Octyl alcohol	658.7	662.0	0.51
		Average	0 71
8. *Ethers*			
Dimethyl ether	400.1	397.0	−0.77
Diethyl ether	465.8	466.0	0.04
Ethyl propyl ether	500.6	501.5	0.18
Vinyl ethyl ether	475.0	481.0	1.26
Ethyl methyl ether	437.9	431.0	−1.57
		Average	0.76
9. *Ketones*			
Acetone	509.1	510.0	0.18
Ethyl methyl ketone	535.0	534.0	−0.19
Diethyl ketone	561.0	559.0	−0.36
Methyl n-propyl ketone	564.0	559.0	−0.88
		Average	0.40
10. *Acids*			
Acetic acid	594.8	591.5	−0.49
Propionic acid	612.7	602.5	−1.67
n-Butyric acid	628.0	627.0	0.16
n-Valeric acid	651.5	652.5	0.15
		Average	0.62

TABLE 1—(*concld.*)

Experimental and calculated values of critical temperatures

	T_c, °K Expl.	Calc.	% Error
11. *Aromatics*			
Benzene	562.1	565.0	0.52
Toluene	592.0	590.0	−0.34
Ethyl benzene	617.1	615.0	−0.34
n-Propyl benzene	638.4	640.0	0.25
n-Butyl benzene	661.0	665.0	0.61
n-Pentyl benzene	678.9	683.0	0.61
		Average	0.43
12. *Organic Halides*			
Methyl chloride	416.3	417.0	0.17
Methyl bromide	467.2	477.0	2.10
Methyl fluoride	317.8	319.5	0.53
Ethyl chloride	460.4	456.5	−0.85
Ethyl bromide	503.9	518.0	2.80
Carbon tetrachloride	556.4	551.5	−0.80
Propyl chloride	503.2	488.0	−3.02
		Average	1.46

TABLE 2

Values of constants in Equation [1] and comparison between experimental and calculated values.

SERIES	Number considered	A	B	% average error in T_c calculated by the method of					
				Present	Vowels(1)	Riedel(1)	Lydersen(1)	Thodos(1)	Eduljee
1a Paraffins	25	810	4,000	1.76	1.03 (6)	0.4 (6)	0.27 (6)	0.47 (6)	0.75 (10)
1b Paraffins	7	700	30,000	0.54					
2 Alkenes	6	815	1,500	0.63	1.3 (3)	0.35 (2)	4.0 (3)	0.23 (3)	0.56 (8)
3 Alkynes	10	745	22,000	0.93					
4 Cyclo-pentanes	10	775	17,000	0.82	3.45 (2)	0.25 (2)	0.5 (2)		
5 Cyclohexanes	10	742	24.000	0.37	2.5 (1)	0.0 (1)	0.0 (1)		
6 Esters	33	760	34,300	1.72	0.66 (3)	0.63 (3)	0.53 (3)		1.44
7 Alcohols	8	840	26,000	0.71	3.2 (3)	0.60 (3)	0.8 (3)		0.73 (14)
8 Ethers	5	800	14,000	0.72	0.4 (2)	0.85 (2)	0.5 (2)		0.59 (12)
9 Ketones	4	805	30,000	0.40	3.0 (1)	0.60 (1)	0.8 (1)		0.88 (7)
10 Acids	4	938	35,000	0.62	0.8 (1)	0.30 (1)	0.5 (1)		1.55 (7)
11 Aromatics	6	770	12,000	0.43	0.4 (6)	0.41 (6)	0.8 (8)		0.8 (24)
12 Organic halides	7	850	11,500	1.46	0.4	0.35	0.5		
	135	Average error		0.95	1.56 (35)	0.43 (34)	0.84 (35)	0.35 (9)	0.91 (115)

The numbers in brackets indicate the number of compounds considered if different from present investigation.
% Error=[(Calcd.—Expl.)/Expl.]×100.

TABLE 3

Systems investigated for multi-component Mixtures

	Number of mixtures	Average deviation	Maximum deviation	
			Present method	Thodos method
Binary systems				
Ethane-propane (11)	7	0.78	1.63	0.69
Ethane-n-butane (18)	5	1.25	3.45	0.34
Ethane-n pentane (14)	8	1.20	1.35	0.34
Propane-n butane (12)	5	0.84	0.51	1.24
Propane-n pentane (13)	4	0.50	0.20	0.25
n Butane- n heptane (19)	5	0.61	1.21	0.26
n Pentane-n hexane (9)	5	0.74	0.87	0.45
Benzene-toluene (9)	4	0.10	0.16	
Ethane-cyclohexane (20)	4	1.20	2.45	0.82
n Pentane-benzene (9)	5	0.34	0.68	1.83
n Pentane-toluene (9)	4	0.95	0.49	0.80
n Pentane-cyclohexane (9)	5	1.12	1.51	1.00
n Hexane-benzene (9)	6	0.16	0.47	0.64
n Hexane-toluene (9)	3	0.42	0.54	1.23
n Hexane-cyclohexane (9)	3	0.89	1.06	0.22
Cyclohexane-benzene (9)	6	0.36	0.60	
Cyclohexane-toluene (9)	4	0.35	0.54	
Average		0.69	1.05	0.72
Ternary systems				
Ethane-propane-n pentane (10)	1		1.32	0.56
Propane-n butane-n pentane (10)	1		1.00	0.39
n Butane-n pentane-n hexane (10)	1		1.43	0.74
Quaternary systems				
Ethane-propane-n butane-n pentane (10)	1		0	0.41
Propane-n butane-n pentane- n hexane (10)	1		0.82	0.27
Quinary systems				
Ethane-propane-n butane n pentane-n hexane (10)	1		1.18	0.58
Methane-ethane propane-n butane-n pentane (10)	1		0.43	1.68
Average			0.88	0.66

SYMBOLS USED

T_c = Critical temperature, °K
$[P]$ = Parachor
R_D = Molar refraction
A, B = Constants in Equations 1 and 2
x = Mole fraction

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