Short communication

Simple method for reliable predicting flash points of unsaturated hydrocarbons

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ABSTRACT

This work introduces a simple method for prediction of the flash point of different classes of unsaturated hydrocarbons including alkenes, alkynes and aromatics. Elemental composition is used as a core function that can be revised for some compounds by a correcting function. The predicted flash points for a data set of 173 unsaturated hydrocarbons are in good agreement with the measured values such that the root mean square (rms) error is 9 K. The estimated flash points for 76 furthers compounds have been compared with two new group additivity methods, where these methods can be applied, that the new method gives a lower rms value. It is shown that the new model can easily be used for any unsaturated hydrocarbons with complex molecular structures.

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1. Introduction

The flash point is frequently used to characterize the flammability of combustible liquids. It can be defined as the lowest temperature at which the mixture of vapor and air above the surface of the liquid can be ignited. However, it can be used to assess the fire hazard associated with designing process, transportation and storage systems of flammable substance. Although the measured flash point values are available for many organic compounds, there are many important chemicals or new synthesized compounds for which no flash point data are given.

There are various approaches for predicting flash points of different classes of organic compounds, which have been reviewed elsewhere [1–4]. Since the flash point of an organic compound depends on its volatility, some authors have introduced different correlations between the flash point of general organic compounds and thermodynamic data related to volatility such as vapor pressure, boiling point and enthalpy of vaporization [1–4]. These methods need accurate thermodynamic data to obtain good predictive results for flash points. Moreover, for safety purposes, it is important to have suitable methods for predicting volatilities of new substances or desirable chemicals because some classes of organic compounds may include dangerous properties such as toxicity [5–9]. Neural networks have become an important modeling technique in the field of quantitative structure-property relationships (QSPR), which has also been used extensively in recent years

for the prediction of flash points of organic compounds [10–19]. The QSPR analysis finds optimum quantitative relationships between molecular structure and desired property (e.g. the flash point) through molecular descriptors. However, the compounds with similar molecular structure in training set of the QSPR procedure should be used as test set. Moreover, this method requires special computer softwares such as Dragon [20].

Some predictive methods can be used for estimation of properties related to volatility of solid or liquid organic compounds through molecular structures, such as enthalpy of sublimation of energetic compounds [21–23]. However, several new methods have been recently developed for estimation of the flash points of different classes of general organic compounds from structural contributions [24–30]. They are advantageous because these methods may be applied for those classes of organic compounds where their thermodynamic data are not available as well as they do not require specialized software to implement. For saturated hydrocarbons, some relationships have been recently introduced to give good predictions of flash points of only acyclic or simultaneously cyclic and acyclic hydrocarbons [24–28]. It was indicated that group contribution methods can also be applied for prediction of flash point of saturated and unsaturated hydrocarbons [29,30]. Group contribution methods cannot be applied for some organic compounds in which the specific group values have not been defined. Moreover, the predicted flash points may be large for some of hydrocarbons.

In contrast to saturated hydrocarbons for which several methods give good predictions of their flash points [24–28], it is necessary to have a reliable model that can be applied for any unsaturated hydrocarbon. The purpose of this work is to introduce a new and simple method for predicting the flash point of different classes of unsaturated compounds containing alkenes, alkynes

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and aromatic hydrocarbons. It is shown that the number of carbon and hydrogen atoms can be used as a core function that may be revised by a correcting function. Correcting function contains two correcting terms that can be determined on the basis of molecular structure of unsaturated hydrocarbons. The predicted results of the new method are compared with experimental data and the estimated values of two of the best available predictive methods.

2. Results and discussion

Since the flash point of unsaturated hydrocarbons depends on their molecular weight and degree of unsaturation as well as the other structural parameters, their flash points can be correlated with suitable parameters [29]. The number of carbon and hydrogen atoms can be used to denote the effect of the two first factors. For hydrocarbons with general formula C_mH_n, the relative values of n with respect to m show degree of unsaturation in different classes of unsaturated hydrocarbons such as multiple double bonds in olefins. The study of the flash points of many unsaturated hydrocarbons reveals that it is possible to correlate their measured values with elemental composition and some molecular structure parameters. The number of carbon and hydrogen atoms has the main contribution for predicting the flash point of the compound with respect to the other parameters. For complex unsaturated compounds like substituted benzene, in addition to the total number of carbon and hydrogen atoms, the flash point depends on the number, type, length and location of branching along the hydrocarbon chain. Moreover, the flash points of alkenes and alkynes depend on the number of carbon atoms attached to double or triple bonds. However, the flash point of unsaturated hydrocarbons with general formula C_mH_n can be expressed as the sum of two functions:

$$FP = constant + (FP)_{core} + (FP)_{correcting} \qquad (1)$$

where $(FP)_{core}$ is a core function containing the number of carbon and hydrogen atoms that has the main contribution to the predicted flash point and $(FP)_{correcting}$ is a correcting function. Table 1 shows the experimental data of different classes of unsaturated hydrocarbons, which have been used to optimize Eqs. (2)–(4) as a function of elemental composition and different structural parameters:

$$FP = 167.1 + (FP)_{core} + (FP)_{correcting} \qquad (2)$$

where

$$(FP)_{core} = 19.68m - 2.915n \qquad (3)$$

$$(FP)_{correcting} = 16.77FP^{(+)} - 32.66FP^{(-)} \qquad (4)$$

The quantities of m and n in Eq. (3) are the number of carbon and hydrogen atoms, respectively. As seen in Eq. (3), $(FP)_{core}$ is a linear function of m and n because it depends on molecular weight and degree of unsaturation of the compound. The factors $FP^{(+)}$ and $FP^{(-)}$ in Eq. (4) are structural parameters of unsaturated hydrocarbons for increasing and decreasing of the flash point on the basis of $(FP)_{core}$, respectively. They can be specified according to the following situations:

(i) $FP^{(+)}$: This parameter can be applied only to polymethyl benzene. The value of $FP^{(+)}$ depends on the number of methyl groups attached to benzene ring in ortho position with respect to each other, which is equal to $0.25n_{CH_3}$. As an example, $FP^{(+)} = 3 \times 0.25 = 0.75$ for 1,2,3-trimethylbenzene. However, the existence of this parameter can increase the value of flash point on the basis of $(FP)_{core}$.

(ii) $FP^{(-)}$: This correcting function is applied to aromatic, alkene and alkyne compounds.

   (a) *Aromatic compounds*: Two different situations can be considered here

1. For the attachment of isopropyl directly to aromatic ring and the presence t-butyl in the molecule, the values of $FP^{(-)}$ are $0.25n_{isopropyl}$ and $0.5n_{t-butyl}$, respectively. As an example, the value of $FP^{(-)} = 3 \times 0.25 = 0.75$ for 1,3,5-triisopropylbenzene.
2. For the attachment of large normal alkyl group ($n' \geq 10$), e.g. dodecylbenzene, $FP^{(-)}$ equals 1.0. The parameter n' is the number of carbon atoms in alkyl group.

   (b) *Alkyne*: For the compounds containing one triple bond with general formula R–C≡C–H, the number of carbon atoms in R determines the value of $FP^{(-)}$. However, $FP^{(-)}$ equals $1.25 - 0.25n'$ where $n' \leq 4$. For example, $FP^{(-)} = 1.25 - 2 \times 0.25 = 0.75$ in 1-butyne.
   (c) *Alkene*: For alkenes with two alkyl groups attached to double bond in form R_1–C═C–R_2, the value of $FP^{(-)}$ is $2.25 - 0.75n'$ where $n' \leq 2$. As an example, $FP^{(-)}$ equals to 1.5 for propene.
   (d) *Two double bonds*: For the existence of two double bonds in form R_1–C═C–C═C–R_2 or R_1–C═C═C–R_2, $FP^{(-)}$ equals $1.0 - 0.5n'$ for which only one of alkyl groups (R_1 or R_2) should be methyl and the other hydrogen atom. For example, $FP^{(-)} = 0.5$ in 2-methylbutadiene.

The flash point of aromatics is a function of the number, type, length and degree of branching of the alkyl groups that are attached to the benzene ring [29]. Two considerable increasing and decreasing effects of $(FP)_{correcting}$ have been seen in above conditions for polymethyl benzene and isopropyl (or t-butyl) substituents in terms of $FP^{(+)}$ and $FP^{(-)}$, respectively. The numerical values before n_{CH_3}, $n_{isopropyl}$ and $n_{t-butyl}$ in these situations have been optimized through choosing different numbers to obtain the suitable coefficient of determination [31].

A multiple linear regression method and experimental data given in Table 1 were used to derive Eqs. (2)–(4) in which the numerical values assigned to the *FP* parameters have been specified [31]. The correcting functions $FP^{(+)}$ and $FP^{(-)}$ have been chosen on the basis of deviations of $(FP)_{core}$ from the measured values. The structural parameters $FP^{(+)}$ and $FP^{(-)}$ are equal to zero if the conditions for giving them various values are not met. The coefficient of determination or the r^2-value of Eqs. (2)–(4) is relatively good, which is equal to 0.976 [31].

Several factors are important in Eqs. (2)–(4) for prediction of the flash point:

(1) The relative contribution of $(FP)_{correcting}$ with respect to $(FP)_{core}$ in Eq. (2) is small. This is an advantage of the new model as compared to group additivity method because omitting or using similar group contribution may give large deviation.
(2) Increasing and decreasing of the parameters of m and n in Eq. (3), respectively, can augment the value of $(FP)_{core}$.
(3) The presence of specified structural parameters in conditions (a)–(d) of part (ii) for $FP^{(-)}$ can reduce the predicted $(FP)_{correcting}$ in Eq. (4), which is not suitable for increasing safety.

The calculated flash points of various unsaturated hydrocarbons compounds are given in Table 1 and compared with corresponding experimental data. It should be mentioned that the measured data from different authors as well as organizations can differ by as much as 30 K [25]. Experimental data of different unsaturated hydrocarbons were also taken from Ref. [32] in which all flash points are from the chemical database of the department of chemistry at the University of Akron (USA). Experimental data in Ref. [32] have been collected for many hazardous chemicals from a large number of scientific sources. As seen in Table 1, the root mean square (rms) deviations of the new method is 9 K. Moreover, maximum deviation

Table 1

Experimental values of unsaturated hydrocarbons [32] for deriving Eqs. (2)–(4). The predicted flash points (K) are also compared with the measured data [32].

No.	Compound	Experimental flash point	Predicted flash point	Deviation
1	Benzene	262	269	7
2	Toluene	280	284	4
3	Ethylbenzene	288	298	10
4	P-Xylene	300	298	−2
5	O-Xylene	303	306	3
6	Propylbenzene	303	312	9
7	Cumene	304	304	0
8	m-Ethyltoluene	311	312	1
9	1,2,3-Trimethylbenzene	324	324	0
10	1,2,4-Trimethylbenzene	321	320	−1
11	1,3,5-Trimethylbenzene	317	312	−5
12	o-Ethyltoluene	312	312	0
13	p-Ethyltoluene	309	312	3
14	Naphthalene	360	344	−17
15	Butylbenzene	331	326	−5
16	1,2,4,5-Tetramethylbenzene	346	343	−3
17	2-Ethyl-p-xylene	329	326	−3
18	3-Ethyl-o-xylene	338	334	−4
19	4-Ethyl-m-xylene	330	326	−4
20	tert-Butylbenzene	307	310	3
21	P-Cymene	320	318	−2
22	o-DiEthylbenzene	322	326	4
23	m-DiEthylbenzene	324	326	2
24	p-DiEthylbenzene	328	326	−2
25	4-Ethyl-1,2-dimethylbenzene	331	334	3
26	1-Methylnaphtalene	355	358	3
27	n-Pentylbenzene	339	340	1
28	IsoPentylbenzene	335	340	5
29	Pentamethylbenzene	364	361	−3
30	p-tert-Butyltoluene	321	324	3
31	2-Phenyl-2methylbutane	338	340	2
32	1-Ethylnaphtalene	380	372	−8
33	2-Ethylnaphtalene	377	372	−5
34	1,3-Dimethylnaphtalene	382	372	−10
35	1,2-Dimethylnaphtalene	374	372	−2
36	Hexylbenzene	356	354	−2
37	Hexamethylbenzene	377	379	2
38	3,5-Dimethyl-tert-butylbenzene	357	338	−19
39	1,2,4-Trimethylbenzene	349	354	5
40	1,3,5-Trimethylbenzene	354	354	0
41	1,4-Diisopropylbenzene	354	338	−16
42	m-Diisopropylbenzene	350	338	−12
43	n-Heptylbenzene	368	368	0
44	1,2,3,4-Tetraethylbenzene	367	383	16
45	2-Phenyloctane	373	383	10
46	n-Octylbenzene	380	383	3
47	n-Nonylbenzene	390	397	7
48	1,3,5-Triisopropylbenzene	359	372	13
49	Decylbenzene	380	378	−2
50	Pentaethylbenzene	386	411	25
51	n-Undecylbenzene	409	392	−17
52	Dodecylbenzene	418	406	−12
53	1,2,4,5-Teraisopropylbenzene	397	406	9
54	1,3,5-Tri-tert-butylbenzene	372	390	18
55	Tridecylbenzene	385	421	36
56	1-Methylanthracene	430	432	2
57	2-Methylanthracene	431	432	1
58	9-Methylanthracene	431	432	1
59	1-methylphenathrene	431	432	1
60	Retene	451	466	15
61	Phenylacetylene	303	309	6
62	Styrene	304	304	−1
63	2-Vinyltoluene	320	318	−2
64	3-vinyltoluene	324	318	−6
65	Allylbenzene	310	318	8
66	beta-Methylstyrene	333	318	−15
67	cis-1-Propenylbenzene	325	318	−7
68	Isopropenylbenzene	313	318	5
69	trans-1-phenyl-1-propene	331	318	−13
70	m-Divinylbenzene	338	338	0
71	p-Divinylbenzene	337	338	1
72	1-Butynylbenzene	341	338	−3
73	3-Ethylstyrene	333	332	−1
74	4-Ethylstyrene	335	332	−3
75	2,4-Dimethylstyrene	333	332	−1

Table 1 (*Continued*)

No.	Compound	Experimental flash point	Predicted flash point	Deviation
76	Acetylene	155	160	5
77	Propyne	186	183	−3
78	1-Pentyne	230	227	−3
79	2-Pentyne	253	244	−9
80	3-Methyl-1-butyne	221	227	6
81	1-Hexyne	252	250	−2
82	2-Hexyne	263	258	−5
83	3-Hexyne	259	258	−1
84	3,3-Dimethyl-1-butyne	239	250	11
85	4-Methyl-1-Pentyne	249	250	1
86	1,6-Heptadiyne	282	284	2
87	1-Heptyne	263	272	9
88	2-Heptyne	275	272	−3
89	3-Heptyne	257	272	15
90	3-Methyl-1-hexyne	268	272	4
91	1,7-Octadiyne	296	298	2
92	2,6-Octadiene	307	298	−9
93	1-Octyne	289	286	−3
94	2-Octyne	301	286	−15
95	4-Octyne	291	286	−5
96	1,8-Nonadiyne	314	312	−2
97	1-Nonyne	306	300	−6
98	1-Decyne	323	314	−9
99	1-Undecyne	338	328	−10
100	4-Undecyne	341	328	−13
101	1-Dodecyne	352	343	−9
102	1-Tridecyne	366	357	−9
103	Cyclobutene	202	205	3
104	Cyclopentene	244	244	0
105	Cyclohexene	256	258	2
106	4-Methylcyclopentene	243	258	15
107	Cycloheptene	267	272	5
108	4-Methylcyclohexene	272	272	0
109	3-Methylcyclohexene	270	272	2
110	4-Ethylcyclohexene	286	286	0
111	Ethylene	137	122	−15
112	Propene	165	161	−5
113	Propadiene	177	183	6
114	1,2-Butadiene	197	213	16
115	1,3-Butadiene	197	197	0
116	Butene	194	199	5
117	cis-2-Butene	200	199	−1
118	Isobutylene	197	199	2
119	1,2-Pentadiene	233	244	11
120	2,3-Pentadiene	235	244	9
121	cis-1,3-Pentadiene	232	227	−5
122	2-Methylbutadiene	225	227	2
123	Pentene	229	238	9
124	2-Pentene	253	238	−15
125	cis-2-Pentene	227	238	11
126	trans-2-Pentene	225	238	13
127	Isopentene	211	238	27
128	1,4,-Hexadiene	248	258	10
129	2,4-Hexadiene	264	258	−6
130	1,5-Hexadiene	246	258	12
131	2,3-Dimethyl-1,3-butadiene	251	258	7
132	3-Methyl-1,4-pentadiene	239	258	19
133	2-Methyl-2,3-pentadiene	255	258	3
134	1-Hexene	253	252	−1
135	cis-2-Hexene	252	252	0
136	cis-3-Hexene	261	252	−9
137	trans-3-Hexene	261	252	−9
138	Isohexene	241	252	11
139	2,3-Dimethyl-1-butene	255	252	−3
140	2,3-Dimethyl-2-butene	256	252	−4
141	3,3-Dimethyl-1-butene	244	252	8
142	2-Methyl-1-penene	241	252	11
143	2-Methyl-2-pentene	246	252	6
144	4-Methyl-2-pentene	241	252	11
145	3-Methyl-1-pentene	244	252	8
146	trans-3-Methyl-2-pentene	266	252	−14
147	2-Ethyl-1-butene	243	252	9
148	1,6-Heptadiene	263	272	9
149	1-Heptene	264	266	2
150	cis-2-Heptene	265	266	1
151	trans-2-Heptene	267	266	−1

Table 1 (*Continued*)

No.	Compound	Experimental flash point	Predicted flash point	Deviation
152	trans-3-Heptene	266	266	0
153	2-Methyl-1-hexene	267	266	−1
154	4-Methyl-1-hexene	258	266	8
155	2-Ethyl-1-pentene	263	266	3
156	2,4-Dimethyl-2-pentene	264	266	2
157	2,3,3-Trimethyl-1butene	256	266	10
158	cis-5-Methyl-2-Hexene	268	266	−2
159	trans-5-Methyl-2-Hexene	268	266	−2
160	trans-3-Octene	282	280	−2
161	trans-4-Octene	281	280	−1
162	Cis-4-Octene	294	280	−14
163	1,8-Nonadiene	299	300	1
164	2-Ethyl-1-hexene	279	280	1
165	1-Nonene	298	294	−4
166	1-Undecene	336	323	−13
167	Dodecane	351	337	−14
168	2-Methyl-1-undecene	345	337	−8
169	1-Tridecene	352	351	−1
170	1-Tetradecene	383	365	−18
171	1-Pentadecene	386	379	−7
172	1-Hexadecene	402	393	−9
173	1-Heptadecene	408	407	−1
The rms deviation (K)				9

Table 2
Comparison of the predicted flash points of the new model as well as group contribution methods of Albahri [29] and Rowley et al. [30] with experimental data [32].

No.	Compound	Experimental flash point	New model	Deviation	Albahri	Deviation	Rowley et al.	Deviation
1	sec-Butylbenzene	318	326	8	325	7	325	7
2	IsoButylbenzene	323	326	3	325	2	325	2
3	1,2,3,4-Tetramethylbenzene	341	343	2	333	−8	328	−13
4	1,2,3,5-Tetramethylbenzene	336	339	3	332	−4	328	−8
5	Neopentylbenzene	323	324	1	335	12	330	7
6	M-Cymene	323	318	−5	327	4	325	2
7	2-Methylnaphtalene	371	358	−13	362	−9	366	−5
8	3,4-Dimethylcumene	341	340	−1	344	3	340	−1
9	1,4-Dimethylnaphtalene	383	372	−11	377	−6	381	−2
10	2,3-Dimethylnaphtalene	387	372	−15	377	−10	381	−6
11	Tetradecylbenzene	433	435	2	448	15	468	35
12	1,4-Di-tert-butylbenzene	370	350	−20	371	1	364	−7
13	Diisopropylbenzene	344	338	−6	353	9	353	9
14	9,10-Dimethylanthracene	442	446	4	438	−4	459	17
15	4-Vinyltoluene	318	318	0	314	−4	311	−7
16	cis-(1-Methyl-1-propenyl)benzene	328	332	4	328	0	337	9
17	1-Pentynylbenzene	355	352	−3	357	2	355	0
18	1-Vinylnaphthalene	389	378	−11	375	−14	380	−9
19	1-Butyne	207	205	−2	208	1	215	8
20	5-Methyl-1-hexyne	269	272	3	266	−3	271	2
21	1-Nonadeyne	431	442	11	436	5	450	19
22	1-Eicosyne	440	456	16	445	5	463	23
23	Cyclooctene	298	286	−12	294	−4	280	−19
24	Cyclododecene	367	343	−24	360	−7	319	−49
25	trans-2-Butene	200	199	−1	202	2	215	15
26	2-Methyl-1-butene	226	238	12	221	−5	230	4
27	2-Methyl-2-butene	266	238	−28	226	−40	237	−29
28	2-Methyl-1,4-Pentadiene	271	258	−13	242	−29	248	−23
29	3-Methyl-1,3-Pentadiene	244	258	14	244	0	255	11
30	1,9-Decadiene	314	314	0	315	1	314	0
31	1-Decene	322	309	−14	316	−7	315	−7
32	trans-5-Decene	319	309	−11	319	0	321	2
33	1,7-Octadiene	278	286	8	280	2	282	4
34	1-Octadecene	421	422	1	420	−1	430	9
35	1-Nonadecene	430	436	6	431	1	443	13
36	1-Eicosene	439	450	11	441	2	457	18
37	1-Octene	281	280	−1	282	1	283	2
38	trans-2-Octene	287	280	−7	286	−1	289	2
39	2-Methyl-1,3-Pentadiene	255	258	3	247	−8	255	0
40	2-Methyl-2-hexene	269	266	−3	268	−1	273	4
41	3-Methyl-1-hexene	267	266	−1	261	−6	270	3
42	2-Hexene	253	252	−1	247	−6	254	1
43	trans-2-Hexene	246	252	6	247	1	254	8
44	3-Ethyl-1-pentene	256	266	10	259	3	263	7
45	3-Ethyl-2-pentene	267	266	−1	266	−1	273	6
46	1,4-Pentadiene	277	244	−33	219	−58	227	−50

Table 2 (*Continued*)

No.	Compound	Experimental flash point	New model	Deviation	Albahri	Deviation	Rowley et al.	Deviation
47	1,3-Pentadiene	244	227	−17	224	−21	234	−10
48	Tetradecyne	378	371	−7	379	1	381	3
49	1-Pentadecyne	390	385	−5	391	1	395	5
50	1-Hexadecyne	401	399	−2	403	2	409	8
51	1-Octadecyne	422	427	5	425	3	437	15
52	p-Methylisopropenylbenzene	332	332	0	330	−2	328	−4
53	9-Vinylanthracene	445	452	7	436	−9	459	14
54	1,5-Dimethylnaphtalene	384	372	−12	–	–	381	−3
55	1,6-Dimethylnaphtalene	383	372	−11	–	–	381	−2
56	2,7-Dimethylnaphtalene	382	372	−10	–	–	381	−1
57	2,6-Dimethylnaphtalene	382	372	−10	–	–	381	−1
58	1-Phenylnaphthalene	435	452	17	–	–	448	13
59	2-Phenylnaphthalene	428	452	24	–	–	448	20
60	4,4-DiMethyl-2-Pentyne	263	258	−5	–	–	267	4
61	6-Methyl-2-heptyne	295	286	−9	–	–	294	−1
62	6-Methyl-3-heptyne	289	286	−3	–	–	294	5
63	1-Methylcyclobutene	228	244	16	–	–	254	26
64	1-Methylcyclopentene	256	258	2	–	–	265	9
65	1-Methylcyclohexene	269	272	3	–	–	276	7
66	1,3-Dimethylcyclohexene	285	286	1	–	–	287	2
67	3-Menthene	316	314	−2	–	–	317	1
68	1,5,5-Trimethylcyclohexene	295	300	5	–	–	261	−34
69	2,4-Dimethyl-1,3-Pentadiene	283	272	−11	–	–	274	−9
70	2,5-Dimethyl-1,5-hexadiene	286	286	0	–	–	284	−2
71	2,5-Dimethyl-2,4-hexadiene	302	286	−16	–	–	297	−5
72	2,4,4-Trimethyl-2-Pentane	268	280	12	–	–	278	10
73	2,4,4-Trimethylpentane	256	280	24	–	–	271	15
74	trans-1,2-di-tert-Butylethylene	306	308	2	–	–	297	−9
75	3,7-Dimethyl-1-octene	317	308	9	–	–	310	−7
76	3-Methyl-1,2-butadiene	230	244	14	–	–	–	–
	The rms deviation (K)			11[a]		12[b]		14[c]

[a] The rms deviation of new model is calculated for all compounds.
[b] The rms deviation of Albahri's method [29] is given only for the first 53 compounds. For these compounds, the calculated rms deviation by the new method is also 11 K.
[c] The rms deviation of the method of Rowley et al. [30] is calculated only for the first 75 compounds. The rms deviation of the new method is also 11 K.

of the predicted results of the new model is 36 K from experimental value as indicated in Table 1. Furthermore, the results of the new work are acceptable with respect to uncertainty of experimental data from different sources. Of 173 unsaturated hydrocarbons given in Table 1, 78.0% of the estimated flash points were within ±10 K of the measured flash points. The predicted results of the new model show that it can be easily applied to complex molecular structures of unsaturated hydrocarbons.

3. Comparison of the new correlation with the other methods

Different pathways have been reported in the literature to predict flash points of organic compounds [6–9]. Group contribution method is a suitable approach for prediction of flash points of different classes of hydrocarbons. For unsaturated hydrocarbons, Albahri [29] has introduced some group contributions of olefins and aromatics for predicting their flash points. This method cannot be used for some unsaturated hydrocarbons because several group contribution values have not been defined. Rowley and co-workers [30] have recently introduced a suitable structural contribution method for a wide range of organic compounds including fourteen group contribution values that can be applied only to hydrocarbons. This method cannot be used for those unsaturated hydrocarbons with –C=C=C– structural parameter. For unsaturated hydrocarbons, it will be shown that the reliability of Rowley et al. method [30] is lower than Albahri's method [29].

To test the reliability of new model for those unsaturated compounds that have not been used in deriving Eqs. (2)–(4), the predicted results for 76 different unsaturated hydrocarbons with complex molecular structures have also been given in Table 2. The calculated flash points of two different group additivity methods of Albahri [29] and Rowley et al. [30] have also been used for comparison of the predicted results. As indicated in Table 2, the reliability of the new method is greater than both Albahri [29] and Rowley et al. [30] methods. Furthermore, flash points of twenty-three and one of unsaturated hydrocarbons cannot be calculated by methods of Albahri [29] and Rowley et al. [30], respectively, because the values for some groups have not been defined by them. Although the reliability of Albahri's method is higher than Rowley et al. [30] method but its applications over a wide range of unsaturated hydrocarbons has some limitations. As seen in Table 2, the present method not only can be easily applied to any unsaturated hydrocarbons but also its reliability is higher than two of the best available methods. It should be mentioned that the present method does not differentiate between isomers, e.g. the compounds with nos. 9–11, 22–24, 32–35, 63–69, etc. in Table 1, because it does not account for such isomeric effect.

4. Conclusions

A novel reliable simple correlation has been introduced to predict the flash points of different classes of unsaturated hydrocarbons containing alkenes, alkynes and aromatics. The number of carbon and hydrogen atoms as a core function $(FP)_{core}$ and some structural parameters of the compound as correcting function $(FP)_{correcting}$ were used in the new model. The function $(FP)_{correcting}$ consists of two parameters $FP^{(+)}$ and $FP^{(-)}$, which can be easily found from molecular structure. As compared to Albahri [29] and Rowley et al. [30] methods, the present method provides more reliable results and can be easily applied for different types of unsaturated hydrocarbons without any difficulty.

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