

# Estimation of the acentric factor of organic compounds via a new group contribution method

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## ABSTRACT

To predict the acentric factor of organic compounds, a new second order group contribution method is developed. Some changes are made in the functional groups of Joback and Reid method and these groups are employed as the first order functional groups in this work. Besides, some second order functional groups are considered to improve the accuracy of estimations and distinguish among most structural isomers and stereoisomers. A set of experimental data for the acentric factor of 608 organic compounds containing complex and heavy polycyclic aromatic components are used to determine the group contribution values of 122 functional groups. The collected compounds in this research are hydrocarbons and hydrocarbon derivatives include carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine, and iodine atoms. The MATLAB software is utilized to develop the new model. The average absolute deviation of acentric factor predictions for 608 organic compounds is 0.022 and the percentage of average absolute relative deviation is 4.9%. The results of the new method are compared to the Constantinou, Gani and O'Connell method. It is observed that there is a considerable difference in the accuracy of the new method in comparison to that of the mentioned method.

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## 1. Introduction

Knowledge of physical properties is of great importance for the perception and design of chemical processes. When there is no experimental data for these properties in the literature, utilization of the estimation methods is mandatory. A broadly used constant for the estimation of physical properties of pure compounds and mixtures is the acentric factor [1]. Pitzer [2] in 1955 defined the acentric factor  $\omega$ , as

$$\omega = -\log_{10} \left[ \lim_{(T/T_c)=0.7} (P_{vp}/P_c) \right] - 1.0 \quad (1)$$

According to this definition, the values of critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), and vapor pressure ( $P_{vp}$ ) at the reduced temperature  $(T/T_c) = 0.7$  are required to determine the acentric factor [3]. From the point of molecular interactions, the acentric factor of a pure compound can be considered as the deviation of the intermolecular potential function of that compound from that of spherical simple molecules; the acentric factor is close to zero for

the spherical molecules while it is significantly greater than zero for long-chain molecules [4].

The acentric factor has an important role in the estimation of thermodynamic and transport properties for gases and liquids [5]. Here are some examples of these applications: enthalpy of vaporization [6], heat capacity of real gases [7], saturated density or molar volume of liquids [8], vapor pressure of pure liquids [7], saturated liquid viscosity [9], liquid heat capacity [10], equations of state (EoS) like the Peng-Robinson [11] and the Soave-Redlich-Kwong [12] EoS, and also compressibility factor [2,7].

There are many cases where the acentric factor values are not experimentally available. For instance, when the experimental critical constants are not accessible or the vapor pressure is not measured near/at the reduced temperature  $(T/T_c) = 0.7$ . In these situations, Eq. (1) cannot be used in the determination of the acentric factor; therefore, the estimation methods have to be employed [1]. Although the estimation methods are not as accurate as the experimental approaches, under these circumstances there are no other choices. The group contribution methods include an important part of the various estimation methods of the acentric factor. Only the knowledge of molecular structures is required to employ the group contribution methods for estimation of the properties of the compounds [13]. A brief explanation for the

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estimation methods of the acentric factor is presented in the next section.

The functional groups of this study, have been successfully applied to develop the new estimation methods for the normal boiling temperature by Ghasemtabar and Movagharnejad [14], the enthalpy of vaporization at normal boiling temperature by Abdi et al. [15], and the critical temperature, pressure and volume by Tahami et al. [16] for organic compounds. Right now, these functional groups are employed to develop a new precise method for the estimation of acentric factor of organic compounds without any dependence to the thermophysical data.

## 2. Estimation methods of the acentric factor

A variety of estimation methods of the acentric factor are available in the literature that some of them are briefly discussed in this part.

Edmister [17] in 1958 presented an estimation technique for the acentric factor based on the Clapeyron equation. This method requires the normal boiling temperature, the critical temperature, and the critical pressure for estimating the acentric factor. Lee and Kesler [7] in 1975 proposed an estimation method for the acentric factor by utilizing the same input information as considered by Edmister [17] method. Hoshino et al. [18] in 1982 presented a group contribution approach for the estimation of acentric factor of only alkanes by utilizing the structural information of the compounds. Lin and Chao [19] in 1984 proposed an equation whereby the acentric factor of hydrocarbons and derivatives can be estimated based on the molecular weight, the specific gravity, the normal boiling temperature, and the critical temperature. Magoulas and Tassios [20] in 1990 and Morgan and Kobayashi [21] in 1991 used the number of carbon atoms for estimating the acentric factor of only normal alkanes. In 1993, Chen et al. [1] introduced a correlation based on the Antoine equation to estimate the acentric factor by using the normal boiling temperature, the critical temperature, and the critical pressure. Han and Peng [4] in 1993 developed a group contribution method for estimating the acentric factor of organic compounds. In 1994, Kontogeorgis et al. [22] provided an estimation method for the acentric factor of high molecular weight compounds ( $M_w > 150$ ), using the van der Waals volume.

Constantinou et al. [23] in 1995 presented a useful and widely used estimation technique for the acentric factor of pure compounds. This second order group contribution method, which is based on the UNIFAC groups, can be applied with some confidence for the prediction of acentric factor [3]. This technique is applicable at two levels by employing 121 first and second order functional groups. The basic level of approximation is done by utilizing simple first order groups. The second level provides more reliable predictions especially for isomers by the second order groups. Constantinou et al. method for the acentric factor is given by the following equation:

$$\omega = 0.4085 \left\{ \ln \left[ \sum_k N_k (w1k) + W \sum_j M_j (w2j) + 1.1507 \right] \right\}^{(1/0.505)} \quad (2)$$

In this equation,  $w1k$  is the contribution value for the first order group of type  $k$  which occurs  $N_k$  times and  $w2j$  is the contribution value for the second order group of type  $j$  which has  $M_j$  occurrences in a component. For the first level of calculations, the value of  $W$  is assigned as zero and for the second level, it is assigned as unity.

Korsten [24] in 2000 utilized the normal boiling temperature, the critical temperature, and the critical pressure for developing an estimation method for the acentric factor. In 2012, a position group

contribution method for estimating the acentric factor of organic compounds by the employment of the molecular weight was proposed by Wang et al. [25] which can make distinction among isomers. Hosseiniifar and Jamshidi [26] in 2014, presented a correlation for the estimation of acentric factor by utilizing one input parameter such as the normal boiling temperature, the molecular weight, or the specific gravity. In 2017, Mondejar et al. [13] proposed a group contribution technique to predict the acentric factor of only halogenated olefins. The normal boiling temperature, the critical temperature, and the critical pressure were employed to provide an estimation method for the acentric factor of pure compounds by Hemmati-Sarapardeh et al. [5] in 2018.

In the field of integration of artificial neural networks with group contribution methods for estimating the acentric factor, the Gharagheizi et al. method [27] in 2011 and the Mondejar et al. method [13] in 2017 can be mentioned.

Most of the estimation methods for the acentric factor have some deficiencies such as dependency on critical properties and/or other thermophysical data, limited applicability, determination of the parameters and the contribution values by the employment of limited amount of experimental acentric factor data, low accuracy of the predictions, low prediction ability of the acentric factor of isomeric components, and so on. In this study, a new second order group contribution method is developed for the estimation of acentric factor of organic compounds which only requires the structural information of the components. A number of 608 experimental data for the acentric factor are gathered to determine the group contribution values of 122 functional groups. It is worthwhile to mention that, the acentric factor of most structural isomers and stereoisomers can be obtained with high accuracy by employing the second order functional groups of new estimation technique. As the Constantinou et al. method [23] is the first universal estimation method for the acentric factor [13], the results of the new estimation technique are compared to this method for different classifications of the organic compounds.

## 3. Description of the new method

The new model for the prediction of acentric factor of organic compounds is developed in this work by using the following process:

- Establishment of a comprehensive data bank from the experimental acentric factors
- Determination of the number of first and second order functional groups in all studied compounds
- Development of the new model by utilizing the `fminsearch` algorithm in MATLAB environment in order to obtain optimized coefficients of the model and group contribution values

Development of a comprehensive and correct estimation method strongly depends on the experimental data. In this work, the acentric factor of 608 organic compounds containing complex and heavy polycyclic aromatic components are collected. This set consists of carbon, hydrogen, oxygen, nitrogen, sulfur, fluorine, chlorine, bromine, and iodine atoms. The main part of the experimental acentric factors is selected from the Thermophysical Properties of Chemicals and Hydrocarbons [28] and the DIPPR 801 database [29]. Besides, the Thermodynamic Data for Pure Compounds [30] is used to provide the minor part of the experimental data set.

The collected compounds in this research are classified to several categories consisting of alkanes, cycloalkanes, alkenes, cycloalkenes, alkynes, benzene derivatives, aromatics, alcohols, phenols, ethers, ketones, aldehydes, esters, formates, acids, other

C.H.O components, amines, other nitrogen components, sulfur components, chlorine components, fluorine components, bromine components, iodine components, other halogen components, and other organic components.

Some changes are made in the functional groups of Joback and Reid method [31] and these groups are employed as the first order functional groups in this work. The first order functional groups are listed in Table 1. There are some points for the utilization of this table. When an atom is bonded to an element except hydrogen, (1) represents a single bond, (2) represents 2 single bonds, = represents a double bond and  $\equiv$  represents a triple bond. Moreover, (ss) or single site shows that the group exists in a ring like in naphthenics and (ds) or double site shows that the group exists in a ring like in aromatics. The group AOH is just restricted to the OH which is connected to the ring and does not include the aromatic carbon.

The first order functional groups are appropriate for the prediction of acentric factor of simple compounds and also these groups cannot capture the isomer differences. In so doing, the second order functional groups are considered to enhance the accuracy of estimations, represent a better description of polycyclic and complex polyfunctional compounds, and differentiate among most isomeric species. The second order groups are presented in Table 2 extensively.

Isomers are molecules with the same chemical formula and different chemical structures. The structural isomers (constitutional isomers) and stereoisomers (spatial isomerism) are two main species of the isomers [32]. In the structural isomers, the functional groups and atoms are joined together through different approaches [33]. In the stereoisomers, the bond structures are identical but the geometrical positioning of the functional groups and atoms differs in space. Two forms of the stereoisomers are cis isomers and trans isomers which describe the relative orientation of the functional groups within the molecules [34]. This new method employs the second order groups to present different estimations for the acentric factor of the structural isomers as well as the cis and trans isomers. Generally in this method, the distinction among isomers is made by determining the groups. In this sense, in order to distinguish between cis and trans isomers, 4s order groups are

considered including Cis-, Trans-, Alpha, and Beta that their usage instruction is explained in Table 2.

As shown by Liu and Chen [35], the sensitivity of the acentric factor to errors of the input data is very great. The estimation model for the acentric factor of organic compounds which needs only the structural information of the components, is presented by Eqs. (3)–(7):

$$\omega = S_{\omega 1} \left[ \ln \left[ C + \sum_i N_i \omega_i + \sum_j N_j \omega_j \right] \right]^{S_{\omega 2}} + S_{\omega 3} N_{atoms} \quad (3)$$

$$C = 1.60822 + 0.03531 * N_{rings} \quad (4)$$

$$S_{\omega 1} = \sum_{k=1}^{N_A^*} S_{\omega 1k} \quad (5)$$

$$S_{\omega 2} = \sum_{k=1}^{N_A^*} S_{\omega 2k} \quad (6)$$

$$S_{\omega 3} = \sum_{k=1}^{N_A^*} S_{\omega 3k} \quad (7)$$

In these equations,  $N_i$  reveals the number of first order functional groups of type  $i$  and  $N_j$  reveals the number of second order functional groups of type  $j$  in the compound. The group contribution values for the first order functional groups of type  $i$  are designated with  $\omega_i$  and the group contribution values for the second order functional groups of type  $j$  are designated with  $\omega_j$  which are shown in Tables 1 and 2, respectively. For some groups, the group contributions designated with (-) are not estimated because reliable experimental acentric factors of the compounds containing these groups could not be found in the literature.  $N_{atoms}$  represents the total number of atoms in the molecule and  $N_{rings}$  represents the number of rings in the considered compound.  $S_{\omega 1}$ ,  $S_{\omega 2}$ , and  $S_{\omega 3}$  are

**Table 1**  
First order group contributions for acentric factor.

Group $i$	$\omega_i$	Group $i$	$\omega_i$
1 CH <sub>3</sub> (1)	-0.03727	27 COO (2) (Ester)	0.23436
2 CH <sub>2</sub> (2)	0.14298	28 (C=O)-O-(C=O) (2) (Anhydride)	0.50952
3 CH (3)	0.17362	29 (C=O)-O-(C=O) (ss) (2) (Cyclic Anhydride)	-
4 C (4)	0.07192	30 = O (1)	-0.32618
5 CH <sub>2</sub> (ss) (2)	0.03497	31 NH <sub>2</sub> (1)	0.33248
6 CH (ss) (3)	0.02504	32 NH (2)	0.52206
7 C (ss) (4)	-4.42E-6	33 NH (ss) (2)	0.16305
8 = C (ss) (3)	-	34 N (ss) (3)	0.28522
9 = CH <sub>2</sub> (1)	-0.06899	35 N (3)	0.23709
10 = CH (2)	0.11519	36 = N (2)	-
11 = C (3)	0.08212	37 = N- (ds) (2)	0.06302
12 = C= (2)	0.09374	38 C $\equiv$ N (1)	0.49152
13 $\equiv$ CH (1)	0.08454	39 NO <sub>2</sub> (1)	0.34614
14 $\equiv$ C (2)	0.07498	40 SH (1)	0.16950
15 = CH (ds) (2)	0.01322	41 S (2)	0.32407
16 = C (ds) (3)	0.10738	42 S (ss) (2)	0.22210
17 OH (1) (Alcohol)	0.61229	43 = S (1)	2.20E-4
18 OH (1) (Cyclic Alcohol)	0.20550	44 S=O (2)	-
19 AOH (1) (Phenol)	0.38995	45 S=O (ss) (2)	-
20 O (2) (Ether)	1.38E-9	46 O=S=O (2)	-
21 O (ss) (2) (Ether)	-0.13547	47 O=S=O (ss) (2)	-
22 C=O (2) (Ketone)	0.19400	48 F (1)	2.47E-8
23 C=O (ss) (2) (Ketone)	0.02701	49 Cl (1)	-0.06504
24 CH=O (1) (Aldehyde)	0.06640	50 Br (1)	-0.33018
25 COOH (1) (Acid)	1.11473	51 I (1)	-0.00449
26 HCOO (1) (Formate)	-4.58E-7		

**Table 2**  
Second order group contributions for acentric factor.

Group <i>j</i>	Description	$\omega_j$
1 (CH <sub>3</sub> ) <sub>2</sub> CH-	Two methyl groups connected to the CH group in a chain.	0.07806
2 CH <sub>3</sub> (CH)<	One methyl group connected to the CH in a chain.	0.07739
3 CH <sub>3</sub> -CH <sub>2</sub> (CH-CH <sub>3</sub> )-	One methyl group connected to the CH into CH <sub>3</sub> -CH <sub>2</sub> -CH in a chain.	0.06835
4 (CH <sub>3</sub> ) <sub>3</sub> C-	Three methyl groups connected to the C in a chain.	0.23453
5 (CH <sub>3</sub> ) <sub>2</sub> C<	Two methyl groups connected to the C in a chain.	0.19017
6 CH <sub>3</sub> -CH <sub>2</sub> [C(CH <sub>3</sub> ) <sub>2</sub> ]-	Two methyl groups connected to the C into CH <sub>3</sub> -CH <sub>2</sub> -C in a chain.	0.19330
7 CH <sub>3</sub> -CH <sub>2</sub> (C-CH <sub>3</sub> )<	One methyl group connected to the C into CH <sub>3</sub> -CH <sub>2</sub> -C in a chain.	0.16291
8 CH <sub>3</sub> (C)<	One methyl group connected to the C in a chain.	0.13455
9 CH <sub>2</sub> =CH-	One methylene group connected to the CH in a chain by a double bond.	0.04016
10 CH <sub>2</sub> =(C-CH <sub>3</sub> )-	One methyl group and one methylene group connected to the C in a chain by a double bond.	0.17717
11 CH <sub>2</sub> =C<	One methylene group connected to the C in a chain by a double bond.	-0.20223
12 CH <sub>3</sub> -CH =	One methyl group connected to the CH = in a chain.	0.05264
13 CH <sub>3</sub> -CH <sub>2</sub> -CH =	One CH <sub>3</sub> -CH <sub>2</sub> group connected to the CH = in a chain.	0.03617
14 CH <sub>3</sub> -CH <sub>2</sub> (C-) =	One CH <sub>3</sub> -CH <sub>2</sub> group connected to the C = in a chain.	-3.13E-11
15 CH <sub>3</sub> -CH <sub>2</sub> (C-CH <sub>3</sub> ) =	One methyl group connected to the C = into CH <sub>3</sub> -CH <sub>2</sub> -C = in a chain.	0.16451
16 CH <sub>3</sub> (C-) =	One methyl group connected to the C = in a chain.	0.03934
17 (CH <sub>3</sub> ) <sub>2</sub> C =	Two methyl groups connected to the C = in a chain.	0.14297
18 CH≡C-	One methylidyne group connected to the C in a chain by a triple bond.	0.11118
19 CH <sub>3</sub> -C≡C-	One methyl group connected to the C≡C in a chain.	-
20 CH <sub>3</sub> -CH <sub>2</sub> -C≡C-	One CH <sub>3</sub> -CH <sub>2</sub> group connected to the C≡C in a chain.	-
21 CH <sub>3</sub> -O-	One methyl group connected to the oxygen atom in a chain.	-1.48E-8
22 CH <sub>3</sub> -CH <sub>2</sub> -O-	One CH <sub>3</sub> -CH <sub>2</sub> group connected to the oxygen atom in a chain.	-3.86E-6
23 (CH <sub>3</sub> ) <sub>2</sub> N-	Two methyl groups connected to the nitrogen atom in a chain.	0.07970
24 CH <sub>3</sub> - a e (0-3)	One carbon atom connected to the main chain or ring, exclusive of the above foregoing functional groups (1-23).	0.06664
25 CH <sub>4</sub> CH <sub>b</sub> - a,b e (0-3)	Two carbon atoms connected to the main chain or ring, exclusive of the above foregoing functional groups (1-23).	0.03531
26 CH <sub>4</sub> CH <sub>b</sub> CH <sub>c</sub> -a,b,c e (0-3)	Three carbon atoms connected to the main chain or ring, exclusive of the above foregoing functional groups (1-23).	-0.09148
27 CH <sub>4</sub> CH <sub>b</sub> CH <sub>c</sub> CH <sub>d</sub> -a,b,c,d e (0-3)	Four carbon atoms connected to the main chain or ring, exclusive of the above foregoing functional groups (1-23).	0.06742
28 CH <sub>4</sub> CH <sub>b</sub> CH <sub>c</sub> ...CH <sub>d</sub> -a,b,c,d,...e (0-3)	The other groups higher than four carbon atoms, connected to the main chain or ring, exclusive of the above foregoing functional groups (1-23).	0.09203
29 Ncarbon	Number of carbons into the other groups higher than four carbon atoms. This group is employed when CH <sub>4</sub> CH <sub>b</sub> CH <sub>c</sub> ...CH <sub>d</sub> - is present in the chemical structure.	-8.03E-6
30 Alkene bond	The alkene chain connected to the ring.	-
31 Ring	Number of rings.	0.04077
32 C-C	Number of the common single bonds between connected rings.	-7.91E-9
33 C=C	Number of the common double bonds between connected rings.	0.09959
34 C-C (out)	Number of the single or double bonds between many connected rings by the external connection.	5.22E-5
35 Double bond	Number of double bonds.	-0.03202
36 Triple bond	Number of triple bonds.	-1.21E-12
37 Cis-	Number of cis- positions.	-1.99E-7
38 Trans-	Number of trans- positions.	5.90E-4
39 Alpha	Number of atoms into the alpha position, for cis hydrocarbons alpha is 2 and for trans hydrocarbons alpha is 1.	-0.02333
40 Beta	Number of atoms into the beta position, for cis hydrocarbons beta is 0 and for trans hydrocarbons beta is 1.	-0.00371
41 C <sub>1</sub> ring	All of the ring members must be numbered, the numbering begins from the side chain with lower carbon atoms into a clockwise. This group is the number of side chains on the first carbon atoms into the ring and also the number of atoms except carbon and hydrogen on the first carbon atoms and those which are located instead of the first carbon atoms.	0.01672
42 C <sub>2</sub> ring	This group is the number of side chains on the second carbon atoms into the ring and also the number of atoms except carbon and hydrogen on the second carbon atoms and those which are located instead of the second carbon atoms.	5.15E-10
43 C <sub>3</sub> ring	This group is the number of side chains on the third carbon atoms into the ring and also the number of atoms except carbon and hydrogen on the third carbon atoms and those which are located instead of the third carbon atoms.	0.04556
44 C <sub>4</sub> ring	This group is the number of side chains on the fourth carbon atoms into the ring and also the number of atoms except carbon and hydrogen on the fourth carbon atoms and those which are located instead of the fourth carbon atoms.	0.04929
45 C <sub>5</sub> ring	This group is the number of side chains on the fifth carbon atoms into the ring and also the number of atoms except carbon and hydrogen on the fifth carbon atoms and those which are located instead of the fifth carbon atoms.	0.04962
46 C <sub>6</sub> ring	This group is the number of side chains on the sixth carbon atoms into the ring and also the number of atoms except carbon and hydrogen on the sixth carbon atoms and those which are located instead of the sixth carbon atoms.	0.04243
47 C <sub>1</sub> =C <sub>2</sub>	A double bond between first atom and second atom into the ring.	-0.02329
48 C <sub>2</sub> =C <sub>3</sub>	A double bond between second atom and third atom into the ring.	0.06579
49 C <sub>3</sub> =C <sub>4</sub>	A double bond between third atom and fourth atom into the ring.	1.04E-5
50 C <sub>4</sub> =C <sub>5</sub>	A double bond between fourth atom and fifth atom into the ring.	-0.13020
51 C <sub>5</sub> =C <sub>6</sub>	A double bond between fifth atom and sixth atom into the ring.	0.12066
52 C <sub>6</sub> =C <sub>1</sub>	A double bond between sixth atom and first atom into the ring.	0.16881
53 C <sub>5</sub> =C <sub>1</sub>	A double bond between fifth atom and first atom into the ring.	0.07790
54 Alpha-6	Number of side chains, oxygen, nitrogen and sulfur atoms in alpha position into the six membered ring of bicyclo compounds.	-0.12470
55 Beta-6	Number of side chains, oxygen, nitrogen and sulfur atoms in beta position into the six membered ring of bicyclo compounds.	-9.09E-8
56 Gamma-6	Number of side chains, oxygen, nitrogen and sulfur atoms in gamma position into the six membered ring of bicyclo compounds.	-
57 Alpha-5	Number of side chains, oxygen, nitrogen and sulfur atoms in alpha position into the five membered ring of bicyclo compounds.	-
58 Beta-5	Number of side chains, oxygen, nitrogen and sulfur atoms in beta position into the five membered ring of bicyclo compounds.	0.05565
59 Left ring side chain	Number of side chains, oxygen, nitrogen and sulfur atoms into the left ring of polycyclic compounds.	0.05681
60 Right ring side chain	Number of side chains, oxygen, nitrogen and sulfur atoms into the right ring of polycyclic compounds.	0.26462
61 Middle ring side chain	Number of side chains, oxygen, nitrogen and sulfur atoms into the middle ring of polycyclic compounds.	-0.13263
62 Left ring double bond	Number of double bonds into the left ring of polycyclic compounds.	-0.01802

**Table 2** (continued)

Group <i>j</i>	Description	$\omega_j$
63 Right ring double bond	Number of double bonds into the right ring of polycyclic compounds.	-0.06547
64 Mid ring double bond	Number of double bonds into the middle ring of polycyclic compounds.	0.12856
65 Oxygen	Number of oxygen atoms.	0.18680
66 Nitrogen	Number of nitrogen atoms.	0.10292
67 Sulfur	Number of sulfur atoms.	-0.02236
68 Chlorine	Number of chlorine atoms.	0.09026
69 Fluorine	Number of fluorine atoms.	0.04420
70 Bromine	Number of bromine atoms.	-7.85E-9
71 Iodine	Number of iodine atoms.	1.34E-8

the adjustable parameters for  $\omega$  in Eq. (3). These parameters are related to the existence of different types of atoms except hydrogen in the chemical formula, containing carbon, nitrogen, oxygen, sulfur, fluorine, chlorine, bromine, and iodine atoms, regardless of the number of each type of these atoms. If any of different atom types in Table 3 is present in the molecule, the corresponding  $s_{\omega 1k}$ ,  $s_{\omega 2k}$ , and  $s_{\omega 3k}$  parameters related to each atom types will be utilized from this table. Also,  $N_A^*$  reveals the number of atom types presented in the compound except hydrogen.

The determination of the contributions for the first and second order groups has been performed by using the experimental acentric factor data of 608 organic compounds. The fminsearch algorithm in MATLAB software has been utilized to develop the new model and optimize the values of the group contributions and model coefficients. This algorithm can find the minimum of a scalar function of several variables (the objective function), by using an initial estimate. In order to achieve the high performance of the model in the optimization process, various ranges of digits are considered as initial estimates for all group contribution values and model coefficients. The fminsearch algorithm which is generally attributed to an unconstrained nonlinear optimization, utilizes the Nelder-Mead simplex algorithm as clarified by Lagarias et al. [36]. The algorithm employs a simplex of  $n+1$  points for  $n$ -dimensional vectors  $X$ . Fminsearch first makes a simplex around the initial guess  $X_0$  by adding 5% of each component  $X_0(i)$  to  $X_0$ , and using these  $n$  vectors as elements of the simplex in addition to  $X_0$  (It utilizes 0.00025 as component  $i$  if  $X_0(i) = 0$ ).

The percentage of average absolute relative deviation (%AARD) is the objective function in this study, which is defined according to the following relation:

$$\%AARD = \frac{1}{N} \sum_{k=1}^N \frac{|\omega_{pred,k} - \omega_{exp,k}|}{\omega_{exp,k}} \times 100 \quad (8)$$

where  $\omega_{pred}$  is the predicted acentric factor by the new method,  $\omega_{exp}$  is the experimental acentric factor, and  $N$  stands for the number of data points.

**Table 3**

$s_{\omega 2k}$ , and  $s_{\omega 3k}$  parameters related to each atom types.

Hydrocarbon atoms	$s_{\omega 1k}$	$s_{\omega 2k}$	$s_{\omega 3k}$
Carbon	0.49972	1.73844	-4.44512E-7
Nitrogen	-0.03445	9.68845E-8	-8.59833E-4
Oxygen	-0.02665	-0.25404	5.40165E-4
Sulfur	-0.04603	0.10581	-8.83428E-11
Fluorine	-0.08725	-0.34928	-6.24162E-10
Chlorine	-0.01042	0.16466	-9.10615E-4
Bromine	-0.23908	-1.27707	0.00458
Iodine	4.99970E-7	0.48959	-1.18007E-6
Halogen	0.03575	-0.07105	0.00115

## 4. Results and discussion

For the development of the new estimation method, all the compounds existing in the databank were randomly divided into a training set and a test set. Developing and optimizing the new model for the acentric factor were performed by using the training set to obtain the group contribution values and the model coefficients. Generally, the training sets lead to fair appropriate predictions, because the model has been formed by utilizing these sets; but it does not interpret that the model is completely safe in different practical situations. Therefore, the available components in the test set were used to estimate the acentric factor through the equation and the contribution values previously obtained using the training set. 90% of the whole data was included in the training set and 10% of the data was included in the test set. The estimation results for the training set compounds as well as the test set compounds are shown in Table 4 which confirm the accuracy and reliability of the proposed model. In this table, the percentage of average absolute relative deviation (%AARD) and some other statistical measures are used to evaluate the prediction capability of the new model in comparison to the experimental data. These measures are defined by the following relations:

$$AD = |\omega_{pred} - \omega_{exp}| \quad (9)$$

$$\%ARD = \frac{|\omega_{pred} - \omega_{exp}|}{\omega_{exp}} \times 100 \quad (10)$$

$$AAD = \frac{1}{N} \sum_{k=1}^N |\omega_{pred,k} - \omega_{exp,k}| \quad (11)$$

where  $AD$  represents the absolute deviation,  $\%ARD$  represents the percentage of absolute relative deviation, and  $AAD$  represents the average absolute deviation.  $\omega_{pred}$  and  $\omega_{exp}$  are predicted and

**Table 4**

The estimation results of new method for the training and the test set.

Method	New method	Training set	Test set
Substances	608	548	60
%AARD	4.9	4.9	4.9
AAD	0.022	0.022	0.022
%ARD ≤ 4%	353	317	36
4% < %ARD ≤ 6%	64	57	7
6% < %ARD ≤ 8%	48	41	7
8% < %ARD ≤ 10%	37	34	3
10% < %ARD	106	99	7
AD ≤ 0.02	398	358	40
0.02 < AD ≤ 0.03	59	53	6
0.03 < AD ≤ 0.04	50	43	7
0.04 < AD ≤ 0.05	26	25	1
0.05 < AD	75	69	6



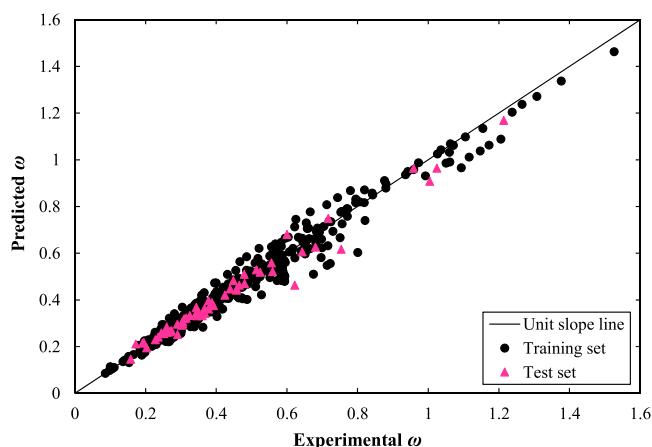


Fig. 1. Comparison of predicted acentric factors by the new method versus experimental data for 608 organic compounds.

experimental acentric factors, respectively. Also,  $N$  stands for the number of data points.

The analysis of the results presented in Table 4 shows that 82.57% of the components have the absolute relative deviation smaller or equal to 10% and also 12.34% of the components have the absolute deviation greater than 0.05. Fig. 1 depicts the comparison of predicted acentric factors obtained by using the new method with respect to the experimental values for 608 organic compounds. As it is obvious in this figure, the test set is in accordance with the training set and also the experimental values fit well with the predicted values in most cases.

The statistical results of the new method are presented in Table 5 for different chemical families of the organic compounds applied in this study. According to this table, the values of percentage of average absolute relative deviation (%AARD) and average absolute deviation (AAD) for the estimation of acentric factor are in the acceptable ranges and also the excellent agreements are observed with the experimental data for all investigated types of

organic compounds.

In order to compare the performance of this model with a universal estimation method for the acentric factor, the Constantinou et al. method [23] is applied for this purpose. As the Constantinou et al. method is not capable of predicting the acentric factor of all 608 studied compounds used to develop the new model, 476 common organic compounds are selected to make comparison between two methods. The statistical summary of this comparison is presented in Table 6 for first and second order estimations. According to this table, the percentage of average absolute relative deviation (%AARD) and the average absolute deviation (AAD) of the new method are much lower than those of the Constantinou et al. method. The results show that in the new method, the utilization of the second order functional groups has more effects on the accuracy of estimations than the Constantinou et al. method. From a meticulous point of view, the new method can estimate 82.77% of the acentric factor data points with the absolute relative deviation smaller or equal to 10% and also 14.50% of the components have the absolute deviation greater than 0.05 by using the first and second order functional groups. The results of second

Table 6

Statistical summary of comparison between new method and Constantinou et al. method.

Method	New method		Constantinou et al. method	
	First Order	Second Order	First Order	Second Order
Substances	476	476	476	476
%AARD	17.2	4.9	22.6	21.8
AAD	0.072	0.024	0.1	0.099
$\%ARD \leq 4\%$	84	280	117	127
$4\% < \%ARD \leq 6\%$	27	47	29	42
$6\% < \%ARD \leq 8\%$	33	36	24	25
$8\% < \%ARD \leq 10\%$	26	31	24	25
$10\% < \%ARD$	306	82	282	257
$AD \leq 0.02$	92	303	133	156
$0.02 < AD \leq 0.03$	37	46	38	36
$0.03 < AD \leq 0.04$	41	38	20	19
$0.04 < AD \leq 0.05$	39	20	17	16
$0.05 < AD$	267	69	268	249

Table 5

The estimation results of new acentric factor model for different chemical families of organic compounds.

Components	Number of components	Number of components in the training set	Number of components in the test set	AAD	%AARD
Alkanes	97	88	9	0.011	2.2
Cyclo alkanes	35	31	4	0.013	4.7
Alkenes	62	56	6	0.010	3.3
Cyclo alkenes	1	1	0	4.23E-7	2.2E-4
Alkynes	2	2	0	6.61E-7	3.4E-4
Benzene derivatives	45	40	5	0.017	4.4
Aromatics	6	6	0	9.71E-4	0.3
Alcohols	39	35	4	0.071	11.5
Phenols	12	10	2	0.031	6.3
Ethers	26	24	2	0.016	4.5
Ketones	28	25	3	0.015	3.5
Aldehydes	14	12	2	0.047	9.6
Esters	38	34	4	0.031	5.5
Formates	6	6	0	0.036	7.8
Acids	33	30	3	0.046	5.8
Other C.H.O compounds	6	5	1	0.086	14.2
Amines	35	32	3	0.021	6.3
Other nitrogen compounds	19	17	2	0.018	4.9
Sulfur compounds	23	20	3	0.007	2.9
Chlorine compounds	19	17	2	0.010	4.5
Fluorine compounds	23	21	2	0.016	5.9
Bromine compounds	7	7	0	0.015	5.9
Iodine compounds	1	1	0	2.43E-6	9.8E-4
Other halogen compounds	24	21	3	0.011	4.5
Other compounds	7	7	0	0.018	6

order estimations by the Constantinou et al. method show that 46.01% of the data points have the absolute relative deviation smaller or equal to 10% and also 52.31% of the components have the absolute deviation greater than 0.05. It is obvious that there is a considerable difference in the accuracy of the second order estimations of the new method in comparison to that of the Constantinou et al. method.

To further show the reliability of the new method, the comparison of predicted acentric factors obtained by the new method and the Constantinou et al. method versus the experimental data for 476 organic compounds is shown in Fig. 2. As it is illustrated in this figure, most of the data points are placed on the unit slope line for the new method. However, the accumulation of the data points around the unit slope line for the Constantinou et al. method is less, in comparison to the proposed method. Furthermore, Fig. 3 shows the comparison of experimental/predicted values of the acentric factor obtained by the two mentioned methods against the molecular weight for 476 organic compounds. Therefore, the developed group contribution method provides a better prediction for the acentric factor than the Constantinou et al. method.

The error analysis of the new method and the Constantinou et al. method is summarized in Table 7 for different types of organic compounds. According to this table, the percentage of average absolute relative deviation (%AARD) and the average absolute deviation (AAD) of the new method are lower than those of the Constantinou et al. method for all studied types of compounds. For further clarification, the comparison of new method and Constantinou et al. method against the published acentric factor values

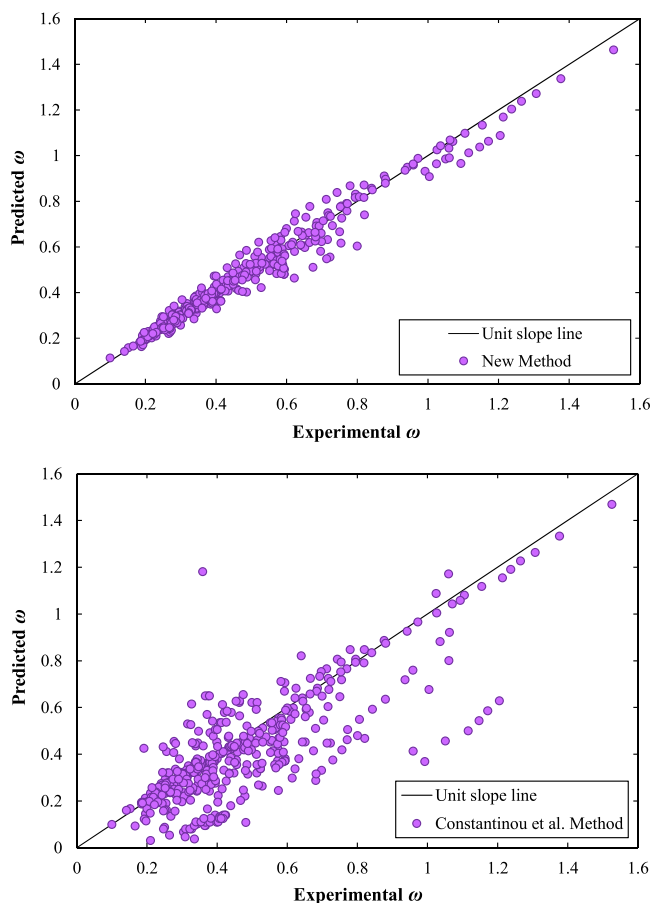


Fig. 2. Comparison of predicted acentric factors by the new method and the Constantinou et al. method versus experimental data for 476 organic compounds.

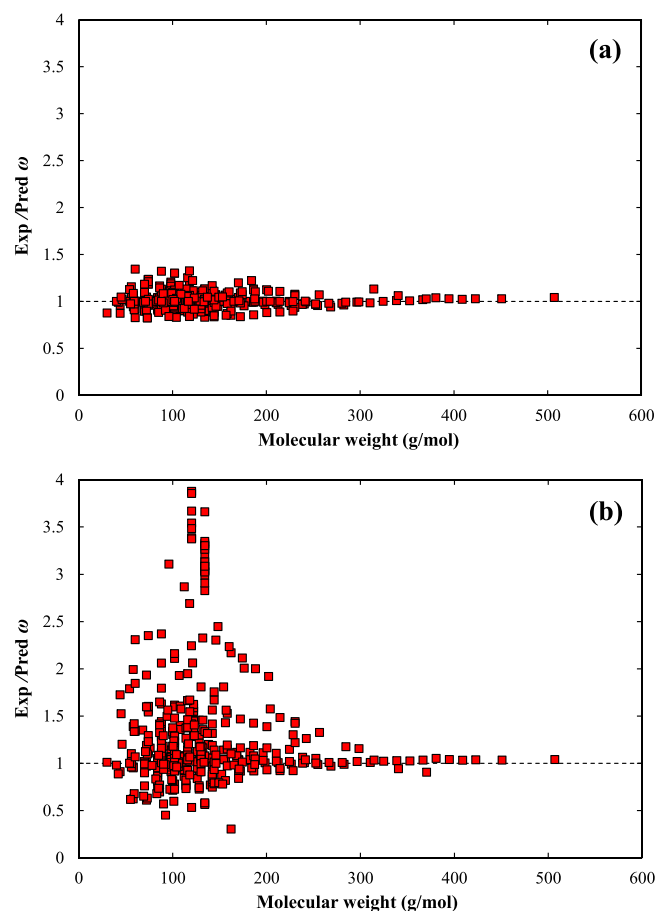


Fig. 3. Comparison of experimental/predicted values of the acentric factor obtained by (a) the new method and (b) the Constantinou et al. method against the molecular weight for 476 organic compounds.

Table 7

Statistical summary of comparison between new method and Constantinou et al. method for different chemical families of organic compounds.

Components	NC <sup>a</sup>	New method		Constantinou et al. method	
		AAD	%AARD	AAD	%AARD
Alkanes	97	0.011	2.2	0.015	3.4
Cyclo alkanes	35	0.013	4.7	0.029	8
Alkenes	58	0.010	3.3	0.018	6.6
Cyclo alkenes	1	4.23E-7	2.2E-4	0.051	26
Alkynes	1	2.61E-7	1.2E-4	0.004	1.9
Benzene derivatives	45	0.017	4.4	0.264	69.5
Aromatics	6	9.71E-4	0.3	0.134	38.2
Alcohols	38	0.073	11.8	0.119	19.7
Phenols	12	0.031	6.3	0.161	31.9
Ethers	19	0.016	4.7	0.059	17.7
Ketones	25	0.015	3.5	0.106	26.2
Aldehydes	12	0.044	8.4	0.122	31.8
Esters	35	0.033	5.7	0.061	12.3
Formates	6	0.036	7.8	0.085	21.2
Acids	30	0.045	5.6	0.353	42.3
Other C.H.O compounds	5	0.097	15.6	0.125	17.7
Amines	14	0.026	7.4	0.109	31.2
Other nitrogen compounds	10	0.018	4.7	0.136	34.4
Sulfur compounds	5	0.009	3.2	0.052	20.2
Chlorine compounds	3	0.014	6.2	0.133	62.7
Fluorine compounds	1	0.047	19.2	0.168	67.8
Bromine compounds	7	0.015	5.9	0.068	26.9
Iodine compounds	1	2.43E-6	9.8E-4	0.090	36.5
Other halogen compounds	5	0.003	1.1	0.019	8.4
Other compounds	5	0.012	4.8	0.134	39.3

<sup>a</sup> The number of components to which the methods was applicable.

**Table 8**  
Comparison of new method and Constantinou et al. method for different isomeric compounds.

Types of isomers	Number of isomers	New method		Constantinou et al. method	
		AAD	%AAD	AAD	%AAD
Structural isomers	330	0.020	4.5	0.098	22.4
Cis isomers	16	0.013	4.3	0.019	6.9
Trans isomers	15	0.013	4.4	0.017	6.2

for some samples is presented in Table S1. These results confirm the sufficiency and the accuracy of the developed method in comparison to the Constantinou et al. method.

In order to survey the capability of the proposed model in the acentric factor prediction of the structural, cis and trans isomers, a comparison between the new model and the Constantinou et al. model is made and the results are reported in Table 8. The Constantinou et al. method cannot accurately predict the acentric factor of isomeric compounds because of the limited functional groups for describing the molecular structures of the isomers. Besides, this method is not capable of differentiating between the cis and trans isomers. While the new method can precisely predict the acentric factor of most structural, cis and trans isomers by applying a set of functional groups containing different poses of atoms and groups, particularly for cis and trans isomers.

## 5. Conclusion

A new generalized group contribution method for the estimation of acentric factor of organic compounds is developed which only requires the structural information of the components. A perfect collection of the first and second order functional groups, an extensive set of substance classes, and a complete data bank containing 608 experimental data for the acentric factor confirm the universality of the new method. The acentric factor of most structural, cis and trans isomers can be obtained with high accuracy by employing the second order functional groups of this estimation technique. It is worth to mention that, this method performs significantly better than the Constantinou et al. method for all investigated classes of organic compounds.

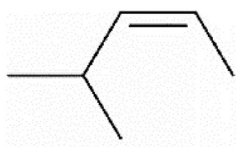
## Acknowledgement

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## Appendix A. Supplementary data

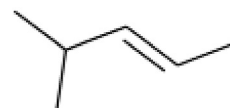
Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fluid.2019.112246>.

**Example 1.** Estimation of the acentric factors of isomeric 4-Methyl-2-Penten-2-ones ( $C_6H_{12}$ ). Functional groups of 4-Methyl-Cis-2-Pentene (experimental value:  $\omega = 0.2442$ ):



First order groups	$N_i$	$N_i\omega_i$	Second order groups	$N_j$	$N_j\omega_j$
$CH_3$ (1)	3	-0.11181	$(CH_3)_2CH-$	1	0.07806
CH (3)	1	0.17362	$CH_3-CH=$	1	0.05264
$=CH$ (2)	2	0.23038	Double bond	1	-0.03202
			Cis-	1	-1.99E-7
			Alpha	2	-0.04666

Functional groups of 4-Methyl-Trans-2-Pentene (experimental value:  $\omega = 0.2552$ ):

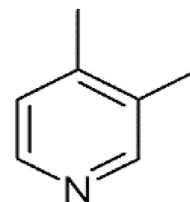


First order groups	$N_i$	$N_i\omega_i$	Second order groups	$N_j$	$N_j\omega_j$
$CH_3$ (1)	3	-0.11181	$(CH_3)_2CH-$	1	0.07806
CH (3)	1	0.17362	$CH_3-CH=$	1	0.05264
$=CH$ (2)	2	0.23038	Double bond	1	-0.03202
			Trans-	1	5.90E-4
			Alpha	1	-0.02333
			Beta	1	-0.00371

$S_{\omega 1k}$ ,  $S_{\omega 2k}$ , and  $S_{\omega 3k}$  parameters are equal for both of these isomers:

Hydrocarbon atoms	$S_{\omega 1k}$	$S_{\omega 2k}$	$S_{\omega 3k}$	
Carbon	0.49972	1.73844	−4.44512E-7	
Compounds	$\omega_{exp}$	$\omega_{pred}$	AD	%ARD
4-Methyl-Cis-2-Pentene	0.2442	0.2485	0.004	1.8
4-Methyl-Trans-2-Pentene	0.2552	0.2552	2.6E-5	0

**Example 2.** Estimation of the acentric factor of 3,4-Dimethylpyridine (experimental value:  $\omega = 0.3063$ ,  $C_7H_9N$ ).

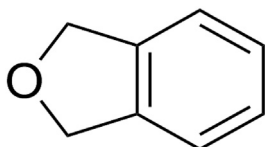


First order groups	$N_i$	$N_i\omega_i$	Second order groups	$N_j$	$N_j\omega_j$
$CH_3$ (1)	2	-0.07454	$CH_3-a \in (0-3)$	2	0.13328
$=CH$ (ds) (2)	3	0.03966	Ring	1	0.04077
$=C$ (ds) (3)	2	0.21476	$C_1$ ring	1	0.01672
$=N-$ (ds) (2)	1	0.06302	$C_2$ ring	1	5.15E-10
			$C_4$ ring	1	0.04929
			$C_1=C_2$	1	-0.02329
			$C_3=C_4$	1	1.04E-5
			$C_5=C_6$	1	0.12066
			Nitrogen	1	0.10292



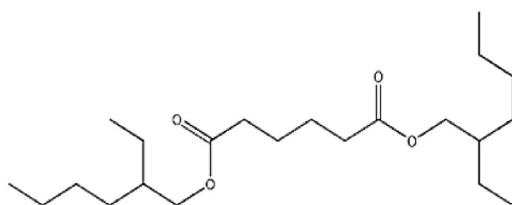
Hydrocarbon atoms	$S_{\omega 1k}$	$S_{\omega 2k}$	$S_{\omega 3k}$
Nitrogen	0.49972 −0.03445	1.73844 9.68845E-8	−4.44512E-7 −8.59833E-4
$\omega_{exp}$	$\omega_{pred}$	AD	%ARD
0.3063	0.3322	0.026	8.4

**Example 3.** Estimation of the acentric factor of Phthalan (experimental value:  $\omega = 0.372$ , C<sub>8</sub>H<sub>8</sub>O).



First order groups	$N_i$	$N_i \omega_i$		$N_j$	$N_j \omega_j$
CH <sub>2</sub> (ss) (2)	2	0.06994	Ring	2	0.08154
=CH (ds) (2)	4	0.05288	C=C	1	0.09959
=C (ds) (3)	2	0.21476	C <sub>3</sub> ring	1	0.04556
O (ss) (2) (Ether)	1	−0.13547	C <sub>1</sub> =C <sub>2</sub>	1	−0.02329
			C <sub>3</sub> =C <sub>4</sub>	1	1.04E-5
			C <sub>5</sub> =C <sub>6</sub>	1	0.12066
			Beta-5	1	0.05565
			Left ring side chain	1	0.05681
			Right ring double bond	3	−0.19641
			Oxygen	1	0.18680
<hr/>					
Hydrocarbon atoms		$S_{\omega 1k}$	$S_{\omega 2k}$	$S_{\omega 3k}$	
Carbon		0.49972	1.73844	−4.44512E-7	
Oxygen		−0.02665	−0.25404	5.40165E-4	
<hr/>					
$\omega_{exp}$		$\omega_{pred}$	AD	%ARD	
<hr/>					
0.372		0.372	2.58E-6	6.9E-4	

**Example 4.** Estimation of the acentric factor of Dioctyl Adipate (experimental value:  $\omega = 1.0598$ , C<sub>22</sub>H<sub>42</sub>O<sub>4</sub>).



First order groups	$N_i$	$N_i \omega_i$	Second order groups	$N_j$	$N_j \omega_j$
CH <sub>3</sub> (1)	4	−0.14908	CH <sub>2</sub> CH <sub>2</sub> - a,b e (0-3)	2	0.07062
CH <sub>2</sub> (2)	14	2.00172	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ...CH <sub>2</sub> -a,b,c,d,...e (0-3)	2	0.18406
CH (3)	2	0.34724	Ncarbon	12	−9.63600E-5
COO (2) (Ester)	2	0.46872	Double bond	2	−0.06404
			Oxygen	4	0.74720

Hydrocarbon atoms	$S_{\omega 1k}$	$S_{\omega 2k}$	$S_{\omega 3k}$
Carbon	0.49972	1.73844	−4.44512E-7
Oxygen	−0.02665	−0.25404	5.40165E-4
$\omega_{exp}$	$\omega_{pred}$	AD	%ARD
1.0598	1.0329	0.027	2.5

#### List of symbols

$M_w$	Molecular weight (g.mol <sup>−1</sup> )
$T$	Absolute Temperature (K)
$P$	Pressure (Pa)
$\omega$	Acentric factor
$N_k, N_i$	Number of first order groups of type $k$ and $i$ , respectively
$M_j, N_j$	Number of second order groups of type $j$
$w_{1k}, \omega_i$	The contribution values of the first order groups
$w_{2j}, \omega_j$	The contribution values of the second order groups
$S_{\omega 1}, S_{\omega 2}, S_{\omega 3}$	Adjustable parameters for prediction of $\omega$ (Eq. (3))
$S_{\omega 1k}, S_{\omega 2k}, S_{\omega 3k}$	The parameters related to each atom types
$N$	Number of data points
$N_A^*$	Number of atom types presented in the molecule except hydrogen
$N_{atoms}$	Total number of atoms in the molecule
$N_{rings}$	Number of rings in the molecule
$W$	Weight for the second order groups in the Constantinou et al. method
AD	Absolute deviation
%ARD	Percentage of absolute relative deviation
AAD	Average absolute deviation
%AAD	Percentage of average absolute relative deviation

#### Subscripts

$v_p$	Vapor pressure
$c$	Critical
$pred$	Predicted
$exp$	Experimental

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