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Prediction of the acentric factor of some halogenated hydrocarbons via group contribution techniques

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Abstract

In this study, trends in the prediction of acentric factors of halogenated alkanes (HAs) were investigated using two group contribution techniques. The examination of discrepancies between predicted and experimental values for both methods served to delineate the precision and constraints of these prediction techniques. It was observed that while predictions for certain compounds conformed closely to experimental data, others manifested substantial deviations, thereby accentuating the intricacies inherent in predicting acentric factors. The discourse extended to practical implications for applications within the realm of engineering, particularly emphasizing the imperative for the refinement of methods and the conduct of comparative analyses to enrich predictive accuracy. The academic contributions of this investigation are notable for the advancement of predictive methodologies over traditional laboratory procedures in addressing environmental concerns associated with halogenated hydrocarbons.

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1. Introduction

The design and implementation of chemical processes require the knowledge of a broad range of physical properties [1, 2]. Inability to source for experimental data of such properties makes prediction methods necessary. One of the constants widely employed in estimating physical properties of compounds is acentric factor (ω). It is particularly suitable for pure compounds and mixtures [3]. When viewed in terms of interaction between molecules, ω measures the deviation of intermolecular potential function of a pure substance from that of a simple spherical molecule. The ω of a spherical molecule approaches zero, whereas that of a long chain molecule will be considerably larger than zero. It is zero for noble gases and greater than zero for polyatomic substances [4, 5].

Acentric factor was proposed and defined by Kenneth Pitzer [6] to portray the non-sphericity of molecular interactions. A substance with ω of 0.5 is often considered to be similar to an ideal gas, while substances with ω values significantly different from 0.5 exhibit non-ideal behavior. The ω is defined as:

$$\omega = -1 - -log_{10}(Pr^{sat}) \text{ at } T_r = 0.7, \tag{1}$$

where $T_r = T/T_c$ is the reduced temperature and $P_r^{Sat} = P^{sat}/P_c$ is the reduced saturation vapor pressure. P_c is the critical pressure, P^{sat} is the vapor pressure at temperature T and T_c is the critical temperature.

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The quantitative difference between the thermodynamic properties of a particular substance and properties predicted by the Corresponding States Principle (CSP) was elucidated by Pitzer's acentric factor. CSP is particularly applicable to fluids which are made up of spherical molecules. The thermodynamic properties of fluids comprising of spherical molecules are markedly distinct from those of fluids consisting of non-spherical molecules. The ω correlates these deviations [7].

When it is not feasible to determine a property from its definition, the use of property prediction techniques becomes handy [8, 9]. Such techniques are basically of two categories: there are models that require the input of parameters like normal boiling temperature, critical temperature, critical pressure, molecular weight or relative density of the compound. In the method of Magoulas and Tassios [10], critical properties were employed and ω was associated with the number of carbon atoms for normal alkanes. Kontogeorgis *et al.* [11] developed a method to predict ω for compounds with high molecular weight. The major input was the van der Waals volume. Lin and Chao's approach [12] required relative density, molecular mass and normal boiling point of the compound. Since experimental data for these properties are not always available for many compounds; it affects their reliability and limits the extent to which such models can be employed. The other models use contributions from groups of atoms that make up the molecular structure of the pure compound or mixture [1, 4, 5, 13].

Halogenated hydrocarbons (HHCs), like chloromethane, bromomethane, and iodomethane, are a chief source of halogens in the atmosphere [14]. HHCs are regarded as xenobiotics due to their inherent anthropogenic characteristics. The presence of halogens like chlorine makes these compounds extremely toxic in comparison with conventional hydrocarbons [14]. Several HAs are used as solvents, foaming agents, refrigerants, and operational fluids for organic heat pumps and Rankine cycles. A number of these haloalkanes, especially the fluorinated alkanes, have ozone depleting or global warming tendencies [7]. The performance of HHCs in industrial applications like refrigeration systems and organic power cycles requires correct information about their thermal and physical properties. This research endeavours to predict and tackle the challenges associated with the ω of HAs through the application of Group Contribution methods (GCMs). Accurate predictions of the ω will enhance the efficiency and accuracy of process design, particularly in industries where separation processes, distillation, and phase equilibrium play pivotal roles.

2. Numerical methods

This section explains the GCMs used to forecast the ω of HAs. The two well-established procedures put forth by Tahami *et al.* [1] and Constantinou *et al.* [5] are the main emphasis.

2.1. The Approach of Tahami et al. [1]

This method incorporates a unique set of functional groups and their associated parameters, providing an alternative perspective on the estimation of ω [1]. It is represented by Equations (2) – (6).

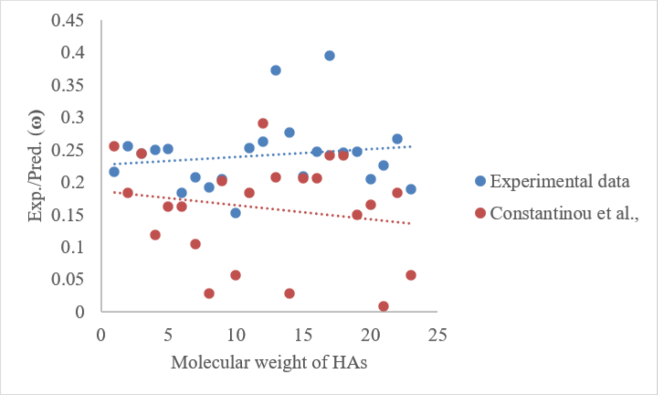

Figure 1. Comparison of experimental/predicted values of (ω) obtained by the method of Constantinou *et al.* [5] against the molecular weight of 23 HAs.

$$\omega = S_{w1}\left[ln\left(C + \sum_i N_i w_i + \sum_j N_j w_j\right)\right]^{S_{w2}} + S_{w3}\, Natoms, \tag{2}$$

$$C = 1 : 60822 + 0 : 03531 * N_{rings}, \tag{3}$$

$$S_{w1} = \sum_{k=1}^{N_A^*} S_{w1k}, \tag{4}$$

$$S_{w2} = \sum_{k=1}^{N_A^*} S_{w2k}, \tag{5}$$

$$S_{w3} = \sum_{k=1}^{N_A^*} S_{w3k}. \tag{6}$$

In these equations, Ni reveals the number of first order functional groups of type i and Nj 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 Wi, and the group contribution values for the second order functional groups of type j are designated with Wj. N_{atoms} represents the total number of atoms in the molecule, and N_{rings} represents the number of rings in the considered compound. S_{w1}, S_{w2}, and S_{w3} are the adjustable parameters. These parameters pertain to the presence of several atom types, other than hydrogen, in the chemical formula. These atom types include carbon, nitrogen, oxygen, sulfur, fluorine, chlorine, bromine, and iodine, irrespective of the quantity of each type.

2.2. The approach of Constantinou et al. [5]

This method involves a comprehensive group list and corresponding contribution values, allowing for the calculation of

Table 1. Predicted acentric factors by the GCMs.

S/N	Compound	Molecular Formular	Tahami *et al.,*	Constantinou *et al.,*
1	1,1,1-trichloroethane	$C_2H_3Cl_3$	-0.0032	0.2552
2	1,1,2-trichlorotrifluoroethane	$Cl_2FC\text{-}CClF_2$	0.0434	0.1835
3	1,1-dichloro-1-fluoroethane	$C_2H_3Cl_2F$	0.0276	0.1835
4	1,1-dichloroethane	$C_2H_4Cl_2$	0.0447	0.2443
5	1,2-dibromotetrafluoroethane	$C_2Br_2F_4$	0.6183	0.1181
6	1,2-dichlorotetrafluoroethane	$C_2Cl_2F_4$	0.0948	0.2417
7	1-chloro-1,1-difluoroethane	$C_2H_3ClF_2$	0.0737	0.1835
8	2,2-dichloro-1,1,1-trifluoroethane	$C_2HCl_2F_3$	0.1193	0.1606
9	2-chloro-1,1,1,2-tetrafluoroethane	C_2HClF_4	0.1827	0.1041
10	Bromobenzene	C_6H_5Br	0.0551	0.1619
11	Bromoethane	C_2H_5Br	0.1007	0.1619
12	Bromotrifluoromethane	CBrF3	0.0207	0.1777
13	Chlorodifluoromethane	$CHClF_2$	0.1460	0.1047
14	Chloropentafluoroethane	C_2ClF_5	0.1541	0.2545
15	Chlorotrifluoromethane	$CClF_3$	0.1170	0.2749
16	Dichlorodifluoromethane	CCl_2F_2	0.1073	0.0084
17	Dichlorofluoromethane	$CHCl_2F$	0.0858	0.1047
18	Dichloromethane	CH_2Cl_2	0.1595	0.0285
19	Ethyl chloride	C_2H_5Cl	0.0721	0.2025
20	Methyl chloride	CH_3Cl	0.0851	0.0568
21	Tetrachloromethane	CCl_4	0.0188	0.1340
22	Trichlorofluoromethane	CCl_3F	0.0529	0.2567
23	1,1,1,2,3,3-hexafluoropropane	$C_3H_2F_6$	0.2416	0.2839
24	1,1,1,2-tetrafluoroethane	$C_2H_2F_4$	0.2251	0.2656
25	1,1,1-trifluoroethane	$C_2H_3F_3$	0.1346	0.1828
26	1,1-difluoroethane	$C_2H_4F_2$	0.2373	0.2904
27	1,1-difluoroethylene	$C_2H_2F_2$	0.2373	0.2904
28	Decafluorobutane	C_4F_{10}	0.1914	0.2081
29	Difluoromethane	CH_2F_2	0.1779	0.0285
30	2-(difluoromethoxy)-1,1,1-trifluoro ethane	$C_3H_3F_5O$	0.1497	0.2486
31	Ethene, 2-chloro-1,1-difluoroethene	C_2HClF_2	0.1601	0.0084
32	Ether, bis(difloromethyl)	$C_2H_2Cl_4O$	0.2707	5.1668
33	Ethyl fluoride	C_2H_5F	0.1318	0.2067
34	Fluorobenzene	C_6H_5F	0.0056	0.2067
35	Hexafluorobenzene	C_6F_6	0.1472	0.2410
36	Hexafluoroethane	C_2F_6	0.2143	0.2410
37	Iodobenzene	C_6H_5I	0.0033	0.1498
38	Methylfluoride	CH_3F	0.1365	0.1656
39	Octafluorocyclobutane	C_4F_8	0.2027	0.0084
40	Octafluoropropane	C_3F_8	0.2336	0.2410
41	Pentafluoroethane	C_2HF_5	0.2443	0.1041
42	Pentane,dodecafluoro	C_5F_{12}	0.2505	0.2410
43	Perfluoro n-decane	$C_{10}F_{22}$	0.5995	0.2410
44	Perfluoromethylcyclopentane	C_6F_{12}	0.2358	0.0084
45	Perfluoro-n-heptane	C_7F_{16}	0.3093	0.2410
46	1,1,2,2,3-pentafluoro- propane	$C_3H_3F_5$	0.1244	0.1828
47	Tetrafluoroethylene	C_2F_4	0.1952	0.0084
48	Trifluoroiodomethane	CF_3I	0.1091	0.1654
49	Trifluoromethane	CHF_3	0.1629	0.1828
50	Vinyl fluoride	C_2H_3F	0.1019	0.0568

the ω for HAs [5]. The basic equation is:

$$\exp(w/a)^b - C = \sum_i N_i W_{1i} + \sum_j M_j W_{2j} \ , \qquad (7)$$

where W_{2j} represents the contribution of the second-order group type j, which happens M_j times in a compound, and W_{li}

Table 2. Deviations of predicted (ω) from available experimental values.

Compounds	Experimental (ω)	Deviations from Tahami *et al.*, Predictions (%)	Deviations from Constantinou *et al.*, Predictions (%)
1,1,1-trichloroethane	0.216	-101.48	18.15
1,1,2-trichlorotrifluoroethane	0.255	-82.98	-28.04
1,1-dichloroethane	0.244	-81.68	0.12
1,2-dibromotetrafluoroethane	0.250	147.32	-52.76
Bromobenzene	0.251	-78.05	-35.50
Bromoethane	0.183	-44.97	-11.53
Dichlorofluoromethane	0.207	-58.55	-49.42
Dichloromethane	0.192	-16.93	-85.16
Ethyl chloride	0.204	-64.66	-0.74
Methyl chloride	0.153	-44.38	-62.88
1,1,1-trifluoroethane	0.253	-46.80	-27.75
1,1-difluoroethane	0.263	-9.77	10.42
Decafluorobutane	0.372	-48.55	-44.06
Difluoromethane	0.276	-35.54	-89.67
Ethyl fluoride	0.209	-36.94	-1.10
Fluorobenzene	0.247	-97.73	-16.32
Hexafluorobenzene	0.395	-62.73	-38.99
Hexafluoroethane	0.245	-12.53	-1.63
Iodobenzene	0.247	-98.66	-39.35
Methylfluoride	0.204	-33.09	-18.82
Tetrafluoroethylene	0.226	-13.63	-96.28
Trifluoromethane	0.267	-38.99	-31.54
Vinyl fluoride	0.189	-46.08	-69.95

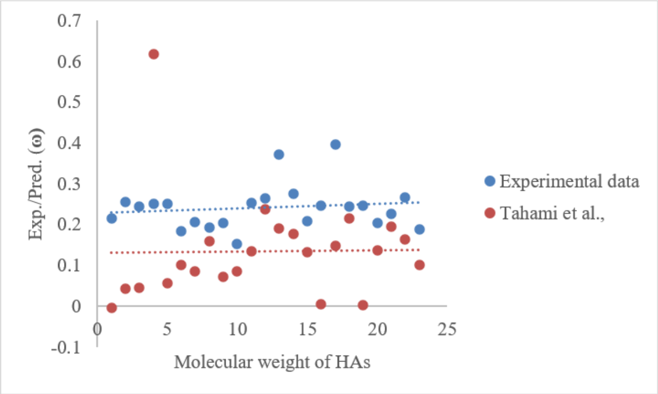

Figure 2. Comparison of experimental/predicted values of (ω) obtained by the method of Tahami *et al.* [1] against the molecular weight of 23 HAs.

represents the contribution of the first-order group type i, which occurs N_i times. In order to achieve optimal additivity of group contributions and dependable extrapolation behavior, the left-hand side of the equation was chosen to optimize the fit of the experimental data [5]. The universal quantities are a, b, and c. The first-level estimation (just a first-order approximation, so A = 0) and the second-level estimation (when both first- and second-order group contributions are included, so A = 1) are distinguished by the constant A.

3. Results and discussion

The ω values predicted by the two techniques adopted for this study are shown in Table 1. Table 2 delineates the disparities between predicted values and experimental data sourced from existing literature. These comparisons furnish insights into the accuracy and reliability of both predictive models, shedding light on potential areas for further refinement and investigation of the properties of HAs. The deviations in Table 2 were calculated according to the following relationship:

$$\text{Deviation}(\%) = \frac{Pred.\,(w) - Exp.\,(w)}{Exp.\,(w)} \times 100 \tag{8}$$

Handbook of Chemical Compound Data for Process Safety was the source of the experimental data [15].

A critical survey of the (ω) values obtained from Constantinou *et al.* [5] GCM showed that compounds like 1,1-dichloroethane and thyl chloride match up pretty well with what we find in experiments. Their differences are close to zero, which means our predictions are pretty accurate. But then there are cases like tetrafluoroethylene and dichloromethane, where the differences are quite big; such outliers are observable in Figure 1. This tells us that there is a difference in the behavior of the molecules of saturated and unsaturated compounds.

Some compounds showed higher (ω) values than expected (like 1,1,1-trichloroethane and 1,1-difluoroethane), while others showed lower values (like 1,1,2-trichlorotrifluoroethane and tetrafluoroethylene). Compounds with similar patterns of halogenation often show similar differences between predicted and experimental values [16].

The Tahami *et al.* [1] GCM yielded (ω) values for the majority of the HAs that were not significantly different from experimental data. Figure 2 shows a reasonable closeness between predicted (ω) values and available experimental data for 23 HAs.

Certain HAs showed positive deviations, which suggest overestimation, while others showed negative deviations, which indicate underestimation. HAs with very high deviations, such as 1,2-dibromotetrafluoroethane, hexafluorobenzene, and iodobenzene, receive special mention here. These cases highlight possible drawbacks or difficulties with the Tahami *et al.* technique. Generally, prediction models show varying degrees of weakness with an increase in chain length and different stereoisomers of organic molecules [17].

Statistical analysis using Pearson correlation coefficients to compare the (ω) values of the twenty-three HAs in Figure 1 was done. The correlation matrix showed that the (ω) values obtained from Tahami *et al.* [1] and Constantinou *et al.* [5] methods had a Pearson correlation coefficient of -0.152 with a non-significant p-value of 0.489. There isn't a strong correlation between these two prediction methods. Conversely, a Pearson correlation coefficient of 0.395 with a p-value of 0.062 obtained from the correlation of experimental data with Constantinou *et al.* [5] values, which is just above the traditional significance threshold, suggests a positive and rather substantial correlation.

On the other hand, the correlation between experimental data and values from the Tahami *et al.* [1] technique yielded a non-significant p-value of 0.398 and a Pearson correlation coefficient of 0.185. This result implies a non-substantial correlation.

4. Conclusion

There are numerous safety and environmental risks associated with halogenated hydrocarbons. Predictive techniques promote efficiency, sustainability, safety, and regulatory compliance when incorporated into the compound development process. Properties like stability and solubility, which are essential for the safe handling and formulation of chemicals, can be estimated via prediction models. These techniques can lower the need for animal testing by precisely forecasting safety profiles, which are compliant with ethical guidelines and less expensive.

The study considered two GCMs for the prediction of (ω). The method of Constantinou *et al.* [5] outperformed the technique presented by Tahami *et al.* [1] for the HAs considered. The latter however, showed impressive accuracy for certain compounds, especially stereoisomers with good agreement between predicted and experimental values. However, observed disparities in certain compounds highlight the intricacies that existing prediction algorithms may fail to reflect effectively. Both methods yielded a wide range of predicted (ω), with significant departures from experimental values across several HAs. The method of Constinou *et al.* [5] requires refinement and additional parameters to address the differences between certain stereoisomers. The Tahami *et al.* [1] method is somewhat cumbersome. The several stages in the operation can be abridged to reduce overestimation or underestimation of (ω).

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