Scientific Paper

MASS-MODIFIED WIENER INDICES AND THE BOILING POINTS FOR LOWER CHLOROALKANES

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Abstract

A criterion for obtaining the chemical graph of a chloroalkane has been proposed by replacing the edge vertex containing CH_3 group with covalently bonded chlorine atom. By introducing α as the group mass ratio of Cl to CH_3 as well as a molecular mass factor $M = M(\alpha, n, n_C)$, a mass-modified Wiener index has been proposed as $W_m = M^P W$ where W is the Wiener index obtainable from the chemical graph, whilst n and n_C correspond to the number of chlorine and carbon atoms respectively in the chloroalkane molecule. The mass factor is defined in such a manner that $W_m = W$ for alkanes in order to maintain consistency. Numerical trials on the boiling point versus Wiener index plane reveal that when $P = 2$ the chloroalkane curve shifts such that it coincides with the alkane curve. In view of the highly established empirical equation for alkanes it is suggested herein that, instead of obtaining separate empirical curves for haloalkanes, there is a good potential for boiling points of haloalkanes be obtainable based on the philosophy of mass factor in order to take advantage of the highly established empirical models of alkanes.

Key words: boiling points, chloroalkanes, mass modification, Wiener index

Introduction

In spite of being in existence for the past 6 decades,[1-5] interest in the Wiener and Wiener-like indices continue to flourish to this day.[6-20] Although being initially applied for correlating with the boiling point of alkanes,[1] the Wiener index has sparked interest in the general application of Quantitative Structure-Activity Relationship (QSAR) and Quantity Structure-Property Relationship (QSPR) for other types of molecules. For example:

(a) Castro et al.[21] applied the Wiener index, the Schultz index and the Randić connectivity index to find the correlation between the boiling point of saturated alcohols and these three indices;[17,21]

(b) Roy et al.[22] used a type of Quantity Structure-Toxicity Relationship (QSTR) to model the toxicity of nitrobenzenes;

(c) Farkas et al.[23] applied Quantitative Structure-Retention Relationship (QSRR) to predict gas chromatographic retention indices for saturated O-, N- and S-heterocyclic compounds; and

(d) A Wiener index for cyclic structures was proposed by Randić.[10]

Recently Charton et al.[24] appreciated the fact that topological parameters for haloalkanes and haloalkenes are function of some combination of polarizability, dipole moment, the number of halogen atoms of each type, and the ratio of the number of branches to the number of atoms along the main polymer chain. In a series of paper, Yang et al.[25-28] demonstrated the usefulness of the vertex electronegativity, the normalized bond length, and the difference of interaction of electrons in the two vertices. The results exhibit good prediction of the retention index of gas chromatography of hydrocarbons, the standard formation enthalpy of methyl halides, halogen-silicon and inorganic compounds containing transition metals. In this paper, we introduce a mass-modified Wiener index for chloroalkanes whereby the atomic mass of chlorine atoms are taken into consideration for correlating with the boiling points of lower chloroalkanes.

Analysis

Although the Wiener index was first defined by Wiener to obtain the sum of distances between carbon atoms in saturated hydrocarbons,[1] it was Hosoya who introduced the formula for Wiener index

$$W = \frac{1}{2}\sum_{i,j=1}^{n} S_{ij} \tag{1}$$

using the distance matrix

$$S_{ij} = \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1n} \\ S_{21} & S_{22} & \cdots & S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ S_{n1} & S_{n2} & \cdots & S_{nn} \end{bmatrix} \tag{2}$$

Customarily, the vertices refer to carbon atoms but not hydrogen atoms. Although halogen compounds are those whereby at least one hydrogen atom is replaced by a halogen atom, these halogen atoms are considered herein as vertices, unlike hydrogen atoms. The justification for such decision is that the halogen atoms are heavier than hydrogen and even the carbon atom. It follows that the halogen atoms need to be differentiated from the carbon atoms. Since it is customary that the carbon atom is considered as a vertex without any weight attached to it, we herein let the carbon atom be of unit weight such that the chlorine atoms are proportionately weighted. As such, we introduce the mass modified Wiener index

$$W_m = M^P W \tag{3}$$

with the molecular mass ratio defined as

$$M = \frac{\alpha n + n_C}{n + n_C} \tag{4}$$

where n =number of chlorine atoms, n_C =number of carbon atoms and α is the mass ratio of the chlorine atom to the CH_3 group,

$$\alpha = \frac{m}{m_C + 3m_H} \tag{5}$$

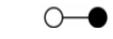
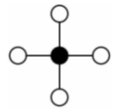
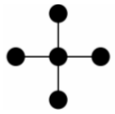
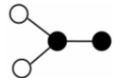
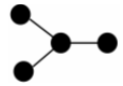
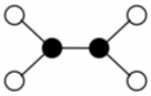
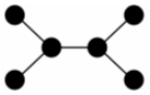
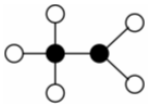
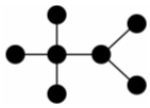
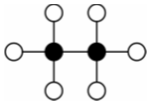
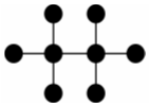
in which m =chlorine atomic mass, m_C =carbon atomic mass and m_H =hydrogen atomic mass. We appreciate the fact that hydrogen mass appears in Equation (5) because this equation considers the replacement of CH3 group with chlorine atom, whilst the hydrogen atom is not considered in Equation (4) due to the neglect of hydrogen atoms as vertices. Table 1 shows the molecular structure and boiling points of chloromethanes and chloroethanes with their corresponding alkanes on the basis of similarity in chemical graphs.[30-33]

Results and discussion

Substituting $m = 35.453$, $m_C = 12.011$ and $m_H = 1.0079$ into Equation (5) gives the Cl-to-CH_3 group mass ratio as $\alpha = 2.358$. Based on this ratio with the number of chlorine and carbon atoms as shown on the left column of Table 1, the molecular mass ratio M is obtained from Equation (4). Needless to say, the molecular mass ratio for alkanes is $M = 1$. Plots of the boiling point in absolute temperature, T_b, versus the

fourth root of the Wiener index for both chloroalkanes and alkanes are furnished in Figure 1.

Table 1. Chloroalkanes and alkanes arranged according to molecular graph with their corresponding boiling points.[30-33]

Chloroalkanes			Alkanes		
Structure	Name	$T_b\,(K)$	Structure	Name	$T_b\,(K)$
	Chloromethane	248.95		Ethane	184.55
	Dichloromethane	312.95		Propane	231.05
	Trichloromethane	334.85		2-methylpropane	261.45
	Tetrachloromethane	349.65		2,2-dimethylpropane	282.65
	Chloroethane	285.45		Propane	231.05
	1,1-dichloroethane	330.45		2-methylpropane	261.45
	1,2-dichloroethane	356.65		Butane	272.65
	1,1,2-trichloroethane	386.95		2-methylbutane	301.05
	1,1,2,2-tetrachloroethane	419.35		2,3-dimethylbutane	331.15
	Pentachloroethane	435.15		2,2,3-trimethylbutane	354.05
	Hexachloroethane	460.15		2,2,3,3-tetramethylbutane	373.96

We observe that data from these two classes of molecules give two separate and distinct data points, whereby for equal Wiener index, chloroalkanes exhibit higher boiling points. It is interesting to note that when we select $P = 2$ in Equation (3), the resulting mass-modified Wiener indices for chloroalkanes increases in such a manner that the corresponding data points fall on the same linear regression as those of alkanes, as shown in Figure 2. The best fit line gives

$$T_b = 92.846\sqrt{M\sqrt{W}} + 111.31 \tag{6}$$

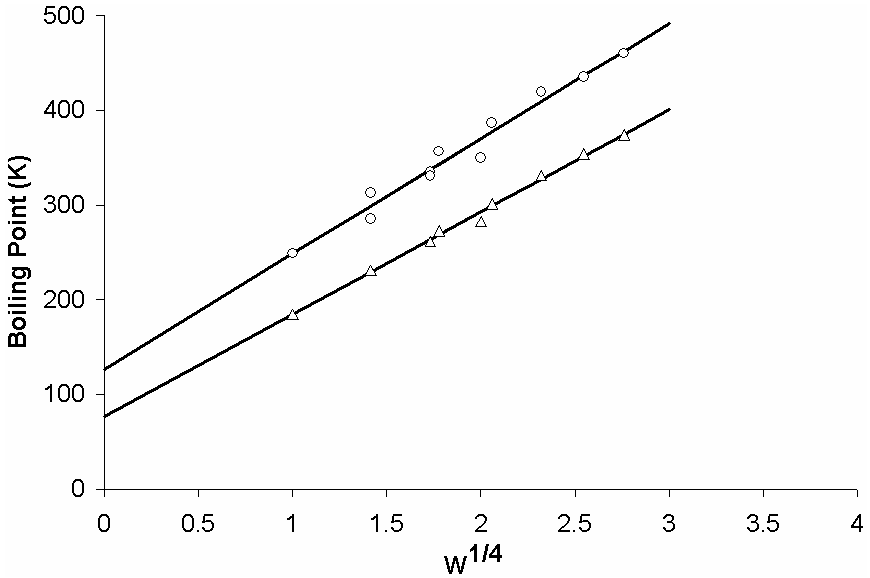


Figure 1. Boiling point of chloroalkanes (circles) and alkanes (triangles) plotted against fourth root of Wiener index.

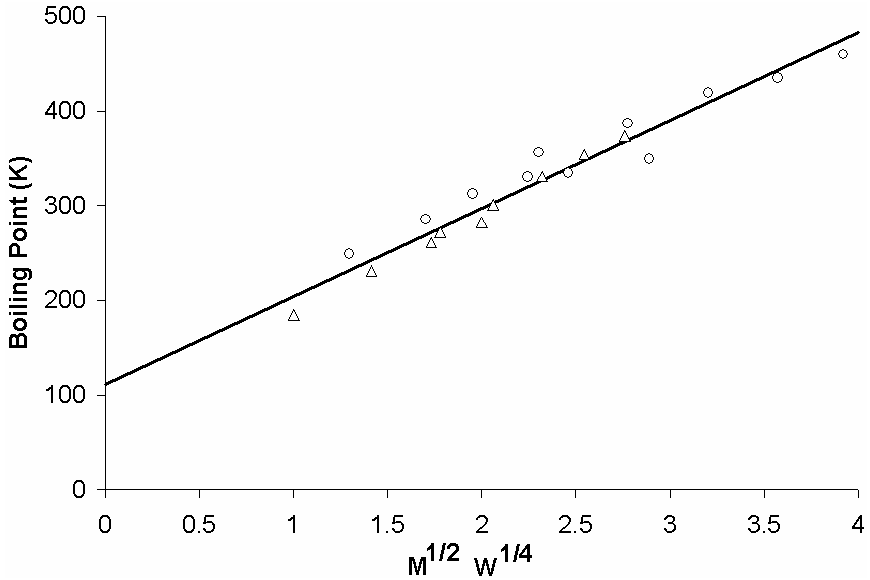


Figure 2. Boiling point of chloroalkanes (circles) and alkanes (triangles) plotted against product of square root of molecular mass ratio and fourth root of Wiener index.

With reference to Figure 3, an improved curve-fit can be obtained when the boiling points are plotted against $W^{0.2283}$ (in which the power 0.2283 has been suggested by Mihalić and Trinajstić),[32] whereby the power of $P = 2$ in Equation (3) is retained. Not surprisingly, a lower index would result in a higher slope, as can be seen in the following curve-fit result,

$$T_b = 109.51\left(M^2W\right)^{0.2283} + 91.524 \tag{7}$$

That Equation (7) appears to exhibit close resemblance to the empirical equation by Mihalić and Trinajstić,[32]

$$T_b = 108.6W^{0.2283} + 95.15 \tag{8}$$

in absolute temperature further suggests that empirical equations of alkanes be used for chloroalkanes by incorporating M. Both exponents of the Wiener index, i.e. 0.25 and 0.2283, were selected due to their capability in producing linear [plots of boiling points versus $W^{1/4}$ or $W^{0.2283}$. The former exponent is convenient whilst the latter was obtained via regression analysis from numerous data of alkanes.

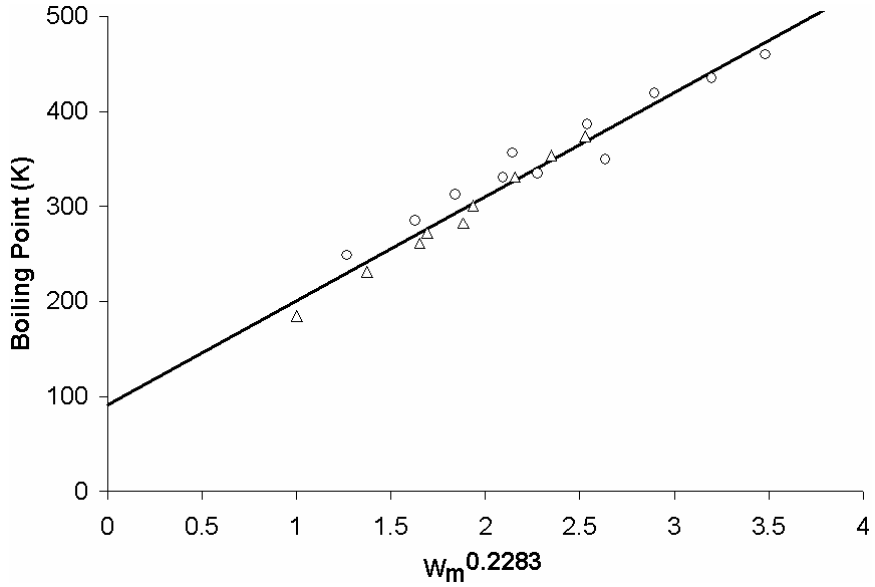


Figure 3. Boiling point of chloroalkanes (circles) and alkanes (triangles) plotted against $W_m^{0.2283}$ whereby $W_m = M^2W$.

Conclusions and Suggestions

A molecular mass modification to the Wiener index has been introduced whereby a factor M is the ratio of the chloroalkane mass in reference to a graph-similar alkane mass. Whether raised to a power of 0.25 or 0.2283, multiplication of the Wiener index with the square of M enables the collapse of chloroalkane data points onto the alkane regression fit. This implies that instead of obtaining a separate empirical equation for haloalkanes, there exists the possibility of extending the empirical equation of alkanes –

which are highly established – for application in haloalkanes by simply factoring the molecular mass ratio M raised to a certain power. In the present paper, a power of 2 has been shown to be suitable for the special case of lower chloroalkanes. Further refinements can be made by considering higher chloroalkanes and their corresponding graph-similar alkanes. Having demonstrated the suitability of the molecular mass ratio in aligning the T_b versus M^2W curve for chloroalkanes, it is suggested that similar work be performed for other haloalkanes in obtaining the parameters P for aligning their T_b versus M^2W curves to that of alkanes.

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Povzetek

Za pripravo kemijskega grafa kloroalkana se kovalentno vezan klorov atom predstavi kot skupino CH_3. Uvede se α kot masno razmerje med Cl in CH_3, molekulski masni faktor M $M = M(\alpha, n, n_c)$ ter masno spremenjeni Wienerjev indeks $W_m = M^P W$, kjer je W Wienerjev indeks, ki ga dobimo iz kemijskega grafa, medtem ko sta n in n_c število klorovih odnosno ogljikovih atomov v molekuli kloroalkana. Masni faktor je definiran tako, da je za alkane $W_m = W$. Če izberemo P=2, se na diagramu vrelišč proti Wienerjevemu indeksu krivulja kloroalkanov premakne tako, da sovpada s krivuljo alkanov. Ker je empirična enačba za vrelišča alkanov dobro uveljavljena, so dobri tudi obeti za ugotavljanje vrelišč haloalkanov s pomočjo masnega faktorja in empiričnih modelov za vrelišča alkanov.