Correlation of Retention Indices with van der Waals' Volumes and Surface Areas: Alkanes and Azo Compounds

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Key Words

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Summary

Van der Waals' volumes (V_W) and surface areas (S_W) of alkanes, (E)-azoalkanes and structurally similar alkenes (R_1–X = X–R_2, X = N, CH) were calculated by a semi-empirical quantum-chemical method (AM1). The calculated data are in reasonable agreement with the experimental values of Bondi and good correlations were found between the calculated data and Kovats' retention indices (I_R). While the V_Ws of alkanes with the same carbon number are very close to one another, the S_Ws follow the scatter of the I_R values for branched alkanes. The difference in the I_R of (E)-azo compounds and the structurally similar alkenes can be explained by the difference in V_Ws.

Introduction

Gas-chromatographic retention indices are of fundamental importance in qualitative gas-chromatographic analysis. James and Martin [1] found a significant correlation between chromatographic retention and carbon number in a homologous series of compounds (alkanes). The retention behaviour of a substance on a given stationary phase can be characterized by the Kovats' retention index (I_R) system [2]. I_R can be used as an experimental measure of the extent of molecular branching in a series of alkanes [3, 4]. On an apolar phase, the interaction of an apolar solute depends on London dispersion forces. The strength of this type of interaction is proportional to the number of electrons in the molecule. Thus, the surface area or the volume of the molecule increases with increasing dispersion forces.

Molecular surface areas have been determined from solubility data and characterized by the cavity surface area in the solvent [5–7]. The molecular shape, characterized by the "shadow area" (projected molecule, covered by its van der Waals' surface, on a plane) calculated theoretically, also correlated with I_R [8].

Bondi [9] calculated the molecular volumes and surface areas ['van der Waals' volumes (V_W) and surface areas (S_W)'] from the recommended non-metallic van der Waals' radii from X-ray diffraction data. An evaluation of the data for hydrocarbons yielded group contributions to V_W and S_W. The hard-sphere volumes were derived from an analysis of the high-pressure equation of state data by Ben-Amotz and Willis [10], and new volume increments for short-chain and long-chain compounds were proposed. Several authors have correlated I_R with V_W [11–19] and I_R with S_W [20]. The surface area and the Randic index [21] correlate closely [22, 23]. Good correlations were also found between V_W, S_W and the Wiberg index [24].

Calixto and Raso [3] estimated V_W for branched and highly branched alkanes with known I_Rs on the basis of the I_R against V_W dependence of n-alkanes (determined by Bondi [9]). The V_Ws obtained are different from those estimated by Bondi [9].

Correlations were found between I_Rs and boiling points, and between differences in I_Rs and differences in boiling points of azo compounds and structurally similar related alkenes (R_1–X = X–R_2, X = N, CH) [25].

V_W and S_W are not directly measured quantities experimentally. Quantum-chemical methods give the prediction of V_W and S_W. In this article correlations of theoretically calculated V_Ws and S_Ws with I_Rs are discussed.

Calculations

The fully optimized geometries of the compounds were calculated for the estimation of V_W, S_W and some other molecular properties (dipole moments, net atomic charges, ionization potentials) by the semi-empirical quantum-chemical method AM1 (Austin Model 1) [26]. Calculations were performed by the software package PcMOL [27, 28]. V_W and S_W of one of the most or the

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most stable conformers were calculated by the Gavezzotti method [29, 30], including PcMOL. The total molecular surface area (volume) was calculated from the sum of the free atomic surface areas (volumes). In the calculations 15000–20000 points/atom were used with the van der Waals' radius (for H 118.5 pm, C 175.0 pm and N 152.5 pm). The average estimated errors in the calculation of S_W and V_W were less than 1.5 % and 0.5 % [29, 30], respectively. For some molecules studied with different conformers however, the difference in S_W and V_W was found to be about 5–8 % and 1 %, respectively. The S_Ws of 2-methylbutane with 1 gauche and 2 gauche interactions are 131.1×10^4 pm^2 and 124.5×10^4 pm^2, respectively. The V_Ws of the same conformers are 96.4×10^6 pm^3 and 96.7×10^6 pm^3, respectively. The more strongly branched the hydrocarbons, the greater are the differences. The geometries of the azo compounds studied were optimized from analogous conformations determined by *ab initio* calculations [31].

Geometry optimization and S_W calculations were also performed for alkanes by molecular mechanics, method PCMODEL [32]. The calculated S_Ws were greater by about 8–10 % for smaller molecules and less by about 5 % for C_7–C_9 molecules than that of calculated by means of PcMOL.

Calculations of correlations were performed and the Figures were drawn by means of PSI-PLOT [33] and DRUGIDEA 2.1 [34].

Results and Discussion

Alkanes

The calculated V_Ws and S_Ws with the I_Rs [35, 36] are listed in Table I. The V_W and S_W data, estimated for some alkanes by the Bondi model [9] or the hard-sphere model [10], the values proposed by Calixto and Raso [3] and those calculated here by the semi-empirical quantum-chemical method AM1 are in Table II. The S_Ws of branched alkanes are about 10 % larger than those calculated by the Bondi additivity rule [9], while the V_Ws are in good agreement with those in Refs. [9, 10]. The data in Ref. [3] are generally lower for branched alkanes.

As expected, the new V_Ws and S_Ws are in good agreement with I_R:

$$I_R = (-48.9 \pm 15.3) + (5.43 \pm 0.11)\, V_W \qquad (1)$$

$$r = 0.989,\ s = 25.6,\ F = 2483,\ MSC = 3.75,\ n = 58$$

$$I_R = (-105.5 \pm 17.6) + (4.48 \pm 0.10)\, S_W \qquad (2)$$

$$r = 0.987,\ s = 27.2,\ F = 2183,\ MSC = 3.62,\ n = 58$$

where r = correlation coefficient, s = standard error, n = number of compounds studied, F is result of Fischer test, and MSC ('model selection criterion') characterizes adequacy of the model, i.e. compares two competing models for the same observed data set [33]. The greater the value of MSC, the more adequate is the model. V_W is in 10^6 pm^3 and S_W is in 10^4 pm^2. The data are depicted in Figures 1 and 2.

Table I. Kovats' retention indices on squalane at 50 °C and calculated van der Waals' surface areas and volumes of alkanes studied[1].

Compounds	I_R	$10^{-4}\, S_W$ pm^{-2}	$10^{-6}\, V_W$ pm^{-3}
Methane	100.0	45.7	28.9
Ethane	200.0	69.1	45.7
Propane	300.0	91.9	63.1
2-M-propane	365.7	108.3	79.5
Butane	400.0	114.2	79.5
2,2-DM-propane	412.6	123.9	96.1
2-M-butane	474.9	131.5	96.5
Pentane	500.0	137.2	96.7
2,2-DM-butane	536.6	144.6	112.8
2,3-DM-butane	567.6	145.9	113.0
2-M-pentane	569.5	156.6	113.1
3-M-pentane	584.0	156.9	113.5
Hexane	600.0	160.4	113.7
2,2-DM-pentane	625.9	166.9	130.1
2,4-DM-pentane	629.9	169.8	130.3
2,2,3-TM-butane	639.8	161.1	129.5
3,3-DM-pentane	658.9	164.4	129.3
2-M-hexane	666.9	177.3	130.4
2,3-DM-pentane	671.7	169.1	129.5
3-M-hexane	676.2	178.8	130.7
3-E-pentane	685.9	167.1	129.9
2,2,4-TM-pentane	690.1	180.9	146.7
Heptane	700.0	183.0	130.5
2,2-DM-hexane	719.7	189.5	147.1
2,2,3,3-TeM-butane	726.1	169.9	145.3
2,5-DM-hexane	728.5	192.4	146.8
2,4-DM-hexane	732.1	193.2	147.4
2,2,3-TM-pentane	737.3	182.9	146.3
3,3-DM-hexane	743.7	186.5	146.5
2,3,4-TM-pentane	752.5	186.0	145.9
2,3,3-TM-pentane	759.8	183.0	145.7
2,3-DM-hexane	760.4	191.5	146.6
2-M-3-E-pentane	761.6	184.9	145.9
2-M-heptane	764.8	202.0	147.3
4-M-heptane	767.5	202.2	147.7
3,4-DM-hexane	770.9	190.6	146.5
3-M-heptane	772.2	203.3	146.9
3-E-hexane	772.9	187.8	147.1
2,2,5-TM-hexane	776.7	207.7	163.5
2,2,4-TM-hexane	789.5	202.2	163.4
Octane	800.0	205.7	147.5
2,4,4-TM-hexane	808.2	198.3	163.3
2,3,5-TM-hexane	812.4	205.0	163.0
2,4-DM-heptane	821.5	214.5	163.4
2,2,3-TM-hexane	821.9	207.3	162.5
2-M-4-E-hexane	824.3	203.3	163.9
4,4-DM-heptane	827.6	209.4	163.1
2,5-DM-heptane	832.9	215.6	163.4
3,5-DM-heptane	833.7	216.9	163.5
2,3,3-TM-hexane	840.0	205.2	162.5
2-M-3-E-hexane	843.7	208.2	162.9
2,3,4-TM-hexane	846.6	201.4	163.0
3,3,4-TM-hexane	853.1	203.7	162.0
3-M-3-E-hexane	853.5	210.0	162.9
3-M-4-E-hexane	854.8	207.3	162.8
3,4-DM-heptane	858.4	213.5	163.3
4-M-octane	863.1	223.8	164.1
Nonane	900.0	228.6	164.4

[1] M: methyl; DM: dimethyl; TM: trimethyl; TeM: tetramethyl, E: ethyl. I_rs from Refs. [35, 36].

Table II. Calculated and estimated van der Waals' surface areas and volumes of some alkanes studied.

Compounds	10^{-4} *S*w pm^{-2}		10^{-6} *V*w pm^{-3}			
	1	**2**	**1**	**2**	**3**	**4**
Methane	45.7	48.1	28.9	28.4	28.4	-
Ethane	69.1	70.4	45.7	45.4	45.4	39.3
2-M-propane	108.3	115.1	79.5	79.4	74.5	72.9
Pentane	137.2	137.6	96.7	96.4	96.4	91.9
2,2-DM-butane	144.6	163.2	112.8	113.3	101.3	106.7
2,3-DM-butane	145.9	159.7	113.0	113.3	106.3	110.4
2-M-pentane	156.6	160.0	113.1	113.3	108.5	110.5
3-M-pentane	156.9	160.0	113.5	113.3	109.8	110.5
Hexane	160.4	160.1	113.7	113.4	113.4	110.7
2,2,3-TM-butane	161.1	185.5	129.5	130.3	118.7	125.4
3,3-DM-pentane	164.4	185.6	129.3	130.3	121.9	125.6
2-M-hexane	177.3	182.3	130.4	130.4	125.4	129.4
2,3-DM-pentane	169.1	182.1	129.5	130.3	124.6	129.2
2,2,4-TM-pentane	180.9	207.9	146.7	147.3	127.8	144.2
2,2-DM-hexane	189.5	208.0	147.1	147.3	135.3	144.4
2,2,3,3-TeM-butane	169.9	211.2	145.3	147.3	134.6	140.4
2,4,4-TM-hexane	198.3	230.3	163.3	164.3	148.3	163.1
2,3,5-TM-hexane	205.0	226.8	163.0	164.3	151.1	166.7
2,4-DM-heptane	214.5	227.0	163.4	164.3	153.2	166.9
3,3,4-TM-hexane	203.7	230.3	162.0	164.3	157.5	163.1
3,4-DM-heptane	213.5	227.0	163.3	164.3	159.9	166.9
Octane	205.7	204.9	147.5	147.3	147.3	148.3

1: quantum-chemical calculations, present work; **2**: [9]; **3**: [3]; **4**: [10].

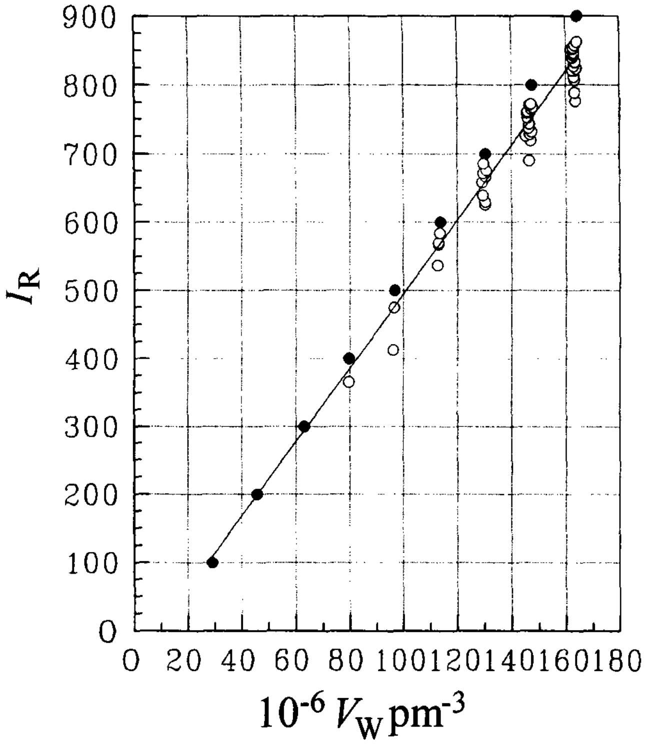

Figure 1
Correlation between Kovats' retention indices (I_R) of hydrocarbons and calculated van der Waals' volumes (V_W). ●: n-alkanes.

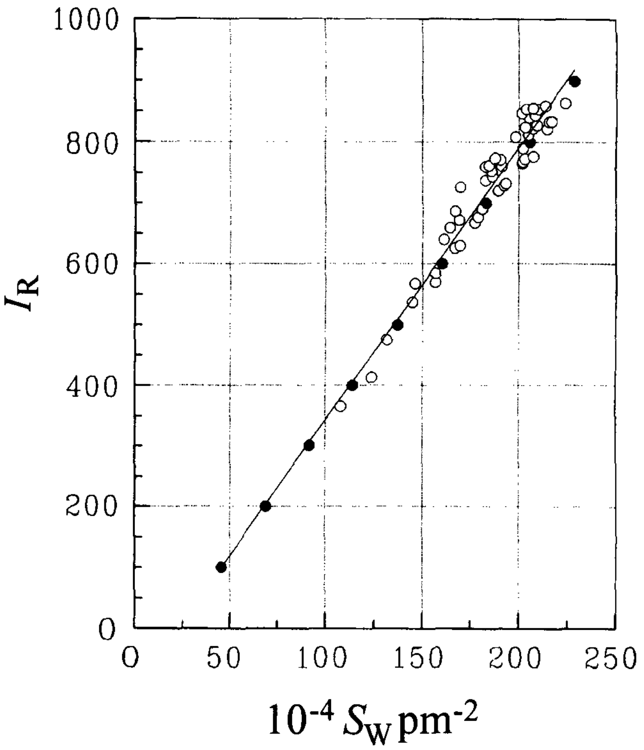

Figure 2
Correlation between Kovats' retention indices (I_R) of hydrocarbons and calculated van der Waals' surface areas (S_W). ●: n-alkanes.

Averaged difference in I_R between the experimental and predicted values calculated via Eqs (1) and (2) for the molecules studied is 20.2 ± 15.1 (standard error 1.98) and 22.8 ± 14.1 (standard error 1.85), respectively. MSCs are only slightly less in the one-parameter linear fitting of I_R and V_W, S_W (3.61 and 3.15, respectively), which suggest that the two-parameter linear model is slightly better statistically for describing the dependence than the single parameter one.

Though the statistics are similar for I_R vs. V_W or S_W plots, the points in the I_R vs. S_W plot are more uniformly distributed than those in the I_R vs. V_W, where the points are crowded (Figures 1 and 2). Figures 1 and 2 show that, while the S_Ws vary roughly continuously with increasing branching, the V_Ws for compounds with the same carbon number are very close to one another and I_R vs. V_W changes in a stepwise manner with increasing carbon number.

Azo Compounds and Structurally Similar Alkenes

Some calculated and experimental molecular properties of (*E*)-azoalkanes [25] and structurally similar alkenes are listed in Table III. The calculated data, lead to the following equations for the I_R vs. V_W and I_R vs. S_W plots:

$$I_R = (125.2 \pm 49.6) + (4.5 \pm 0.4)\, V_W \qquad (3)$$

$$r = 0.955,\ s = 38.1,\ F = 125,\ MSC = 2.15,\ n = 14$$

$$I_R = (7.7 \pm 29.9) + (3.8 \pm 0.2)\, S_W \qquad (4)$$

$$r = 0.988,\ s = 19.6,\ F = 503,\ MSC = 3.47,\ n = 14$$

The averaged differences in I_R between experimental and predicted values calculated via Eqs (3) and (4) for the azo compounds studied, are 25.8 ± 24.9 (standard error is 6.64) and 14.4 ± 11.4 (standard error 3.05), respectively. The values of MSC for one-parameter linear fitting of V_Ws and S_Ws are 1.86 and 3.61, respectively, which differ only slightly from MSC in the two-parameter model.

The linear correlations between experimental boiling points and calculated V_Ws and S_Ws were

$$\text{B.p.} = (-73.8 \pm 14.0) + (1.32 \pm 0.11)\, V_W \qquad (5)$$

$$r = 0.959,\ s = 10.7,\ F = 136,\ n = 14$$

$$\text{B.p.} = (-107.9 \pm 8.5) + (1.13 \pm 0.05)\, S_W \qquad (6)$$

$$r = 0.989,\ s = 5.6,\ F = 535,\ n = 14$$

A less satisfactory correlation was obtained between the ionization potential (I_p) and I_R of azo compounds:

$$I_R = (11662 \pm 2170) - (1169 \pm 231)\, I_p \qquad (7)$$

$$r = 0.825,\ s = 72.5,\ F = 26,\ MSC = 0.82,\ n = 14$$

The differences in the corresponding I_Rs of azo compounds and alkenes were found to correlate with the differences in boiling points [25]. The differences between the I_Rs (ΔI_R), S_Ws (ΔS_W) and V_Ws (ΔV_W) of the alkenes and the structurally similar (*E*)-azo compounds are 27.8 ± 5.0, and 9.9 ± 0.8, respectively. ΔI_R depends linearly on the differences ΔS_W and ΔV_W. The slope of the ΔI_R vs. ΔV_W plot is 2.80 ± 0.63. From the known I_R, for an alkene, I_R for the structurally similar azoalkanes can be predicted.

Conclusion

Good correlations were found between the calculated van der Waals' surface areas and volumes and the Kovats' retention indices of alkanes, alkenes and azo com-

Table III. Kovats retention indices at 50 °C on methyl silicone and calculated van der Waals' surface areas and volumes of trans azo compounds and structurally similar alkenes (R_1–X = X–R_2, X = N, CH), calculated by AM1[1].

Compounds		I_R exp.	S_W/ 10^4 pm^2	V_W/ 10^6 pm^3	I_p/ eV	I_R	S_W/ 10^4 pm^2	V_W/ 10^6 pm^3
R_1	R_2	(*E*)-azo compounds				Alkenes		
CH_3	CH_3	386.8	101.4	63.9	9.597	409.9	116.3	74.6
CH_3	C_2H_5	481.7	124.1	81.8	9.524	507.2	134.5	91.8
C_2H_5	C_2H_5	571.9	147.1	98.2	9.452	601.3	152.9	108.0
C_2H_5	2-C_3H_7	624.1	159.8	116.0	9.422	654.1	168.8	125.1
CH_3	i-C_4H_9	642.2	168.1	115.2	9.449	666.5	181.1	125.2
2-C_3H_7	2-C_3H_7	669.8	176.4	132.0	9.314	703.7	182.7	141.7
C_2H_5	1-C_3H_7	670.4	170.4	115.2	9.426	694.0	177.2	125.1
2-C_3H_7	*t*-C_4H_9	710.7	194.0	149.4	9.281	–	205.1	158.7
2-C_3H_7	1-C_3H_7	721.4	182.5	131.7	9.356	750.7	191.9	143.0
C_2H_5	2-C_4H_9	723.1	178.6	132.6	9.415	762.9	188.5	141.8
C_2H_5	i-C_4H_9	731.7	190.6	132.9	9.381	755.6	200.4	142.0
1-C_3H_7	1-C_3H_7	768.9	192.7	132.0	9.398	792.8	201.6	141.7
C_2H_5	1-C_4H_9	769.4	192.8	131.1	9.425	795.8	193.7	142.7
2-C_4H_9	2-C_4H_9	868.4	228.7	166.9	9.279	–	225.0	176.1

pounds. Van der Waals' volumes estimated on the basis of the Bondi additivity rule are in excellent agreement with the values calculated in this work. The polar effects are not significant for these compounds. It seems that the calculated V_{WS} of alkanes do not reflect the differences in the I_{RS} of branched molecules, while the S_{WS} decrease more or less regularly with the I_{RS}. Correlations were found between the differences in the van der Waals volumes, surface areas and Kovats' retention indices of azo compounds and the structurally similar alkenes.

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