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Research Article

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Investigating the Van Der Waals Equation "A" and "B" Parameters for Hydrocarbons (C₁ to C₂₄) by Computational Modelling

Robson Fernandes de Farias

Universidade Federal do Rio Grande do Norte, Cx. Postal 1664, 59078-970, Natal-RN, Brasil

Abstract In the present work, it is performed a computational chemistry study involving hydrocarbons, from C₁ (methane) to C₂₄ (tetracosane), in order to correlate *a* and *b* parameters of van der Waals equations with polarizability and molecular volume, as well another molecular parameters. The computations were performed usingSpartan'14 (version 1.1.8) by a Density Functional (DFT) method (B3LYP level, 6-31G* basis set, 6-31G* optimized geometry, in vacuum). Linear relationship between *a* andpolarizability, as well as *b* and volume, are observed. The energies of frontier molecular orbital (ϵ HOMO, ϵ LUMO), energy band gap (ϵ LUMO- ϵ HOMO), electronegativity (χ), chemical potential (μ), global hardness (η), global softness (*S*), and global electrophilicity index (ω) were calculated. It is verified that the values of energy gap, and, mainly, η , *S* and ω (this last one, mainly) suffers very small variations or no variations at all, to higher hydrocarbons. So, as the number of carbons increases, the parameters that can be related with attractive and repulsive forces (and related, of course, with *a* and *b* values, both related, in a last reasoning, with the higher or lower deformability of the electron clouds), tends to a "stabilization", making the linear relationship no longer so pronounced.

Keywords Hydrocarbons; Density functional; van der Waals equation; Polarizability

Introduction

The van der Waals equation it is one of the most employed to describe and predict the behaviour of gases when the ideal gas premises are not present in a given system:

 $(\mathbf{P} + a/\mathbf{V}^2) (\mathbf{V} - b) = \mathbf{n}\mathbf{R}\mathbf{T}$

In this equation, coefficients a and b are related with a correction for pressure and volume, respectively. In a broad sense, a is related with the intermolecular attractive forces, whereas b is related with the intermolecular repulsive forces, depending on effective molecular volume.

The van der Waals coefficients a and b are empirically obtained, or can be estimated by using Lennar-Jones parameters, for example [1].

Since to obtain a and b experimental values, specific experimental apparatus and skills (not available everywhere) are required, chemical computations can provide a relatively simple and easy way to obtain reliable values for such parameters.

In the present work, it is performed a computational chemistry study involving hydrocarbons, from C_1 (methane) to C_{24} (tetracosane), in order to correlate the *a* and *b* parameters of van der Waals equations with polarizability and molecular volume, as well another molecular parameters.

Methods

The computations were performed usingSpartan'14 (version 1.1.8) [2] by a Density Functional (DFT) method (B3LYP level, 6-31G* basis set, 6-31G* optimized geometry, in vacuum).



The experimental a and b values were obtained by applying the experimental T_c (critical temperature) and P_c (critical pressure) experimental values [3] to the equations: $a = 27R^2T_c^2/64P_c$; $b = RT_c/8P_c$, where R is the gas constant.

Results and Discussion

The experimental a and b values, as well as the calculated polarizabilities and volumes to hydrocarbons from C₁ (methane) to C₂₄ (tetracosane) are summarized in Table 1. In Figure 1, a experimental values are plotted as function of the calculated polarizabilities. In Figure 2, b experimental values are plotted as function of the calculated volumes (in cubic Angstrons).

Table 1: Experimental *a* and*b*, and theoretical palarizability and volume values.

Formula	name	а	b	Polarizability	Volume/A ³
		(barL ² /mol ²)*	(L/mol)*		
CH_4	methane	2.30	0.0434	40.83	33.18
C_2H_6	ethane	5.58	0.0651	42.73	51.79
C_3H_8	propane	9.39	0.0905	44.38	70.22
C_4H_{10}	butane	13.89	0.1164	45.93	88.67
$C_{5}H_{12}$	pentane	19.09	0.1449	47.47	107.11
$C_{6}H_{14}$	hexane	24.84	0.1744	49.02	125.56
$C_{7}H_{16}$	heptane	31.06	0.2050	50.55	144.01
C_8H_{18}	octane	37.88	0.2374	52.07	162.45
C_9H_{20}	nonane	45.02	0.2698	53.59	180.89
$C_{10}H_{22}$	decane	52.73	0.3042	55.10	199.35
$C_{11}H_{24}$	undecane	60.14	0.3354	56.62	217.79
$C_{12}H_{26}$	dodecane	69.37	0.3757	58.12	236.24
$C_{13}H_{28}$	tridecane	77.09	0.4176	59.63	254.68
$C_{14}H_{30}$	tetradecane	89.20	0.4587	61.14	273.13
$C_{15}H_{32}$	pentadecane	98.77	0.4972	62.64	291.58
$C_{16}H_{34}$	haxadecane	108.88	0.5367	64.14	310.03
$C_{17}H_{36}$	heptadecane	117.88	0.5708	65.64	328.48
$C_{18}H_{38}$	octadecane	126.14	0.6018	67.14	346.92
$C_{19}H_{40}$	nonadecane	143.30	0.6764	68.64	365.37
$C_{20}H_{42}$	eicosane	160.75	0.7459	70.15	383.82
$C_{21}H_{44}$	heneicosane	171.37	0.7850	71.65	402.27
$C_{22}H_{46}$	docosane	183.83	0.8335	73.14	420.71
$C_{23}H_{48}$	tricosane	197.82	0.8924	74.64	439.16
$C_{24}H_{50}$	tetracosane	214.52	0.9556	76.14	457.60



Figure 1: "a" as function of polarizability for hydrocarbons (C_1 to C_{24}). Linear correlation coefficient = 0.983.



Figure 2: "b" as function of volume (cubic Angstrons for hydrocarbons (C_1 to C_{24}). Linear correlation coefficient = 0.9920.

As can be verified, in both curves, linear relationships are obtained. Of course, if in the abscissa axis, instead of polarizabilities or volumes are employed the number of carbons or the molar masses, linear relationships are also obtained. However, parameters such as number of carbons or molar mass are only "apparently" related with *a* and *b* values, and such linear relationships are observed only due to the fact that we are dealing with linear hydrocarbons. If the number of carbons are increased (in a branch hydrocarbon for example) but the polarizability it is not, a linear relationship it is not observed, any more.

In order to illustrate such fact, the partition coefficient (P), and the standard entropy (S^o) were also calculated and are summarized in Table 2. Both parameters exhibits linear relationships with a and b values, but such fact is only consequence of the linear nature of the studied hydrocarbons. So, in order to obtain reliable relationships and equations, it is necessary to employ the parameters "really" related with a and b.

In order to make a most profound discussion, the energies of frontier molecular orbital ϵ HOMO and ϵ LUMO (Table 2), energy band gap (ϵ LUMO- ϵ HOMO), electro negativity (χ), chemical potential (μ), global hardness (η), global softness (S), and global electrophilicity index (ω) were calculated (Table 3). This last parameters were calculated as follows: $\chi = -1/2$ (ϵ LUMO+ ϵ HOMO); $\mu = -\chi$; $\eta = (\epsilon$ LUMO- ϵ HOMO)/2; $\omega = -\mu^2/2\eta$ and $S = 1/2\eta$ [4-7].

As can be verified from Table 3 data, as the number of carbons increases, the values of energy gap, and, mainly, η , *S* and ω (this last one, mainly) suffers very small variations or not variations at all. So, as the number of carbons increases, the parameters that can be related with attractive and repulsive forces (and related, of course, with *a* and *b* values, both parameters related, in a last reasoning, with the higher or lower deformability of the electron clouds), tends to a "stabilization", making the linear relationship no longer so pronounced.

Table 2: Theoretical log P, S°, E_{HOMO} and E_{LUMO} data to hydrocarbons from C ₁ to C ₂₄ .							
Formula	name	log P	S° J/mol	ε _{HOMO} /eV	ε _{LUMO} /eV		
CH_4	methane	1.09	186.09	-10.59	3.21		
C_2H_6	ethane	1.33	227.45	-9.25	2.85		
C_3H_8	propane	1.75	267.22	-8.83	2.61		
C_4H_{10}	butane	2.17	295.62	-8.63	2.58		
$C_{5}H_{12}$	pentane	2.58	318.67	-8.46	2.55		
$C_{6}H_{14}$	hexane	3.00	341.42	-8.28	2.52		
$C_{7}H_{16}$	heptane	3.42	363.51	-8.15	2.50		
C_8H_{18}	octane	3.84	384.82	-8.05	2.49		
C_9H_{20}	nonane	4.25	405.13	-7.97	2.47		
$C_{10}H_{22}$	decane	4.67	425.49	-7.90	2.46		
$C_{11}H_{24}$	undecane	5.09	445.02	-7.85	2.46		
$C_{12}H_{26}$	dodecane	5.51	463.62	-7.80	2.45		
$C_{13}H_{28}$	tridecane	5.92	482.35	-7.76	2.44		
$C_{14}H_{30}$	tetradecane	6.34	501.13	-7.73	2.44		
$C_{15}H_{32}$	pentadecane	6.76	519.17	-7.70	2.44		
$C_{16}H_{34}$	haxadecane	7.18	537.46	-7.68	2.43		

As an illustrative example, the *a* values as function of η are shown in Figure 3. **Table 2:** Theoretical log P. S^o Evolution of η are shown in Figure 3.



$C_{17}H_{36}$	heptadecane	7.59	555.80	-7.66	2.43
$C_{18}H_{38}$	octadecane	8.01	573.54	-7.64	2.43
$C_{19}H_{40}$	nonadecane	8.43	591.46	-7.63	2.43
$C_{20}H_{42}$	eicosane	8.84	609.45	-7.61	2.42
$C_{21}H_{44}$	heneicosane	9.26	626.93	-7.60	2.42
$C_{22}H_{46}$	docosane	9.68	644.21	-7.59	2.42
$C_{23}H_{48}$	tricosane	10.10	661.66	-7.58	2.42
$C_{24}H_{50}$	tetracosane	10.51	678.83	-7.57	2.42

Table 3: Energy band gap (ϵ LUMO- ϵ HOMO), electro negativity (χ), chemical potential (μ), global hardness (η), global softness (S), and global electrophilicity index (ω).

Formula	name	Energy	band	χ	μ	η	ω	S
		gap/eV				•		
CH_4	methane	13.80		3.69	-3.69	6.90	0.99	0.07
C_2H_6	ethane	12.10		3.20	-3.20	6.05	0.85	0.08
C_3H_8	propane	11.44		3.11	-3.11	5.72	0.85	0.09
C_4H_{10}	butane	11.21		3.03	-3.03	5.61	0.82	0.09
$C_{5}H_{12}$	pentane	11.01		2.96	-2.96	5.51	0.79	0.09
$C_{6}H_{14}$	hexane	10.80		2.88	-2.88	5.40	0.77	0.09
$C_{7}H_{16}$	heptane	10.65		2.83	-2.83	5.33	0.75	0.09
C_8H_{18}	octane	10.54		2.78	-2.78	5.27	0.73	0.09
C_9H_{20}	nonane	10.44		2.75	-2.75	5.22	0.72	0.10
$C_{10}H_{22}$	decane	10.36		2.72	-2.72	5.18	0.71	0.10
$C_{11}H_{24}$	undecane	10.31		2.70	-2.70	5.16	0.70	0.10
$C_{12}H_{26}$	dodecane	10.25		2.68	-2.68	5.13	0.70	0.10
$C_{13}H_{28}$	tridecane	10.20		2.66	-2.66	5.10	0.69	0.10
$C_{14}H_{30}$	tetradecane	10.17		2.65	-2.65	5.09	0.69	0.10
$C_{15}H_{32}$	pentadecane	10.14		2.63	-2.63	5.07	0.68	0.10
$C_{16}H_{34}$	haxadecane	10.11		2.63	-2.63	5.06	0.68	0.10
$C_{17}H_{36}$	heptadecane	10.09		2.62	-2.62	5.05	0.68	0.10
$C_{18}H_{38}$	octadecane	10.07		2.61	-2.61	5.04	0.67	0.10
$C_{19}H_{40}$	nonadecane	10.06		2.60	-2.60	5.03	0.67	0.10
$C_{20}H_{42}$	eicosane	10.03		2.60	-2.60	5.02	0.67	0.10
$C_{21}H_{44}$	heneicosane	10.02		2.59	-2.59	5.01	0.67	0.10
$C_{22}H_{46}$	docosane	10.01		2.59	-2.59	5.00	0.67	0.10
$C_{23}H_{48}$	tricosane	10.00		2.58	-2.58	5.00	0.67	0.10
$C_{24}H_{50}$	tetracosane	9.99		2.58	-2.58	4.99	0.66	0.10



Figure 3: "a" as function of global hardness (η)

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