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News Aspects Theoric and Experimental to Paraffins Compounds

*Eloi Alves da Silva Filho, Fabrício Uliana
and Arlan da Silva Gonçalves*

Abstract

The paraffinic compounds are important to new investigation on the properties physics and its correlation with theoric dates, because in literature no is completely clarified. However, there are some studies on the formalism for developing asymptotic behavior correlation for homologous series paraffin compounds. In this work is show that the effect of parameters theoric obtained by molecular modeling can be correlated with experimental dates. To paraffins as pure, for example, n-hexane, C_6H_{14} , MW 158 g/mol, is composed of two groups CH_3 and four groups CH_2 and its can depending of structure molecular ramification to predict what your dependency with thermodynamics data. Therefore, the molecular modeling of paraffinic compounds uses a methodology that looks for data correlated with the structure of the molecule complemented with experimental data. The objective this study is correlated this molecular data with some thermodynamics data as enthalpy of formation and other parameters.

Keywords: thermodynamics data, molecular modeling, paraffins compounds, theoric properties, molecular structure

1. Introduction

Paraffins compounds can be found in all phases of the petroleum production and very researched due to the industrial interest, mainly in what concerns the generation of energy and combustible material. Thermodynamic properties, such as heats of vaporization, specific heats, free energies, internal energies, entropies and enthalpies or interacting heat contents for petroleum hydrocarbons and their mixtures like paraffins compounds are very importance in chemical and work associated with petroleum refinery operations like other activities in this field. With the help of literature data and complementing with computational calculations of the thermodynamic properties of paraffins today it becomes possible to correlate theoretical data with experimental data [1].

In literature has been reported some study with a general equation for correlating the thermodynamic properties of n-paraffins and n-olefins, and other homologous series [2–6]. The recent work show that the modeling the thermal conductivity of n-alkanes via the use of density scalling for molecular liquids has proven to be a powerful estimation technique for transport properties [7]. It is important to

Molecular Formula	Name	Molecular Mass(u)	Boiling point b.p.(K)	Melting point m.p.(K)
CH ₄	Methane	16	111.0	90.5
C ₂ H ₆	Ethane	30	184.4	101.0
C ₃ H ₈	Propane	44	230.9	85.3
C ₄ H ₁₀	Butane	58	272.4	134.6
C ₅ H ₁₂	Pentane	72	309.1	143.3
C ₆ H ₁₄	Hexane	86	341.9	178.5
C ₇ H ₁₆	Heptane	100	371.4	182.4
C ₈ H ₁₈	Octane	114	398.7	216.2
C ₉ H ₂₀	Nonane	128	423.8	222.0
C ₁₀ H ₂₂	Decane	142	447.1	243.3

Table 1.
Physical properties of melting point and boiling point to Paraffins.

highlight that a database query can find many thermodynamic properties and are available for free on the internet, for example, NIST Chemistry WebBook [8], but no have data to interaction energy for paraffins. In preview work, Hadjieva and collaborators [9] showed that the increasing industrial interest in finding heat storage materials for efficient use of thermal energy in corresponding applications stimulates the investigation of phase change materials. Paraffin mixtures have been evaluated as suitable thermal storage materials (TSM) with melting points in the temperature range of 25–100 °C.

In general the paraffins compounds have little reactivity but it has a good inter-action molecular due to being apolar structure and its directs some studies of its interaction energy ($\Delta_{\text{int}}E/\text{kJ}\cdot\text{mol}^{-1}$) when interactions occur between two n-alkenes such as pentane binding to another pentane where weak van der Waals interactions predominate. Therefore, the paraffins, the longer the chain (-CH₂), the more interatomic sites there are for interactions between the molecules with a larger and stronger attractions or lower vapor pressures with higher boiling points. The literature [10, 11] shows that indeed boiling points for n-alkanes increase with increasing chain length. While often this trend is thought of as increasing boiling point with molecular wight (**Table 1**), it is really the increasing of the intermolecular forces that cause this not the increasing mass. The first four molecules, C1 to C4 are gases, C5 to C17 are liquids and those containing 18 carbon atoms or more are solids at 298 K.

The conformations of C2, ethane, is special, and the torsional strain and eclipsed form maximum torsional strain, it can be that rotation around C-C bond in is not completely free, and can affect the melting point.

In this work, the interaction energy, $\Delta_{\text{int}}E$ and formation enthalpy, Δ_fH were studied for five paraffins compounds like pentene, hexane, octane, undecane and tetradecane respectively, by computational calculate and correlation with experimental data, for evaluation of linearity found between experimental and theoretical data.

2. Methodology

2.1 Computational

The computational calculate in this work was used a machine with core proces-sor i5-5200u 2.20GH and with 8G of RAM, 250D SSD, gforce 920 m video card running Xubuntu Core operating system (Linux distribution based on Ubuntu 16.04) and molecular modeling software distributed free of charge.

The work began with the construction of the geometry of the reagents used in the AVOGADRO program. In this program the graphical interface is used for the disposition of atoms and bonds in their proper places generating a three-dimensional representation of the molecules. The generated structures can be recorded in coordinate files that specify the positions of each atom in a Cartesian space (Cartesian coordinates) or indicate the bond length, angles and dihedral for each atom of the system (z-matrix) like is showed in **Table 2**.

The generated structure is then optimized so that the values of bond lengths, angles and dihedra are optimized in order to obtain geometries closer to those experimentally determined. To perform this optimization, one needs to use a set of parameter data for several atoms in several different chemical environments called the force field.

Once created and optimized, the system is saved to the PDB file. Using the program OPEM BABEL, the PDB file containing the reagents for the input files of MOPAC2016 was generated, thus generating a file <FileName> .mop.

In the .mop file the first line of the is intended for the insertion of the keywords that will determine what type of calculation the program should carry out the second line is a space to put comments that may be relevant and the other lines are the set of coordinates that representation the system. The following **Figures 1–4** show three-dimensional structure obtained from some paraffinic compounds used this computational methodology.

File	Edit	Format	Display	Help
20				
	Energy:			–5.4744410
C		–3.07778		0.34773 0.00881
C		–1.76950		1.11704 0.09877
H		–3.92678		1.02945 0.12005
H		–3.14344		–0.40822 0.79784
H		–3.17101		–0.15594 0.95864
C		–0.56337		0.19053 –0.05321
H		–1.72241		1.63457 1.06399
H		–1.74982		1.88544 0.68281
C		0.75059		0.96820 0.03782
H		–0.61754		–0.32775 –1.01837
H		–0.59011		–0.57856 0.72836
C		1.95672		0.04170 –0.11414
H		0.80476		1.48650 1.00297
H		0.77733		1.73729 –0.74377
C		3.26500		0.81102 –0.02427
H		1.90961		–0.47590 –1.07933
H		1.93706		–0.72666 0.66749
H		3.33064		1.56690 –0.81337
H		4.11399		0.12929 –0.13547
H		3.35824		1.31477 0.94314

Table 2.
Recorded in coordinate files.

Figure 1.
Three-dimensional representation of the pentane molecule.

Figure 2.
Three-dimensional representation of the hexane molecule.

Figure 3.
Three-dimensional representation of the octane molecule.

Figure 4.
Three-dimensional representation of the undecane molecule.

3. Results and discussion

The result of interacting energy, separate are in the **Table 3** and graphic in **Figure 5**, shows that a energy of interaction increasing with molecular mass, with a good correlation between each data, $r^2 = 0.99627$. This show that the interacting

Molecule	Interacting Energy (kJ · mol ⁻¹)	Separate energy (kJ · mol ⁻¹)	ΔintE (kJ · mol ⁻¹)	Boiling point Experimental (°C) [8]
Pentane	-295.48	-278.27	17.21	36.0
Hexane	-342.00	-320.16	21.84	68.71
Octane	-436.05	-404.45	31.60	125.59
Decane	-436.05	-532.31	44.69	196.21
Tetradecane	-718.54	-661.68	56.86	255.09

Table 3.
Values for energy of interaction between the molecules and the experimental boiling point.

Figure 5.
Correlation between the calculated interaction energy and the experimental boiling point.

energy is a important parameter thermodynamic to explain the fact that intermolecular van der Waals increase with increase of the molecular size or the surface area of the paraffins molecule.

On the other hand the paraffins compounds can have infinite number of conformations by rotation around –C-C- single bonds and consequently generates of 1–20 kJ/mol in small energy barrier due weak interaction between adjacent bonds as called torsional strain. Then to obtain a stable molecule of paraffinic compounds it is necessary a more complete analysis of other parameters thermodynamics such as the enthalpy of formation ($\Delta_f H^\circ$) that in this work was calculate using the program MOPAC201 where $\Delta_f H^\circ$ were compared with experimental data, as can be observed in the **Figure 6**.

This formation enthalpy are very agreement until C_5H_{12} but the C_6H_{14} there is an increase in the difference that can be attribute a phase change and also in your properties physics as boiling point.

Thus, the ionization energy (IE) is also very important for understanding this linearity in **Figure 6** and have been investigated with results in **Figure 7**.

Figure 6.
Formation enthalpy experimental compared with theoric.

Figure 7.
Ionization energy experimental compared with theoric.

The ionization energy, also called ionization potential (IE) was defined according to IUPAC in 1994 like the minimum energy required to remove an electron from an molecular entity (its vibrational ground state) in the gaseous phase [12]. If the resulting molecular entity is considered to be in its vibrational ground state, one refers to the energy as the “adiabatic ionization energy”. If molecular entity produced possesses the vibrational energy determined by the Franck Condon principle (according to which the electron ejection takes place without an accompanying change in molecular geometry), the energy is called the “vertical ionization energy”. The ionization energy of a stable species, that is, any molecule that may exist, is always positive.

In the **Figure 7**, was observed that experimental data were higher than the theoretically obtained data, for example, Decane have a difference of the $\Delta = 1.117$ and this discrepancies between computed and experimental results can be accounted for theoretical contributions, that are often based on the atomic groups or chemical bonds. This ionization energy also lowered by delocalization of charge as the molecular size is increased and related to some molecular property, common to paraffinic compounds.

Figure 8.
 HOMO energy orbital to CH paraffinic groups.

Hall [13] in earlier paper reported that the ionization potentials of some paraffinic molecules could be obtained of antisymmetrical molecular orbital localized over the CH bonds. In the **Figure 8**, was observed that to Paraffinic molecules of C_7H_{16} to $C_{12}H_{26}$ are more stable to the ejection of an electron from the highest occupied molecular orbital (HOMO).

According of Cao and Yuan [14] reported that is more easily polarized the paraffinic molecule, the more stable the final-state (charged molecule), and furthermore, the lower the ionization potential will be. That is to say, the substituent polarizability effect can facilitate the ionization.

4. Conclusions

We conclude that the interaction energy, $\Delta_{\text{int}}E$ and formation enthalpy, $\Delta_f H$ were by computational calculate and correlation with experimental data, for to $C_2 - C_{12}$ were important in this study due a good linearity found between experimental and theoretical data. With this model of computational calculate can be applied to other types of branched paraffinic compounds. The results of this study show that molecular orbital HOMO and polarizability are an mportant parameter to ionization energy of Paraffinic compounds.

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Conflict of interest

No.

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Author details

Eloi Alves da Silva Filho^{1*}, Fabrício Uliana¹ and Arlan da Silva Gonçalves²

1 Department of Chemistry, Federal University of Espírito Santo, Vitória, ES, Brazil

2 Federal Institute of Education, Science and Technology of Espírito Santo, Vila Velha, ES, Brazil

*Address all correspondence to: eloi.silva@ufes.br

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