Molecular Orbital Nature of Solubility of Shot Chain n-Alkanes in Water and Their Reaction Rate Constants with Nitronium Cations: A DFT Study

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Abstract

The new theoretical models describe both the solubility S of the shot chain n-alkanes in water at 298.15 K, and their reaction rate constants k with nitronium cation NO_2^+ at 293.15 K on the basis of their molecular orbital characteristics. It is shown that both the quantities S and k are determined by the energies E_{orb} of the specific virtual (for S) and occupied (for k) molecular orbitals of these n-alkanes. The obtained regression equations confirm the theoretically found dependences of S and k on the absolute value of E_{orb}. This fact demonstrates that the electronic structure particularities of the studied n-alkanes play a crucial role in both their above-mentioned physicochemical properties.

Keywords

Solubility in Water, Reaction Rate Constants, n-Alkanes, Nitronium Cations, Orbital Controlled Interactions, DFT Calculations

1. Introduction

It has been shown in our previous work [1] that some specific occupied molecular orbitals (SMOs) of the shot chain n-alkanes (from ethane up to n-decane) are responsible for their different physicochemical properties. It is about the surface tension σ of these n-alkanes at their normal boiling points and their reaction rate constants k_r with hydroxyl radicals (at the absolute temperature T = 297 ± 2 K and the pressure P = 0.1 MPa in the gaseous phase). The molecular orbitals

(MOs) defining both these properties are the same ones (see [1]). These orbitals (called in [1] as "SMOs") possess the following characteristics. Firstly, they are occupied MOs, whose energies E_{orb} are close to the HOMOs ones of the studied n-alkanes. That is, these orbitals are the MOs of the following types: HOMO-1, HOMO-2, HOMO-3. Secondly, these MOs ("SMOs") contain the 1s atomic orbitals (1s-AOs) of all the hydrogen atoms entering the molecular structures of the considered n-alkanes. It is to be noted here that for any of the studied n-alkanes, all its hydrogen atoms 1s-AOs are present in their SMOs with one common sign ("+" or "−"). It was also shown in [1] that the energies E_{orb} of the SMOs of the given n-alkanes play a key role in the adequate quantitative description of their above-mentioned quantities σ and k_r.

So, the following equation obtained in [1] describes the dependence of k_r on the absolute value (module) of $|E_{orb}|$:

$$\log_{10} k_r = C + \frac{Z}{E_i - |E_{orb}|}. \tag{1}$$

In Equation (1), C and Z are constants for all the studied n-alkanes. Their numerical values are $C = 8.1254$ and $Z = 496.25$ kJ·mol^{-1} [1]. $|E_{orb}|$ is the energy of the SMO of the considered n-alkane, and, therefore, it depends on its nature. In its turn, E_i is the molecular orbital energy of the unpaired electron of OH$^•$. The numerical value of E_i defined in [1] equals to 1003.13 kJ·mol^{-1}. It has been also shown in [1] that the surface tension of the studied n-alkanes (considered at their normal boiling points) depends on their values $|E_{orb}|$.

Further, it was shown in the work [2] that for different organic near-boiling liquids, whose molecules possess the hyperconjugation between their π-electronic systems and their methyl groups, their surface tension can be described by means of the following equation:

$$\sigma = |\varepsilon_0| \left(1 - T/T_c\right) \left(\mu V^{2/3}\right)^{-1} \tag{2}$$

Here T and V are respectively absolute temperature and molar volume of a near-boiling liquid; T_c is its critical temperature; μ is some constant for all the studied liquids. In its turn, $|\varepsilon_0|$ is the absolute value of some average zero-point one-particle binding energy of one separate molecule in the volume of this liquid. It was shown in [2] that the quantity $|\varepsilon_0|$ can be presented as:

$$|\varepsilon_0| = fN |E_{orb}|, \tag{3}$$

where f is the constant coefficient of proportionality which does not depend on the nature of the studied liquid; $|E_{orb}|$ is the absolute value of the energy of some occupied molecular orbital which belongs to the active valence zone of the above-mentioned separate molecule of this liquid. N is the number of its atoms, whose AOs enter the given MO with the great values of their coefficients. It was also shown in [2] (in accordance with the data of the work [3]) that the molecular orbitals, whose energies $|E_{orb}|$ enter Equation (3), are energetically close to the HOMOs of the molecules of the investigated liquids or they are the HOMOs of the given molecules.

Here it is to be noted that the main results of the works [1] [2] consist in the common conclusion that the energies $|E_{orb}|$ of some specific MOs of the molecules of the studied organic compounds define their essentially different quantities: σ and k_r.

Bearing in mind the given conclusion, it seems to be very interesting and important to find (using the above shot chain n-alkanes as an example) their other physicochemical properties which could be connected with their energies $|E_{orb}|$ describing some new specific molecular orbitals of these compounds. Thus, the aim of the present work is to find their new physicochemical quantities depending on $|E_{orb}|$.

2. Theory

2.1. Solubility of the Shot-Chain n-Alkanes in Water at 298.15 K

In order to consider the above property of the studied n-alkanes (from CH_4 to n-$C_{10}H_{12}$) we shall use the van't Hoff isochore equation (see [4] [5]) written in its logarithmic form:

$$\log_{10} S = A + \frac{B\Delta H}{RT} = A + B'\Delta H .\qquad(4)$$

Here S is solubility of a chemical compound (in our case any of the considered n-alkanes). The quantity S is usually expressed in molar fraction [4] and [5]. ΔH is the partial molar enthalpy connected with formation of a saturated aqueous solution for each of the studied n-alkanes. R is the gas constant. A and B' are some constant quantities depending on the nature of the considered n-alkane. T is the absolute temperature at that the dissolution of the n-alkanes takes place. As we consider the solubility of the n-alkanes at the constant T ($T = 298.15$ K) and at the normal atmospheric pressure P ($P = 0.1$ MPa), so we can include the quantities R and T into the constant B, forming some new constant B' ($B' = B/RT$).

Further, since for the studied n-alkanes their S values are of the order of 10^{-4} mol·L^{-1} [6], we consider them rather small in the sense that they lead to insignificant changes in volume during the formation of joint "alkane-water" systems. In other words, these volume changes are small enough to consider the dissolution process to be isochoric and described by the van't Hoff isochore equation. Thus, for the quantity ΔH we can write the following approximate equality:

$$\Delta H = \Delta E + P\Delta V \approx \Delta E\qquad(5)$$

Here ΔE is the partial molar energy change which accompanies the formation of the aqueous solution for any of the n-alkanes under study.

Now we have to define the quantity ΔE. In order to do it, we shall take into account the following reasons. At first, let us consider one n-alkane molecule which belongs to the studied aqueous solution and is surrounded by water molecules from all sides. We can consider that this molecule creates some cavity in the surrounding aqueous medium. Obviously, the creation of the given cavity requires some amount of energy ΔE and, thus, it is an endothermic process. Let, further, the quantity of the surface of this cavity be equal to Q. Then the quantity

ΔE_1 can be defined as some work which is done against the forces responsible for the surface tension σ of water at the considered temperature T. In this case we can write for ΔE_1 the following equation:

$$\Delta E_1 = \sigma Q \tag{6}$$

Further, in the present work we shall consider that the value of Q is proportional to the number n_m of the methylene groups entering the molecular structure of the studied n-alkane. It should be noted here that the molecular structure of all the n-alkanes under study (including methane) are considered as consisting of a certain number of methylene groups and two terminal hydrogen atoms. So, we can rewrite Equation (6) as:

$$\Delta E_1 = c\sigma n_m \tag{7}$$

Here c is some coefficient of proportionality between Q and n_m, which is supposed constant for all the n-alkanes.

Now we have to define the second addendum ΔE_2 in the total energy quantity ΔE. If the first addendum ΔE_1 describes (see above) the formation of the one-particle cavity in an aqueous medium containing the considered n-alkanes, then, in its turn, ΔE_2 is the energy addendum to ΔE, which is being defined by the intermolecular interaction between the MOs of the considered n-alkane molecule and the MOs of the water molecules surrounding it and forming its aqueous shell. It has been shown in the recent work [7] that all the O-H bonds of the above water molecules are situated within the surface of the given shell. In its turn, some part of the lone electronic pairs of these water molecules is directed towards the given n-alkane molecule. Thus, based on these data, in the present work we suppose that the above interaction is being realized by means of interaction of some specific unoccupied molecular orbitals of the n-alkanes and the MOs belonging to the water molecules of the mentioned aqueous shell and describing some number n_p of the lone electronic pairs of these water molecules.

Further, let the energy of the above-mentioned specific MO of the n-alkane molecule be E_{orb} and the number of the hydrogen atoms, whose 1s-AOs enter the given SMO with great values of their molecular-orbital coefficients, be n_H. Then, based on the data of the work [3], we can consider that the energy effect, describing the interaction of the n-alkane molecule with the surrounding water molecules will be proportional to the product $|E_{orb}| \cdot n_H$, or $E_{orb} \cdot n_H$ (here we write E_{orb} instead of $|E_{orb}|$, based on the above-mentioned virtual character of the SMO of the n-alkane molecule; it means that its energy is positive and, therefore, $|E_{orb}| = E_{orb}$).

At the same time, the quantity ΔE_2 will be proportional to both the just considered product $E_{orb} \cdot n_H$ and the above-mentioned number n_p. Thus, we can write for the quantity ΔE_2 the following equation:

$$\Delta E_2 = \chi E_{orb} n_H n_p , \tag{8}$$

where the coefficient of proportionality χ is supposed to be constant for all the n-alkanes under study. In its turn, the number n_p is proportional to the surface

Q of the aqueous shell, surrounding the considered n-alkane molecule, and Q is proportional to the number n_m of its methylene groups (see Equations (6) and (7) above), so we can rewrite Equation (8) in the final form:

$$\Delta E_2 = \gamma E_{orb} n_H n_m , \tag{9}$$

where γ is some constant coefficient of proportionality for all the studied n-alkanes.

Now, using the one-particle quantities ΔE_1 and ΔE_2 (see Equations (7) and (9), which fit only for one n-alkane molecule under consideration, we can write the following equation:

$$\Delta E = N_A \left(\Delta E_1 + \Delta E_2 \right) = c N_A \sigma n_m + \gamma N_A E_{orb} n_H n_m , \tag{10}$$

which holds for the molar quantity ΔE (see Equation (5)). In Equation (10) N_A is Avogadro number. Further, using Equations (5) and (10), Equation (4) can be presented as:

$$\log_{10} S = A + c N_A B' \sigma n_m + \gamma N_A B' E_{orb} \cdot n_m n_H , \tag{11}$$

or in the following final form:

$$\log_{10} S = A + \xi n_m + \mu E_{orb} \cdot n_m n_H . \tag{12}$$

In Equation (12), the constants ξ and μ include the corresponding constants from Equation (11) and do not depend on the nature of the n-alkanes under study. The quantity of the surface tension of water σ is included in ξ, as it is also constant (as T is constant, $T = 298.15$ K).

2.2. Relationship "n-Alkanes Electronic Structure—Reaction Rate Constants with Nitronium Cation"

In order to reveal the above relationship, it seems reasonable that the new equation which is similar to Equation (1) (received in the work [1]) fits also for the new reaction type of the studied shot chain n-alkanes with the new reagent: nitronium cation. Really, Equation (1) holds for the calculation of the reaction rate constants describing the elimination of hydrogen atoms from molecules of the studied n-alkanes by means of hydroxyl radicals. At the same time, in the case of nitronium cations, the hydrogen atom transfer from n-alkanes to NO_2^+ occurs simultaneously with the corresponding electron transfer from the same SMO which earlier contained the electron of the given hydrogen atom (see the work [8]). Therefore, the transfer of the corresponding hydride anion H^-, whose electrons have left the same SMO of the n-alkane, occurs through the $NO_2^+ \cdots H \cdots C$ three-center bond. This conclusion is also confirmed by our DFT calculations performed for the $[n\text{-}C_nH_{2n+1}]^+$ systems. Thus, the same SMOs are responsible both for the abstraction of a hydrogen atom in the case of the reaction of n-alkanes with hydroxyl radicals [1] and for the transfer of the hydride anion in the reaction of n-alkanes with nitronium cations.

3. Computational Details

All the parameters of the electronic structure and geometry of the investigated

compounds have been calculated by means of the DFT method, using Becke's three-parameter nonlocal exchange functional [9] with the correlation functional of Lee, Yang and Parr (B3LYP) [10]. For all the studied molecular systems, their full geometry optimization was performed with the use of the 6 - 31* basis set with polarization functions for all the atoms [11]. All the calculations were done by means of the GAUSSIAN 09 program package [12].

4. Results and Discussion

4.1. Solubility of the n-Alkanes in Water

In order to verify Equation (12) received in the previous Section we have investigated the n-alkanes presented in Table 1. Beginning from ethane, all these compounds possess linear hydrocarbon chains. The geometry optimization of all the considered systems shows that their molecules have the planar carbon chains in which any four consecutive carbon atoms are in the trans-configuration. The subsequent analysis of the virtual MOs of the given n-alkanes (see Section 2.2) show that their LUMOs satisfy all the above-mentioned criteria for their consideration as the sought SMOs. Indeed, these LUMOs contain 1s-AOs of all the hydrogen atoms and, moreover, with one common sign ("+" or "−") of the corresponding MO coefficients. For the case of methane, propane, n-pentane, and n-octane their LUMOs (their SMOs) are shown in Figure 1.

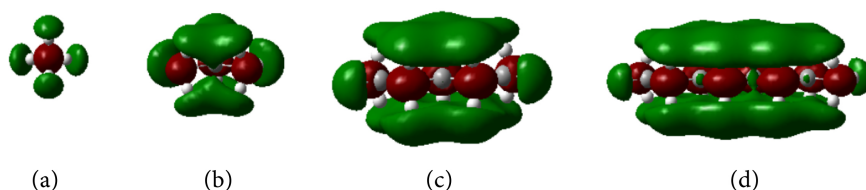
| (a) | (b) | (c) | (d) |

Figure 1. The SMOs (the LUMOs) of some studied n-alkanes responsible for their solubility S: methane (a), propane (b), n-pentane (c), and n-octane (d).

Table 1. The data necessary to obtain equation (13) and the subsequent calculation of $-\log_{10}S$.

No	Alkane	n_m	n_H	E_{orb} (kJ/mol)	$-\log_{10}S$ Exp.	$-\log_{10}S$ Calc.	$-\log_{10}S$ LOOCV
1	Methane	1	4	309.63	0.90	0.89	0.89
2	Ethane	2	6	275.17	1.36	1.40	1.42
3	Propane	3	8	252.37	1.94	1.94	1.94
4	n-Butane	4	10	249.27	2.57	2.53	2.52
5	n-Pentane	5	12	246.01	3.18	3.15	3.15
6	n-Hexane	6	14	243.72	3.84	3.82	3.81
7	n-Heptane	7	16	241.63	4.53	4.52	4.52
8	n-Octane	8	18	240.06	5.24	5.26	5.27
9	n-Nonane	9	20	238.80	5.88	6.04	6.10
10	n-Decane	10	22	237.84	6.98	6.86	6.67

In order to demonstrate that namely the considered virtual orbitals are responsible for the interaction of n-alkanes with neighboring water molecules, we have calculated the interaction between the two molecules, namely, n-pentane and water. The results of this DFT calculation are presented in **Figure 2**. One can see that there is a clear-cut interaction between the lone electronic pairs of the oxygen atom of the water molecule and the SMO (the LUMO) of the n-pentane one.

For each of the studied n-alkanes, **Table 1** contains their quantities n_m, n_H, and E_{orb}, along with the experimental values $-\log_{10} S$ taken from the work [6].

Further, the numerical values of the constants A, ξ, and μ (see Equation (12)) were defined by means of the least square method applied to the data set in **Table 1**. The usage of the found values of A, ξ, and μ in Equation (12) allows one to write it in the following final form:

$$-\log_{10} S = 0.4220 + 0.4198 n_m + 4.28287 \times 10^{-5} E_{orb} n_m n_H .\qquad(13)$$

The last but one column of **Table 1** contains the values of $-\log_{10} S$ of the studied n-alkanes calculated by means of Equation (13). The last column of **Table 1** includes the values of $-\log_{10} S$ which were obtained by the use of the so-called "Leave-one-out" Cross-Validation Scheme (LOOCV). The given statistical method consists of consequent removal of one of the investigated compounds from the regression analysis and subsequent calculation of the predicted quantity for the removed compound.

The comparison of the values of $-\log_{10} S$ presented in the last three columns of **Table 1** shows that these values are very close to each other and to the corresponding experimental ones. It means that Equation (13) (and, therefore, Equation (12)) describes the solubility of the studied n-alkanes in water adequately.
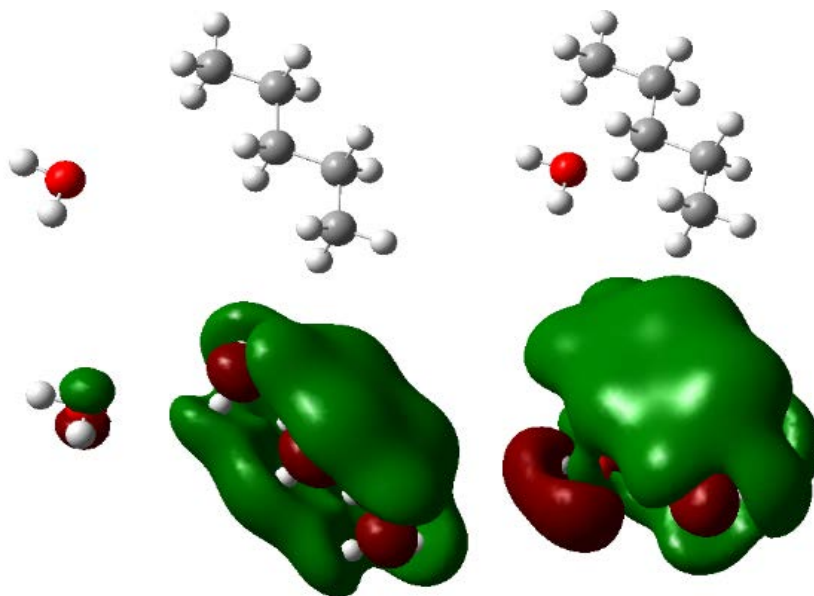

Figure 2. The interaction of the lone electronic pair of a molecule of water with the virtual SMO (the LUMO) of n-pentane.

4.2. Rate Constants for the Reaction $n\text{-}C_nH_{2n+2} + NO_2^+ = [n\text{-}C_nH_{2n+1}]^+ + HNO_2$

In our previous work [1] we have investigated the rate constants for the reaction of shot chain n-alkanes (C_2 - C_{10}) with hydroxyl radicals in the gaseous phase at $T = 298.15 \pm 2$ K and P = 0.1 MPa. Unlike [1], in the present paper, we consider the rate constants for the reaction of some n-alkanes with nitronium cations in the HNO_3-93 wt% H_2SO_4 solution at 293 K (see the work [13]). Thus, in the present work we deal with the new type of the reaction of n-alkanes: their electrophilic nitration which is being realized in the liquid phase (instead of the earlier considered gaseous one).

Since we consider the electrophilic nitration of the n-alkanes by means of nitronium cations, their occupied SMOs determined in [1] will interact with a certain virtual molecular orbital of nitronium cation. The given MO of NO_2^+ can be characterized, firstly, by its negative energy (because of the electrophilic nature of nitronium cations) and, secondly, by its significant spatial extent. Our DFT calculations show that the MO of nitronium cation with the absolute value of its energy 702.88 kJ·mol^{-1}, fits both the above-mentioned requirements. Figure 3 demonstrates the spacial shape of this MO along with that of the SMO of n-pentane, and the MO of the optimized joint system [$n\text{-}C_5H_{12}$ & NO_2^+], arising due to the interaction between nitronium cation and n-pentane.

As noted in Section 2.2, the rate constants for the reactions of alkanes with NO_2^+ can be calculated by Equation (1), in which E_i is the energy of the just discussed unoccupied MO of the studied cation. This redefinition of E_i will also lead to a change in the values of C and Z in Equation (1). In order to determine the new values of C and Z, which are constant for all the studied n-alkanes, we have used the experimental values of their reaction rate constants k with NO_2^+ [13]. The new C and Z were defined by means of the least square method. Thus, for the rate constants of the studied nitration reaction, Equation (1) has the following final form:

$$-\log_{10} k = 5.5360 + \frac{664.59}{702.88 - |E_{orb}|}. \tag{14}$$

Table 2 contains the experimental values of k [13] and $-\log_{10}k$, along with the earlier calculated (and taken from [1]) values of E_{orb} of the studied n-alkanes. It contains also the values of $-\log_{10}k$ calculated by means of Equation (14). The last column of Table 2 includes the values of $-\log_{10}k$ calculated by means of the LOOCV scheme (see above). The comparison of the values $-\log_{10}k$ presented in the three last columns of Table 2 shows that for each of the studied n-alkanes the corresponding values of $-\log_{10}k$ are very close to each other. Thus, Equation (14) describes the rate constants for the electrophilic nitration of the considered n-alkanes adequately.

It is to be noted that in this work we limited ourselves to consideration of n-alkanes, since, as our calculations show, when passing to branched systems, significant changes in the SMOs (the LUMOs) occur, which, in turn, depend on the branching site of the corresponding molecules.
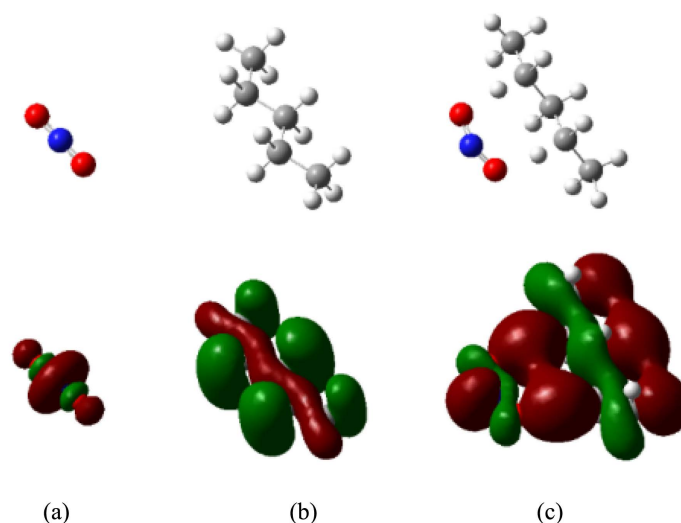
(a)   (b)   (c)

Figure 3. The interaction of the virtual MO of NO_2^+ (a) with the occupied SMO of n-C_5H_{12} (b) leading to the bonding MO of the complex [n-C_5H_{12} & NO_2^+] (c).

Table 2. The data necessary to obtain equation (14) and the subsequent calculation of $-\log_{10}k$.

No	Alkane	k_{exp} (kg·mol⁻¹·s⁻¹)	E_{orb} (kJ·mol⁻¹)	$-\log_{10}k$		
				Exp.	Calc.	LOOCV
1	Propane	0.0196	873.56	1.71	1.64	1.53
2	n-Butane	0.052	863.34	1.28	1.39	1.46
3	n-Pentane	0.12	845.16	0.92	0.87	0.85
4	n-Hexane	0.18	841.27	0.74	0.73	0.73
5	n-Heptane	0.23	837.02	0.64	0.58	0.56
6	n-Octane	0.35	835.47	0.45	0.52	0.56

5. Conclusions

The following conclusions can be drawn. It is shown that for the studied shot chain n-alkanes, namely the lowest unoccupied molecular orbitals of their molecules are the specific molecular orbitals which are responsible for the quantities of their solubility in water. The given LUMOs interact with lone electronic pairs of water molecules, and the values of the molecular orbital energies of these NUMOs enter the equation which allows one to calculate the above-mentioned solubility.

In their turn, the specific molecular orbitals of the studied n-alkanes, describing the rate constants in the nitration reaction with nitronium cation, are the same occupied molecular orbitals which were defined earlier [1] for the reaction of these n-alkanes with hydroxyl radical. Both the obtained equations allow one to calculate the solubility of the n-alkanes in water and their rate constants in the nitration reaction with cations adequately.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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