

Short communication

Analysis of the mechanism of retention on graphitic carbon by a computational chemical method

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Abstract

Retention mechanism on a graphitic carbon was analyzed by computational chemical calculation. The model graphitic carbon phase was a large polycyclic aromatic hydrocarbon (PAH) and analytes were carbohydrates and hydrocarbons separated by liquid and gas chromatography. Molecular mechanics calculation was fast and suggested their retention order and main retention force. Molecular orbital package calculation (MOPAC) demonstrated their complex form.

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1. Introduction

The retention mechanisms on graphitic carbon and the chromatographic applications were reviewed [1]. The hydrophobic compounds and anions are retained on a graphitic carbon column but not cations in liquid chromatography. The chemical and physical stability performed in both chromatography and extraction, especially for polar compounds. The disadvantage is difficult desorption of non-polar compounds adsorbed on the surface. The computational chemical analysis indicated that molecular size related to Van der Waals energy and electrostatic potential contributed the retention of hydrophobic compounds and anions, respectively. Further details of ion retention were analyzed based on the retention of guanidino compounds [2]. According to Hosoya [3], a graphitic carbon molecule should consist of over 10^5 carbons. However, the molecular size was limited by the capacity of the computer used for computational chemical analysis. A small model phase of graphitic carbon is a polycyclic aromatic hydrocarbon (PAH). The molecular size depended on the calculation capacity of a computer, however, the calculated results demonstrated that the net atomic charge of center carbons was positive, and the value was smaller at the center of a larger size polycyclic aromatic hydrocarbon. Atomic charge of the outer carbons was negative by an extended Hückel calculation. The electron potential

was low at the center and high at the edge of a graphitic carbon model. This indicated the existence of two types of molecular interactions; hydrophobic interaction at the center of a graphitic carbon molecule and electrostatic interaction at the edge of graphitic carbon. In this study, the retention mechanism of volatile hydrocarbons in gas chromatography and carbohydrates in liquid chromatography were analyzed by molecular mechanics (MM2) and molecular orbital package calculations (MOPACs) as molecular interaction energy between a polycyclic aromatic hydrocarbon and an analyte.

2. Experimental

Further study of the retention mechanism on graphitic carbon was achieved using a more powerful computer than that previously used. The computer used was a Dell model Latitude C840 equipped with a 2 GHz processor and 1024 MB memory. The molecular properties of analytes and model phases and molecular interactions (1:1 complex) were calculated by molecular mechanics (MM2) and the MOPAC from version 5 of the CAChe program from Fujitsu, Tokyo, Japan. The standard parameters used for MM2 force fields were bond stretch, bond angle, dihedral angle, improper torsion, Van der Waals, hydrogen bond and electrostatic (MM2 bond dipoles). The Van der Waals cut-off distance was 9 Å. The optimized energy value was less than 0.00001 kcal/mol. The energy unit was kcal/mol (1 kJ/mol = 4.18 kcal/mol). The MOPAC settings were analytical geometry search

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option (minimize gradient by EF, optimize geometry by EF) with XYZ and properties of Mulliken population polarizabilities and localized orbitals. The Cricket-Graph program from Computer Associates (San Diego, CA, USA) was used for data handling. The standard compounds used were isobutane, 1-butene, *n*-butane, *trans*-2-butene, benzene, 1,3,5-trihexene, 1,3-dihexene, 1-hexene, *n*-hexane, cyclohexane, ribose, mannose, α - and β -glucose, and α - and β -galactose.

3. Results and discussion

A 22-ring polycyclic aromatic hydrocarbon was first constructed as a model graphitic carbon phase, and the molecular interaction energy between this model phase and a standard compound was calculated using molecu-

lar mechanics (MM2) and AM1 of the MOPAC routine in the CAChe program. The calculated energy values are summarized in Tables 1 and 2. When two molecules form a complex, the energy value decreases from the sum of two molecule's energy value due to a formation of stable structure. When the energy value of a pair of molecules is the same as the sum of two molecule's energy value, a complex formation is not occurred. When the energy value of a complex is higher than the sum of two molecule's energy value, the complex is an excited stage to make a new compound. Therefore, the molecular interaction energy (Δ energy) value was calculated by subtracting the energy value of the complex from the sum of individual energy values and the energy value of model phase. The molecular mechanics calculation of one pair of molecular interactions was completed within a few minutes, while the MOPAC calculation required 6 h to optimize the complex form.

Table 1

Contribution of energy values calculated using molecular mechanics calculation for retention

Chemicals	Δ Final energy (eV)	Δ Van der Waals energy (eV)	Δ Hydrogen bonding energy (eV)	Δ Electro static energy (eV)	Retention energy (min)
β -Glucose	32.8246	3.415	33.711	19.831	2.40
β -Galactose	39.5774	6.903	40.627	17.348	2.60
α -Glucose	39.4049	6.094	37.769	34.864	2.62
α -Galactose	43.3891	5.434	39.738	33.195	3.05
Ribose	27.5529	5.128	25.891	13.618	2.30
β -Mannose	35.0325	6.515	30.271	19.071	2.50
Isobutane	6.6641	6.677	0	0	–
<i>n</i> -Butane	7.9056	7.954	0	0	–
1-Butene	8.0887	6.825	0	0	–
<i>trans</i> -2-Butene	11.2118	6.998	0.198	0	–
Cyclohexane	8.2060	8.241	0	0	–
Benzene	8.5939	8.615	0	0	–
1,3,5-Hexene	9.8368	9.859	0	0	–
1,3-Hexene	10.4864	9.576	0	0	–
1-Hexene	11.2417	10.222	0	0	–
Hexane	11.2554	11.315	0	0	–

Table 2

Contribution of energy values calculated using MOPAC calculation for complex formation

Chemicals	Δ Heat of formation (Kcal)	Δ Total energy (eV)	Δ Electronic energy (eV)	Δ Core-core repulsion (eV)	Δ Ionization potential
β -Glucose	–230.2	–10.0	31566.3	–31576.3	11.1
β -Galactose	–225.5	–9.8	31128.5	–31138.2	11.2
α -Glucose	–235.6	–10.2	33320.5	–33330.7	11.2
α -Galactose	–241.7	–10.5	24757.5	–24768.0	11.2
Ribose	–231.8	–10.0	20782.6	–20792.7	11.4
β -Mannose	–233.8	–10.1	30751.3	–30761.5	11.3
Isobutane	–234.9	–10.2	14695.9	–14706.0	11.9
<i>n</i> -Butane	–234.8	–10.2	14848.7	–14858.9	11.8
1-Butene	–234.8	–10.2	13761.2	–13771.4	10.5
<i>trans</i> -2-Butene	–233.8	–10.1	13859.2	–13869.4	10.1
Cyclohexane	–235.3	–10.2	19618.3	–19628.5	11.5
Benzene	–234.9	–10.2	17500.3	–17510.5	10.2
1,3,5-Hexene	–234.8	–10.2	18458.0	–18468.2	9.3
1,3-Hexene	–234.8	–10.2	18736.9	–18747.1	9.6
1-Hexene	–235.0	–10.2	18739.2	–18749.4	10.5
Hexane	–235.3	–10.2	18903.3	–18913.5	11.6

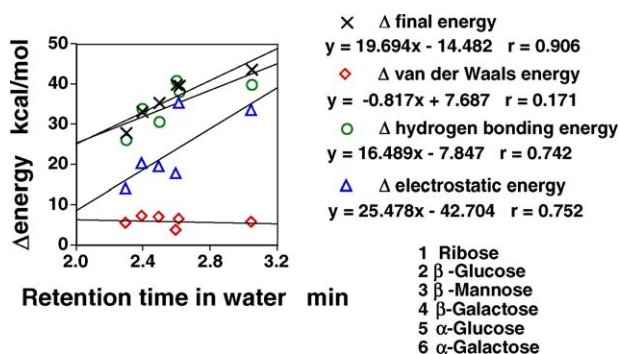


Fig. 1. Contribution of energy values for the retention of saccharides.

The retention mechanism of polar compounds was studied by analysis of retention of saccharides in liquid chromatography. The retention times measured in water was obtained from the literature [4] and collected in Table 1.

The correlation coefficient between these retention times and final structure energy was 0.906, $n = 6$. That between those and hydrogen bonding and electrostatic energy was 0.742 and 0.752, respectively. However, that between those and Van der Waals energy was 0.171. These results indicated that hydrogen bonding and electrostatic energy contributed to the retention of saccharides on a graphitic carbon in liquid chromatography as shown in Fig. 1. The Van der Waals energy values were nearly equal and there was no contribution to retention observed.

The MOPAC calculation did not indicate a specific contribution to molecular interaction. However, the heat of formation was related with the retention time of saccharides. The correlation coefficient between retention times and heat of formation or total energy was 0.684 ($n = 6$) as shown in Fig. 2.

Only a few retention data of similar organic volatile compounds were found in the literature on gas chromatographic analysis where a graphitic carbon column was used for gas analysis. Unsaturated compounds eluted faster than saturated compounds in general. The retention time of ethylene was shorter than that of ethane [5], and benzene eluted before *n*-hexane [6]. The retention order of 4 carbon hydrocarbons was isobutane, 1-butene, *n*-butane and trans-2-butene [7]. Therefore, the retention mechanism was studied using model standard compounds. No retention time measured at

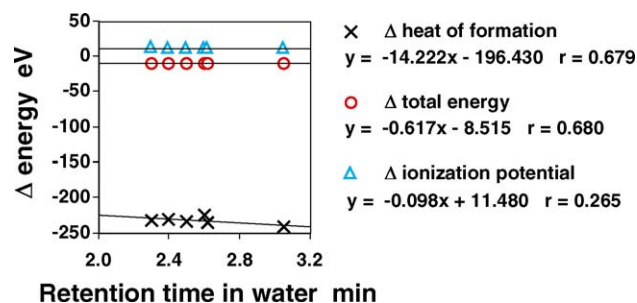


Fig. 2. Contribution of energy values calculated using MOPAC for the retention of saccharides.

isocratic condition was obtained, therefore, the correlation coefficient was not calculated. It seemed that the final structure energy should be related to the retention time, and Van der Waals energy contributed to the retention, while other energy values did not contribute according to MM2 calculation as summarized in Table 1.

The MOPAC calculation did not indicate clear evidence of the retention mechanism, however, electronic energy values seemed to be important to study the retention of hydrocarbons on a graphitic carbon even if the energy value did not change significantly as summarized in Table 2.

At present, molecular mechanics calculation, MM2, is useful to study the retention order in chromatography. MOPAC calculation did not clearly indicate the contribution force of molecular interaction. However, it demonstrated the molecular interaction center from the constructed electron density map by the tabulator of CAChe program, and the change of atomic partial charge before and after the optimization of the complex form. These hydrocarbons interacted at the center of PAH molecule, and these carbohydrates interacted at the edge of PAH with hydrogen bonding, where anions were retained by ion–ion interaction [1] as seen in Figs. 3 and 4.

Atomic partial charge of the model phase and these hydrocarbons did not change significantly after optimized the complex form of these hydrocarbons, while the electron potential was slightly shifted toward the molecular interaction side. On the other hand, a carbohydrate was first put on the center of the model phase, but it was shifted to the edge of model phase after the optimization. The result was the same for all compounds used. The atomic partial charge of atoms at hydrogen bonding site was changed about 0.01 eV. These results indicated clearly the existence of different retention mechanisms on graphitic carbon phase, hydrophobic and electrostatic interaction.

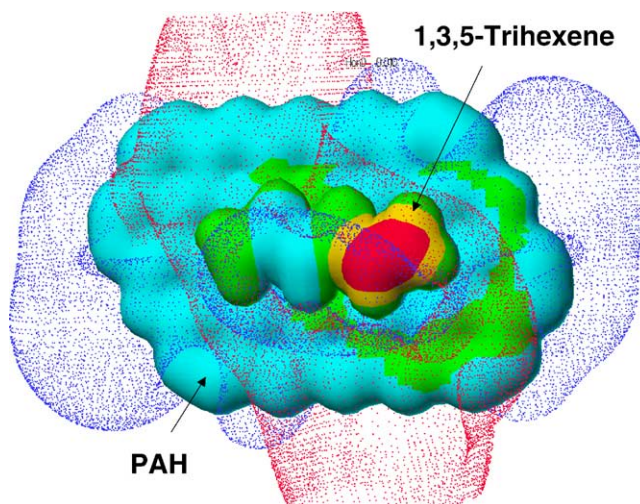


Fig. 3. Electrostatic potential (shaded shape) and electron density (dotted shape) of 1,3,5-trihexene-PAH complex. Darker the location, richer the electron on the surface of electron potential.

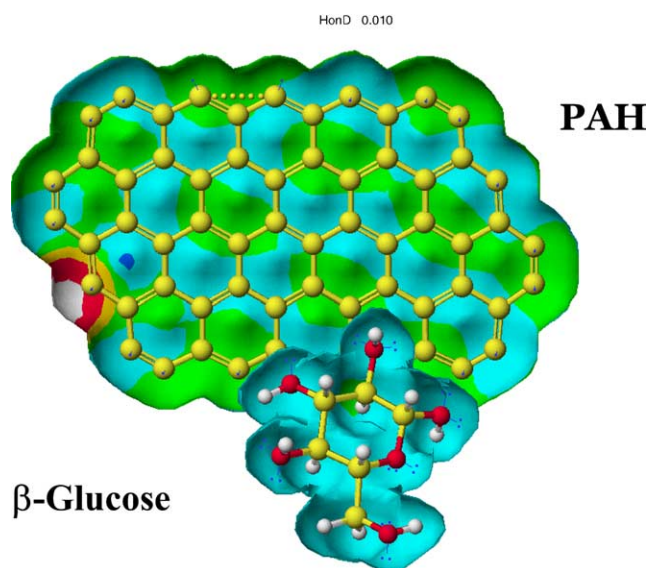


Fig. 4. Electrostatic potential of β -glucose-PAH complex: large grey ball: carbon; small grey ball: hydrogen; large black ball: oxygen.

4. Conclusion

This analysis indicated that MM2 calculation was sufficiently powerful to predict retention time at moment.

This simple calculation method was used to predict retention time of phenolic compounds measured in reversed-phase liquid chromatography using a pentyl-bonded phase with high precision instead of octanol-water partition coefficients ($\log P$ values) as previously used [8]. Further study using MM2 calculation with a suitable model phase will facilitate optimization in chromatographic separation, and MOPAC calculation will clarify the molecular interaction formation. Further study of the effect of solvent may improve precision, but this is not simple with the present computational system.

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