Using Connolly Surface to Characterize the Adsorption of Methyldibenzothiophenes and Methyldibenzofurans, and Their Chemical Mechanism as Molecular Tracer for Oil Filling Pathways

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Abstract: According to the geochromatographic effect, we can infer the general trend of oil migration based on the change of hydrocarbon composition in oil. In the oil migration carrier bed, oil is the mobile liquid mobile phase medium; the adsorbed water and bound water are stationary liquid fixed phase medium. The compounds in petroleum have a liquid-liquid geochromatographic fractional effect with adsorbed water and bound water. Due to the difference of adsorption function between the isomers of methyldibenzothiophene (MDBT) and methyldibenzofuran (MDBF), its relative content will change regularly with the migration of oil. In this paper, the Conolly molecular surface algorithm and DMol3 are used to calculate the molecular surface area and volume of target molecules. The water molecule with a radius of 1.5Å is used as a probe to make it roll on the surface of target molecules 1-MDBT, 4-MDBT and 1-MDBF, 4-MDBF respectively. The calculation results show that the surface area of 1-MDBT is 200.21Å2 and the volume is 184.28Å3; the surface area of 4-MDBT is 204.32Å2 and the volume is 186.34Å3; the dipole moment of 4-MDBT is larger. The surface area of 1-MDBF is 193.60Å2 and the volume is 175.06Å3; the surface area of 4-MDBF is 196.88Å2 and the volume is 174.77Å3, the dipole moment of 1-MDBF is much larger than that of 4-MDBF. Comparatively speaking, 4-MDBT and 1-MDBF have stronger adsorption. Therefore, when oil moves in the carrier bed, with the increase of migration distance, the parameters 4-/1-MDBT and 1-/4-MDBF decrease gradually.

1. Introduction

Dibenzothiophenes (DBTs) sulfur-containing heterocyclic aromatics and dibenzofurans (DBFs) oxygen-containing heterocyclic aromatics are ubiquitous in crude oils and sedimentary organic matters. As important molecular markers, they have been widely used in indicating the sedimentary environment of organic matters and classifying the petroleum origin types and maturity degrees [1]. Based on the thermal stability of the molecular structure and the mechanism of hydrogen bond formation, in recent years, a series of DBTs and DBFs indicators have been proposed to trace regional petroleum filling orientation and pathways. The method has been successfully applied in the Neogene sandstone reservoirs in the Pearl River Mouth Basin, the Paleogene sandstone reservoirs in the Beibu Gulf Basin and the Ordovician carbonate reservoirs in the Tarim Basin [2-6]. However, there are multiple interactions among the molecules of compounds in petroleum and between the molecules and the stratum medium. To generalize the parameters of various highly efficient DBTs and DBFs in tracing regional petroleum filling orientation and pathways, it is necessary to continuously study the chemical mechanism of the migration fractionation effect of these compounds.

The nitrogen-containing compound carbazole (shown in Figure 1a) is a common indicator to trace reservoir filling. The electronegativity of its N atom is 3.04 and the dipole moment is 1.70D

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(Debye), which is a polar compound. The carbazole molecules in petroleum can form hydrogen bond with the negative electric atoms in the medium through the hydrogen atom on the N-H functional group in the petroleum carrier bed, which leads to the adsorption of molecules and the migration fractionation effect. The structures of DBT and DBF molecules are similar to that of carbazole; they are symmetrical structures with high thermal stability and stable existence in highly mature oil. The contents in petroleum are generally higher than that of carbazole [2-6]. The sulfur atom of DBT (shown in shown in Figure 1b) has an electronegativity of 2.58, and a dipole moment of 0.84D; it is also a polar molecule. DBTs in petroleum can form hydrogen bonds with hydrogen atoms in the medium through lone pair electrons of sulfur atoms on thiophene rings, leading to the adsorption of molecules and the migration fractionation effect [2-6]. The electronegativity of oxygen and nitrogen atoms in DBF (shown in Figure 1c) is very high (3.44 and 3.04 respectively). Oxygen atoms can provide electrons and form hydrogen bonds with hydrogen atoms in the medium of the carrier bed, so that DBF can have a certain polarity. They can also produce the migration fractionation effect by acting on the carrier bed. According to the adsorption degrees of different compounds, a series of DBTs and DBFs indicators in regional petroleum filling orientation and pathways were proposed, such as 4-/ 1-methyl dibenzothiophene (4-/ 1-MDBT), 2,4-/1, 4-dimethyl dibenzothiophene, total alkyl dibenzothiophene, total DBFs, and 1-/ 4-MDBT [2-6].

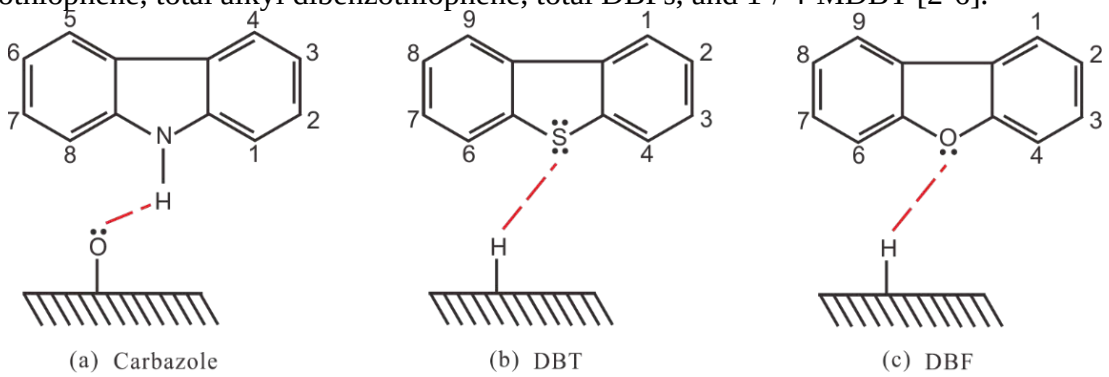

Fig.1 Hydrogen-Bond Interaction between Carbazole, Dibenzothiophene, Dibenzofuran and Electronegative Atoms in the Medium.

According to the adsorbability principle of the tracer, the molecular surface area and volume of DBTs and DBFs were calculated by the Connolly molecular surface algorithm [7]. The difference of adsorbing ability between adsorbed water and bound water by the molecular surface area was analyzed in order to further reveal the geochromic fractionation effect of petroleum in the carrier bed.

2. Characterization of Connolly Molecular Surface Adsorption

In the stratum, water coexists with the rock and accompanies the whole diagenesis process. Generally, rocks are hydrophilic, while water molecules have a certain polarity; they are easy to be absorbed by rocks to form adsorbed water, as shown in Figure 2. When oil transports in the pores filled with formation water, it will continuously expulse the formation water. However, the expulsion process will not be complete, and there is still a layer of irreducible water film on the surface of rock particles. That is, the oil mainly in direct contact with water molecules, rather than rock or mineral particles. Then, some compounds in oil will interact with water molecules, such as the hydrogen atom on N-H functional group in nitrogen compounds and the sulfur atom in sulfur compounds, which form a hydrogen bond with the negative electric atom (oxygen atom) and hydrogen atom in water medium respectively. As a result of hydrogen bonding, the compounds in petroleum will have a liquid-liquid chromatographic fractional effect with adsorbed and bound water (Figure 2).

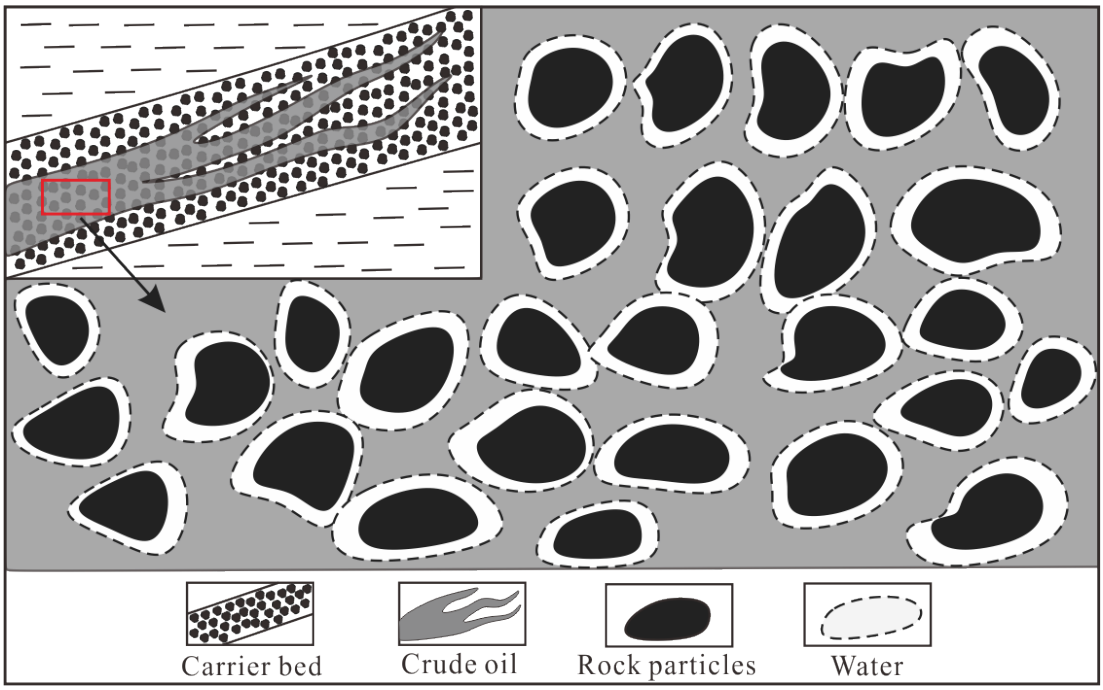

Fig.2 Migration of Crude Oil in Carrier Bed.

To characterize and calculate the surface properties of compound molecules is an important way to determine the molecular stability and recognize the molecular interactions in media. Connolly [7] first proposed the method of molecular point surface and triangulation of the surface. That is, by injecting a solvent molecular probe of appropriate size, it can roll along the target molecule, and the track passed by the inner concave surface of the probe molecule is the surface of the target molecule (Figure 3). Among them, if the molecular probe is tangent to an atom of the target molecule, the surface experienced on the atom is called a convex sphere (Figure 4a); if the molecular probe is tangent to two atoms, the surface experienced by the arc connecting the two point of contact on the probe is called the saddle sphere (Figure 4b); the triangular region formed by three atoms tangent to each other on the surface of the sphere facing the target molecule is called a concave sphere (Figure 4c). The sum of the convex sphere, the saddle sphere and the concave sphere of the target molecule is the molecular surface area represented by Connolly's surface algorithm. And the volume enclosed by the three is the molecular volume represented by Connolly's algorithm. In addition, when the probe molecule rolls on the target molecule's surface, the trajectory of the probe molecule's spherical center is the solvent-accessible surface. Comparatively speaking, the solvent-accessible surface is larger than the molecular surface.

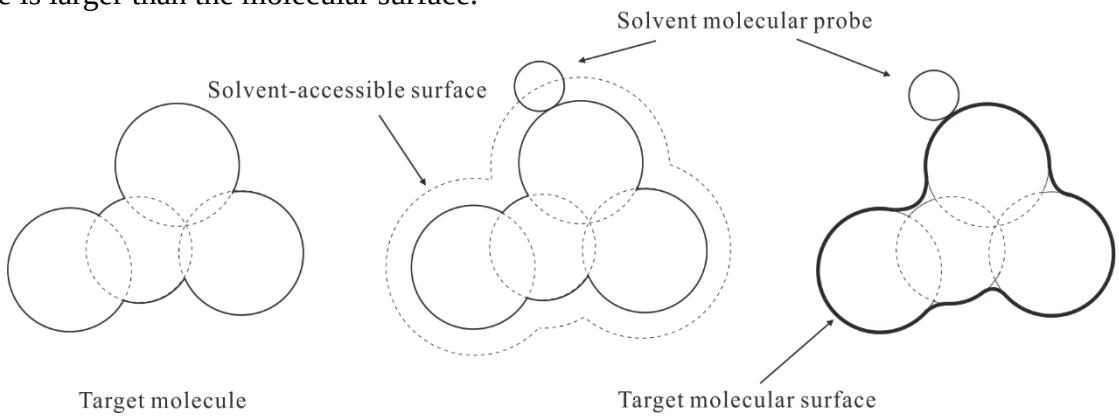

Fig.3 Connolly Surface Calculation of an Atomic Complex.

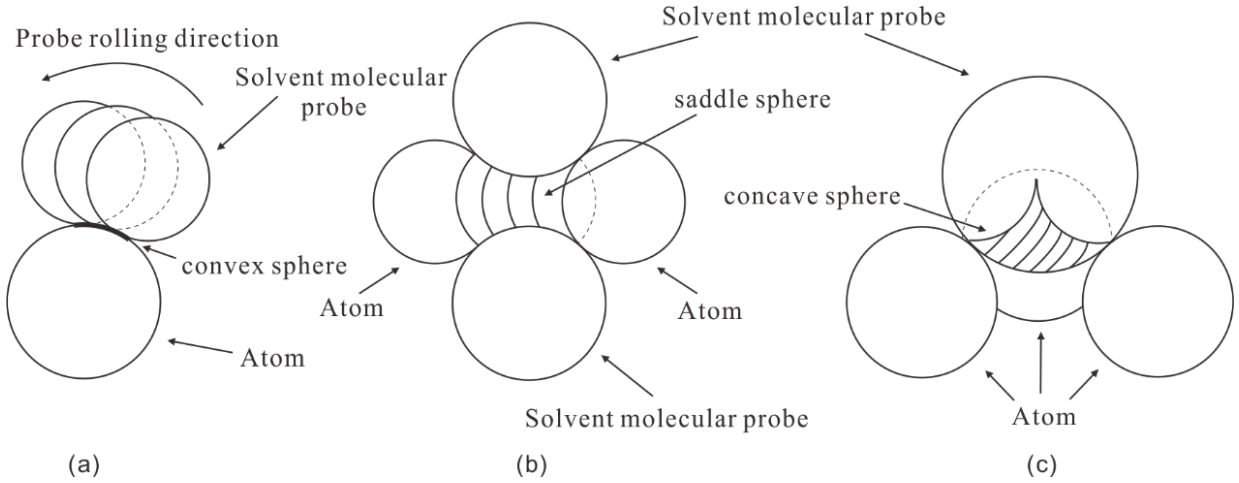

Fig.4 Types of Connolly Surface. [8]

In this paper, the calculation of the molecular surface of the compound is based on the density functional theory (DFT) method of all electrons, which is realized by the DMol3 software package [9]. The Grimme method is used for the DFT-D dispersion correction of the exchange-correlation function of GGA-PBE [9]. In geometrical structures optimization, the allowable relaxation guidance energy, the maximum force and the maximum displacement of all systems are less than 1×10^{-5}Ha, 0.001Ha/Å and 0.005Å respectively. The optimized equilibrium structure was then used to calculate the Connolly molecular surface and molecular volume of the compound with the atomic volume and surface area tools provided by Material Studio [10].

3. Molecular Surface Characterization of Mdbt and Mdbf

When the Connolly surface was calculated, the grid interval, Van Der Waals scale factor, the values of iso-surface and the radius of injected water molecular probe were 0.15Å, 1.00Å, 0.05 and 1.5Å respectively.

3.1 Characterization of Mdbt Molecular Surface

The experimental results showed that the surface area of the 1-MDBT molecule was 200.21Å^2 and the volume was 184.28Å^3; 4 - MDBT molecule had the surface area of 204.32Å^2 and the volume of 186.34 Å^3 (shown in Figure 5). The differences in measured values are small, but in terms of the size of molecules, especially isomers, even small differences can have a significant effect. Compared with the 1-MDBT molecule, the surface area and volume of the 4-MDBT molecule are larger, and the solvent-accessible surface formed by the water molecular probe is also larger. The larger the surface area of the compound, the more water molecules it can contact with.

In the oil migration carrier bed, the contact relationship between oil and water medium is similar to the contact between target molecules and water molecular probes in the experiment. Therefore, in the oil of the liquid mobile phase, Connolly molecules with larger the surface areas have larger contact areas with the adsorbed and bound water in the fixed phase. In combination with the experiment, the 4-MDBT with a large molecular surface area is more easily absorbed by the adsorbed water and bound water in petroleum than the 1-MDBT. It shows that the surface area of compound molecules in petroleum can be used as parameters determine its adsorption to the formation water of fixed phase. In addition, the dipole moment is 1.1687D for 4-MDBT and 1.1476D for 1-MDBT (shown in Figure 5)), indicating that the polarity of 4-MDBT is stronger than that of 1-MDBT, which further proves that 4-MDBT is more adsorbent.

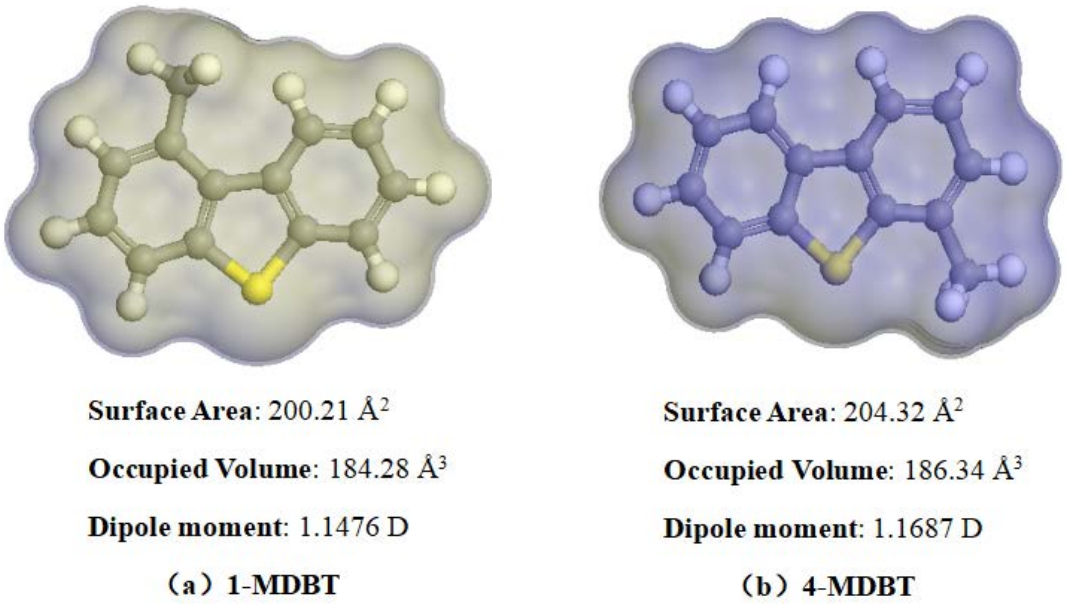

Fig.5 Connolly Surfaces of 1-Methyldibenzothiophene and 4-Methyldibenzothiophene.

Therefore, when the petroleum in mobile phase migrates in pores filled with formation water, the chromatographic fractionation effect between the oil of mobile phase with the adsorbed water and bound water of fixed phase occurs. As the migration distance increase, the number of compounds with stronger adsorption decreased, resulting in the gradual decrease of parameter 4-MDBT/1-MDBT.

3.2 Characterization of Mdbf Molecular Surface

The surface area of 1-MDBF molecule is 193.60Å^2, and the volume is 175.06Å^3. The surface area of the 4-MDBF molecule is 196.88Å^2, and the volume is 174.77Å^3. The surface area of the 4-MDBF molecule is slightly larger than that of 1-MDBF, but the volume is smaller. The dipole moment links the microcosmic structure and the macroscopic performance characteristics. The calculated molecular dipole moment is 1.1628D for 1-MDBF and 0.2977D for 4-MDBF. The dipole moment of 1-MDBF is much larger than that of 4-MDBF, indicating that the polarity of 1-MDBF is also much larger than that of 4-MDBF.

According to the analysis of molecular surface area, volume and molecular dipole moment, it is found that the molecular dipole moment is the decisive factor for the adsorbing ability of 1-MDBF and 4-MDBF. The adsorption property of 1-MDBF is stronger than that of 4-MDBF. In the oil migration carrier bed, the oxygen atoms in 1-MDBF are more likely to form hydrogen bonds with the hydrogen atoms in the water medium, and then be absorbed by the adsorbed water and the bound water. In the carrier bed, oil is the mobile liquid phase medium; adsorbed water and bound water are the stationary liquid phase medium. In the process of migration, liquid-liquid chromatographic fractional occurs between petroleum compounds and adsorbed water and bound water.

Therefore, when oil is transported in pores filled with formation water, the number of 1-MDBF with stronger adsorption decreases faster with the increase of migration distance, and the parameter 1-MDBF/4-MDBF also decreases gradually.

4. Conclusion

In the oil migration carrier bed, oil is the mobile liquid mobile phase medium; adsorbed water and bound water are stationary liquid fixed phase media. The hydrogen atom on the N-H functional group in nitrogen-containing compounds and the sulfur atom in the sulfur-containing compounds will form hydrogen bonds with the negative electric atom (oxygen atom) and the hydrogen atom in

the water medium respectively, and then be adsorbed. Compounds in petroleum will have liquid-liquid chromatographic fractional effect with adsorbed water and bound water.

The results of Connolly molecular characterization show that the surface area of 1-MDBT molecule is 200.21Å^2 and the volume is 184.28Å^3. The surface area of the 4-MDBT molecule is 204.32Å^2 and the volume is 186.34Å^3. The molecular surface area and volume of 4-MDBT isomers are larger than that of 1-MDBT isomers, and the contact area with water molecules is also larger. In addition, the polarity of 4-MDBT is stronger than that of 1-MDBT, so the adsorption ability of 4-MDBT is stronger. The surface area of 1-MDBF molecule is 193.60Å^2, and the volume is 175.06Å^3. The surface area of the 4-MDBF molecule is 196.88Å^2 and the volume is 174.77Å^3. The surface area of the 4-MDBF molecule is slightly larger than that of 1-MDBF, but the volume is smaller. The dipole moment of 1-MDBF is much larger than that of 4-MDBF. The comprehensive analysis shows that 1-MDBF has stronger adsorption capacity. Therefore, as the migration distance of oil in the carrier bed increases, the parameters 4-MDBT/1-MDBT and 1-MDBF/4-MDBF gradually decrease.

Acknowledgment

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