COMPOSITIONAL SPACE BOUNDARIES FOR ORGANIC COMPOUNDS

Vladislav V. Lobodin[1]; Chang S. Hsu[2]; Alan G. Marshall[1,3]

[1] Ion Cyclotron Resonance Program, NHMFL, Tallahassee, FL 32310
[2] Future Fuels Institute, Florida State University, Tallahassee, FL 32310
[3] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306.

Introduction

Analysis of complex organic mixtures provided by ultrahigh-resolution FT-ICR mass spectrometry enables us to assign an elemental composition for a myriad of components in petroleum and oils derived from fossil resources and bio-masses. The compositional boundary equation may be used to eliminate impossible or inaccessible chemical formulae from all possible elemental combinations found by computer matching of the measured accurate mass within a defined mass window.

Recently we introduced a linear equation DBE=0.9C# (where DBE is number of rings plus double bonds and C# is a number of carbon atoms in a molecule) to determine the upper limit of compositional boundaries for fossil hydrocarbons.[1] We called it “90% rule” that means that no hydrocarbon molecule in fossil resources (petroleum, coal etc.) is possible with DBE exceeding 90% of carbon number value. The lowest limit is DBE = 0, corresponding to alkanes (C_cH_{2c+2}), and coincides with the abscissa of a plot of DBE versus carbon number.

In this work we extend our studies to all hydrocarbons including polyynes structures and bucky bowls (not present in fossil resources) and organic compounds containing heteroatoms (S, O, N, P, Cl, etc.) in both natural resources and synthetic products.

Results and Discussions

For hydrocarbons in fossil oils, the upper boundary is determined by the maximally condensed aromatic structures to define a "planar aromatic limit” by a generalized equation of DBE=0.9*C# (Figure 1). However, non-planar aromatic structures formed by the inclusion of five-member rings surrounded by six-member rings, such as “bucky-bowls”, can be synthesized.[2] Although no such molecules have yet been reported in petroleum our generalized linear equation derived for the "planar aromatic limit" is still valid for all of the synthetic buckybowls.

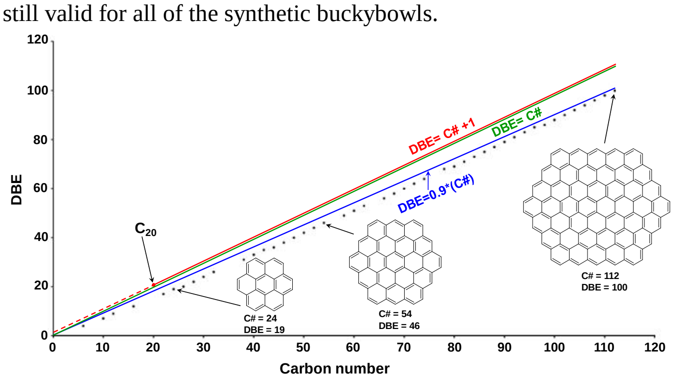

Figure 1. DBE vs. carbon number plot. Equation DBE=0.9*C# (blue line) defines the upper compositional boundaries for fossil hydrocarbons. Eq. DBE=C# (green line) corresponds to polyynes which covers all hydrocarbons. Eq. DBE=C#+1 (red line) determines the absolute upper limit for all compounds not containing any N atoms.

However, the upper boundary equation defined for fossil hydrocarbons is not always applicable to synthetic chemicals, such as the compounds containing triple bonds. The smallest molecule, acetylene, is an important petrochemical. Synthetic polymers with multiple acetylene units can be produced. The triple bond is equivalent to two double bonds and is accounted as DBE=2 for every triple bond. The upper compositional boundary for hydrocarbons containing triple bonds in polyynes having a general formula of C_CH_2 is determined by an equation of DBE=C# (green line on Figure 1). In nature, polyyne substructures have been reported in living organisms.[3] The same boundary equation can be applied to the cyano group having a triple bond between carbon and nitrogen by counting each nitrogen as carbon. For example, cyanogen C_2N_2 has a DBE=4, or DBE=C#+N#.

Three main criteria: DBE, number of carbon atoms and number of heteroatoms (N,O,S) are used to define the compositional boundaries for naturally occurring organic compounds. In general, the presence of O and S does not affect the DBE to carbon atom. Nitrogen-containing compounds, on the other hand, the number of nitrogen atoms would need to be considered due to its odd valence. As for fossil hydrocarbons, the upper boundary of heteroatom-containing compounds is also determined by the maximally condensed aromatic structures and generalized equation of DBE=0.9(C#+N#), where N# is number of nitrogen atoms in the molecule.[4] For example, Figure 2 shows DBE vs. carbon number plot for N_1 class of the severely thermo-treated asphaltene residue analyzed by (+) ESI FT-ICR MS. The upper compositional space boundary (dashed red line) is defined by the equation DBE = 0.9 x (C#+1), because number of nitrogen atoms (N#) in this class (N_1) is 1.

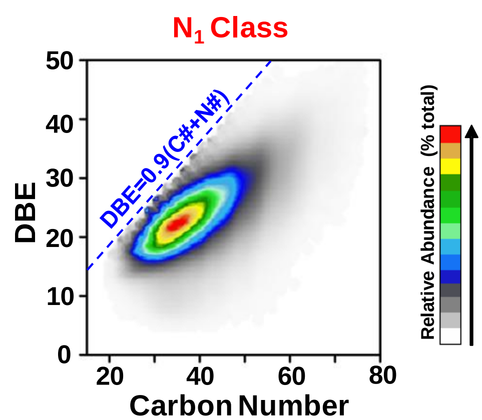

Figure 2. DBE vs. carbon number plot for N_1 class of the severely thermo-treated asphaltene residue. The sample was analyzed by (+) ESI FT-ICR MS. Compositional space boundary (dashed blue line) for N_1 class is based on the equation DBE = 0.9 x (C#+ N#).

To obtain the absolute upper boundary for all compounds including those without hydrogen atom, such as CS_2, we use fullerenes as a reference to derive an equation of DBE=C#+1 (solid red line on Figure1).

Conclusions

We have defined the absolute compositional boundaries for organic compounds.

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References

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