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Highly Efficient Separation of Phenolic Compounds from Oil Mixtures by Imidazolium-Based Dicationic Ionic Liquids via Forming Deep Eutectic Solvents

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Review

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Geochemical Evolution of Occluded Hydrocarbons inside Geomacromolecules: A Review

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ABSTRACT: Within geomacromolecules, such as kerogen, asphaltene, and solid bitumen, other compounds can be adsorbed and even occluded as free molecules. The occluded components have been well preserved by the macromolecular structure, and retain some of the primary geochemical information. In this work we try to probe the geochemical evolution of occluded hydrocarbons inside geomacromolecules associated with the geomacromolecule evolution from kerogen → asphaltene → solid bitumen. The results show that occluded hydrocarbons can be transferred steadily from kerogen → asphaltene → solid bitumen. Later-evolved geomacromolecules not only inherit the occluded hydrocarbons from the former ones, but can also occlude some new free molecules. Occluded hydrocarbons are subject to a relatively independent thermal evolution, whereas the evolution of adsorbed molecules is constrained by other factors besides thermal stress. Elucidation of the geochemical evolution of occluded hydrocarbons inside geomacromolecules will be helpful in oil (bitumen)−source correlation, identification of mixed-source reservoirs, and characterization of hydrocarbon accumulation and evolution.

1. INTRODUCTION

During geological history, dead organisms successively undergo the geological processes of sedimentation, diagenesis, catagenesis, and metagenesis, accompanied by the occurrence of a variety of biochemical or chemical reactions and the formation of geomacromolecules. Fulvic acid, humic acid, and humin usually form during the deposition of organic matter through the processes of microbial degradation, polymerization, and condensation; kerogen is generated through sediment diagenesis, and then asphaltene is derived from the kerogen cracking (Figure 1).[1] Solid bitumen can also be formed during the degradation of kerogen,[2] although it is mainly derived from crude oil evolution processes, including thermal alteration, deasphalting, or biodegradation.[3] Thus, such geomacromolecules are the products of sedimentary organic matter in different evolution stages and contain a significant amount of geochemical information, making them some of the most studied objects in many fields, such as biogeochemistry, environmental geochemistry, and oil/gas geochemistry.

Geomacromolecules generally have high molecular weights and complex chemical structures (but no regular molecular formula), and are actually admixtures. Some conceptual structure models representing the largest possible set of physicochemical analytical data for geomacromolecules have previously been used to represent the structures of humic matter,[4−6] kerogen,[7,8] and asphaltene.[9−11] Specific acids or alkalis are usually used to isolate humic matter[12] and kerogen,[8] whereas asphaltene[13] and solid bitumen[14,15] are obtained by treatment with appropriate organic solvents.

As representative geomacromolecules from source rock or oil reservoirs, kerogen, asphaltene, and solid bitumen are important study objects for the geochemical information encoded with them. Their macromolecular structures can adsorb and even occlude other small molecules (e.g., biomarkers).[16−19] The occluded molecules can be well preserved by the macromolecular structure and thus prevented from contact with extraneous reagents, catalysts, microbes, or surface-derived formation waters flowing through the deposit.[20−22] Therefore, the occluded fraction can retain primary organic geochemical information over the geological time.[20−22] Besides the free molecules occluded inside the geomacromolecular structure, some biomarkers are covalently bonded to the geomacromolecular structure so that they retain earlier geochemical characterization.[23−25]

In studies on the adsorbed and occluded components of geomacromolecules, researchers have detected many biomarkers among the occluded compounds. These biomarkers have proved to be useful in studies of organic matter with depleted soluble fractions,[17] oil (bitumen)-source correlation,[16,26] identification of mixed-source reservoirs,[27−29] and characterization of hydrocarbon accumulation and evolution.[19]

2. ADSORPTION−OCCLUSION IN GEOMACROMOLECULES

2.1. Adsorption−Occlusion Phenomena Inside the Structure of Geomacromolecules. In the extraction of kerogen using different solvents, such as chloroform, a mixture of methanol/acetone/chloroform, or a mixture of CS_2 and *N*-methyl-2-pyrrolidinone, extraction yields typically increase with increasing polarity of the organic solvents, indicating an abundance of noncovalent bond interactions between the organic matter and the kerogen structure.[30,31] Asphaltene, from the oils suffered from serious biodegradation and depleted in *n*-alkanes, has been dissolved in toluene and reprecipitated from

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