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Time of flight-secondary ion mass spectrometry (TOF-SIMS) study of diverse asphaltenes

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ABSTRACT

Mass spectrometry has been used to elucidate a large variety of properties of asphaltenes. Here, time-of-flight secondary ion mass spectrometry (TOF-SIMS) is used to probe three diverse asphaltene types with wide ranging fractions of alkyl carbon to the sum of alkyl plus aromatic carbon (Rc), immature source rock asphaltenes (ISA with Rc ~ 0.75); petroleum asphaltenes (PA with Rc ~ 0.5); and coal-derived asphaltenes (CDA with Rc ~ 0.25). In addition, the asphaltenes from a commercial bitumen are examined. Primary ion surface bombardment using the Bi_3^+ ion yields high energy density of deposition and significant molecular fragmentation with secondary ion formation. Formation of free radical cation fragments is generally suppressed especially for smaller fragments except for specific cases. Possible structures, especially cations of common aromatic compounds, are suggested for fragments with relatively large cross section of formation. Principal component analysis of the fragmentograms allows identification of key properties of the complex fragmentation patterns for the different samples. Comparisons of TOF-SIMS fragmentograms show a fundamental difference for small fragments between CDAs and all petroleum derived asphaltenes with CDAs being dominated by aromatic carbon fragments whereas all petroleum derived asphaltenes show a large fraction of fragments from alkyl carbon. However, the type of alkyl carbon fragments did not exhibit systematic trends with Rc, nor with the extent of chemical reaction or chemical processing of the materials. Consequently, it appears that having an appreciable alkane fraction is a basic property of petroleum derived asphaltenes, but the exact type of alkane carbon for differing samples of these asphaltenes is more idiosyncratic than systematic.

1. Introduction

Almost all chemical properties of asphaltenes have been subject to significant debate [1–3]. Perhaps the most fundamental debate has addressed the molecular weight of asphaltenes; other concerns include the molecular architecture of asphaltenes, the nanoaggregate aggregation number, the binding strength of asphaltene nanoaggregates, and the critical nanoaggregate concentration; mass spectrometry has played a very important and, at times, decisive role in resolving these issues. The uncertainty in molecular weight spanned a huge range of one or more decades [4]. Early mass spectrometry results indicated the molecular weight distribution of (petroleum) asphaltenes peaked below one kilodalton [5]. Nevertheless, some confusion arose from the application of colligative techniques such as vapor pressure osmometry to molecular weight, in spite of the countervailing properties for VPO measurements of asphaltenes of requiring high concentrations and being very sensitive to aggregation [4]. Moreover, laser desorption ionization mass spectrometry (LDI MS) applied to asphaltenes gave variable results [4]. Molecular diffusion helped clarify the issue; measurements employing low concentrations indicated that asphaltene molecular weights are around 750 Da [6–9]. Moreover, the artifact of molecular aggregation on LDI MS was shown to occur when high laser power and high surface concentrations of asphaltenes were employed [10,11]. Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS) yields ultrahigh resolution and gives asphaltene molecular weights in the 700 Da range [12]. The complementary method of utilizing ESI ionization with an orbitrap mass analyzer gives comparable results [13]. Atmospheric pressure chemical ionization (APCI) [14] and laser induced acoustic desorption mass spectrometry [15] confirmed these results. Two-step laser desorption laser ionization (L^2MS) has been shown to avoid both aggregation and fragmentation [16], and yields 650 Da asphaltene molecular weights [17–27].

The existence and dominance of island molecular architecture of

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asphaltenes, with a single, relatively large polycyclic aromatic hydrocarbon (PAH) per molecule, was first indicated by time resolved fluorescence depolarization studies [6,7,28,29]. L^2MS studies utilizing 25 island and archipelago model compounds show that asphaltenes are dominated by island architecture; all archipelago models compounds underwent unimolecular decomposition at high laser power, while none of the island compounds nor the asphaltenes exhibited this behavior under identical conditions [22]. In addition, the L^2MS method has been shown to have relatively constant cross section for a wide variety of molecular structures [18]. Other mass spectrometry studies employing electron ionization and collisional assisted decomposition (CAD) obtained fragmentation patterns more consistent with island architecture [30]. While unimolecular decomposition studies support the island molecular architecture for asphaltenes [22,30], bulk decomposition studies of asphaltenes are much less definitive in part because bulk decomposition studies of island model compounds result in the fabrication of archipelago compounds [31]. Presumably, bulk decomposition of archipelago model compounds would yield islands compounds as well. Consequently, while bulk decomposition of asphaltenes delineates degradation products, these methods are evidently not effective at determining unaltered, original asphaltene chemical structures.

Recently high resolution scanning tunneling microscopy (STM) and atomic force microscopy (AFM) studies have confirmed island architecture dominates in asphaltenes from a large variety of samples [32,33]. A study of archipelago model compounds shows that the flash heating under ultrahigh vacuum conditions employed by the IBM Zurich group in the asphaltene studies readily resolve “traditional archipelago” structures which have PAHs linked with an alkane chain. Especially, IBM Zurich and collaborators showed that BPE (1,2-dipyrenylethane) was successfully transferred, and not a single BPE molecule was fragmented among about one hundred molecules imaged, despite the presence of a very weak CC bond (65 kcal/mol, compared to 85 kcal/mol for a typical CC bond) [34]. It showed the flash heating under high vacuum condition is quite mild in preserving molecules from thermal cracking, and is consistent with earlier data which suggested that the rate of fragmentation is not competitive to desorption under similar conditions [35].

Mass spectrometry has also been key in determination of the aggregation number of asphaltenes. Surface assisted laser ionization mass spectrometry (SALDI MS) employs gentle desorption due to indirect heating of the sample. This method can preserve asphaltene nanoaggregates if the laser power is kept sufficiently low [20,24,26]. By measurement of molecular weight by L^2MS and nanoaggregate weight by SALDI MS, aggregation numbers can be determined. For diverse asphaltenes similar to those use here, ISAs, PAs, and CDAs, the aggregation numbers have all been shown to be roughly 7 [24,26]. This aggregation number is very similar to estimates from other methods including NMR [36], centrifugation studies [37], equilibrated gravitational gradients [38,39], and DC-conductivity studies [40,41]. The critical nanoaggregate number (CNAC) of asphaltenes has been determined by many methods including high-Q ultrasonics [42,43], NMR [36], centrifugation studies [37], and DC-conductivity studies [40,41]. Mass spectrometry has also been used to obtain the asphaltene CNAC which obtained results in agreement with other studies [44].

Mass spectrometry has contributed to understanding the strength of binding in the nanoaggregate. SALDI MS studies of asphaltenes shows that the nanoaggregates are preserved only at the lowest laser power suggesting weakly bound nanoaggregates [20,24,26,27]. At higher laser powers, asphaltene nanoaggregates are disaggregated to small multimers [20]. The greater heating typical in L^2MS methods is not compatible with preservation of asphaltene nanoaggregates [20,22,45], while L^2MS methods also suppress fragmentation [45]. These results are also consistent with direct molecular imaging analyses of asphaltenes, where a rapidly heated filament for sample transfer disaggregated all asphaltene nanoaggregates [32,33]. This low binding energy of asphaltene nanoaggregates is consistent with the CNAC of asphaltenes in toluene being ~2 × 10^{-4} Molar [36,37,40–44]. Using the approximation, $\Delta G^0_{\text{CNAC}} = RT\ln(\text{CNAC})$; one obtains $\Delta G^0_{\text{CNAC}} = 5$ kcal/mole, similar to a physisorption interaction with much lower energy than a covalent bond. Moreover, the small temperature dependence of the CNAC indicates that nanoaggregate formation is driven primarily by entropy and to a lesser extent enthalpy [36,41]. The observation of nanoaggregates [38,46,47] and clusters [47,48] in oilfield reservoirs with temperatures in excess of 100 °C is consistent with a small temperature dependence of the aggregation concentrations of these species; a large temperature dependence could preclude aggregate formation in reservoirs. This result is consistent with the fact that the formation of surfactant micelles in aqueous systems is dominated by entropy; the solvent entropy increases more than the surfactant entropy decreases in micelle formation. In addition, a recent study indicates that for different asphaltenes the nanoaggregate aggregation number is rather invariant. Nevertheless, the extent of π-stacking in the nanoaggregate depends significantly and inversely on the fraction of alkane carbon in the nanoaggregate [24]. This is consistent with a lesser role played by enthalpy in that the extent of π -stacking would be expected to impact enthalpy. One mass spectrometry study did indicate a tightly bound nanoaggregate, and also indicated a somewhat larger aggregation number than other studies [44]; perhaps these two observations are correlated.

All of these previous mass spectral studies of asphaltenes have utilized relatively small excess energies in order to probe asphaltene properties with little chemical alteration. Even for studies where covalent bonds were being broken, the objective remained to minimize fragmentation. For example, the L^2MS experiments which show that the island architecture dominates by comparing fragmentation patterns of 23 model compounds with asphaltenes, the ionizing laser power was increased from low values until the threshold for fragmentation was obtained.

In this paper time-of-flight, secondary ion mass spectrometry is used to probe diverse asphaltenes. Here, enormous fragmentation energies are used. Very high energy densities are obtained using heavy ion bombardment (Bi_3^+ ion) at 25 keV. This process yields energy densities far higher than often used in mass spectrometry, for example with 70 eV electron ionization mass spectrometry. In this paper, we are not attempting to address a particular chemical attribute of asphaltenes such as molecular weight, but rather we are exploring the behavior of diverse asphaltenes in very energetic fragmentation. Here, we explore cations only. The selection against free radical cation formation is generally important for smaller fragments. Many fragmentograms exhibit large peaks plausibly associated with specific aromatic compounds. Some distinction of fragmentograms on sample origin is observed, specifically for coal-derived asphaltenes with high fractions of aromatic carbon vs. all petroleum-derived asphaltenes with lower fractions of aromatic carbon. For larger fragments, the fragmentograms for all asphaltene samples here are fairly similar.

2. Experimental section

2.1. Sample preparation

Asphaltenes were extracted from three sources, as described previously [24,49]. The sources include petroleum asphaltenes (PA), coal-derived asphaltenes (CDA), and immature shale asphaltenes (ISA). The PA samples are UG8 and BG5, both extracted from Kuwaiti black oils. The CDA samples are Adaru and Wyoming, both extracted from coal liquefaction and distillation processes [50–52]. The ISA sample is Eagle Ford, extracted from an unweathered outcrop of an immature section of the Eagle Ford [19].

For each sample, the asphaltenes were isolated from the liquid feedstock (the dead crude oil for the PA, liquified and distilled coal for the CDA, and bitumen extracted from the shale by 9:1 DCM:MeOH for