CHARACTERIZATION OF HIGH-MOLECULAR WEIGHT SULFUR CONTAINING AROMATICS IN VACUUM RESIDUES USING FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

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Introduction

Millions of tons of vacuum residues are produced annually in oil refineries worldwide. Although being potentially valuable resources for petrochemistry, their further processing is hampered by the fairly large amounts of sulfur present in these heavy fractions. Removal of the largely polycyclic aromatic sulfur heterocycles (PASH) by hydrodesulfurization (HDS) is more inefficient than for lighter petroleum fractions[1]. A better structural knowledge of the recalcitrant PASHs is therefore desirable for the development of new catalysts.

Previous studies proved that even after several chromatographic simplification steps the complexity of the sample is tremendous. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has demonstrated the capability to resolve thousands of compounds in similar samples[2]. Nitrogen and polar compounds were investigated and more than 11,000 unique exact masses were identified. However, a selective measurement of PASHs is not easily feasible with present methods.

To study specifically the sulfur heterocycles in vacuum residues, we are investigating the methylation of the sulfur atoms of the target molecules to methylsulfonium salts[3]. Thus, these compounds are effectively "tagged" in a highly selective reaction prior to injection into the mass spectrometer. The computed mass data show the presence of PASHs with mainly one and two sulfur atoms per molecule in the vacuum residue before and after partial hydrodesulfurization.

Experimental

Vacuum Residue Samples. The residue samples investigated in this study were taken from a Safaniya crude oil before (feed) and after (effluent) partial hydrotreatment with a catalyst. The sample residues were provided by the Institut français du pétrole, Vernaison, France. After removal of asphaltenes by precipitation, the aromatic fraction was isolated by preparative liquid chromatography in order to separate saturate-aromatic-resin compounds according to the SARA method[4]. The aromatic fraction contained 4.66 % sulfur before and 2.91 % after hydrodesulfurization

Ligand exchange chromatography provided a group separation of PASHs from the polycyclic aromatic hydrocarbons (PAH). This separation was achieved using a Pd(II)-bonded stationary phase as described previously[5]. Two fractions were easily separated by using eluents of different polarity and are referred to as the PAH and the PASH fraction.

Methylation of sulfur compounds. PASHs were selectively methylated at the sulfur atom, thus efficiently charging PASHs with a positive charge using a procedure described by Acheson et al[3]. PAH and PASH fractions of 50 mg "feed" and "effluent" and 1 mmol of iodomethane were dissolved in 3 mL of dry 1,2-dichloroethane (DCE). A solution of 1 mmol silver tetrafluoroborate in 2 mL DCE was added and allowed to react for 48 h. The precipitated silver iodide was removed by centrifugation and DCE was distilled off under reduced pressure. The resulting sulfonium salt was dried under vacuum before mass spectrometric analysis. To investigate the influence of alkyl substitution on the efficiency of the methylation, reference compounds were methylated as well. The following compounds were employed: dibenzothiophene, 4-methyldibenzothiophene, 4-ethyldibenzothiophene, 2,4,6,8-tetramethyldibenzothiophene, and 2,7-dimethylbenzothiophene. Except for the commercial dibenzothiophene, they were synthesized in our laboratory[6].

High resolution mass spectrometry. Mass spectra were acquired using an APEX III Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a 7 T magnet and an Agilent electrospray (ESI) ion source. For introduction the samples were dissolved in a 50:50 (v/v) solution of dichloromethane/methanol and injected in the infusion mode using flow rates of 2 µL/min. Typical electrospray conditions were 4.5 kV spray voltage. After ionization the ions were accumulated for 0.5 s in the hexapol before transfer to the cyclotron cell. For a good signal-to-noise ratio at least 64 scans were accumulated. Internal and external calibration was done using the Agilent electrospray calibration solution with the masses 322.04812, 622.02896, 922.00980 covering the mass whole range of the samples.

Calculation of compound classes from accurate mass data. For each mass signal several most probable elemental compositions were calculated using the software "Molecular Weight Calculator" [7], Version 6.25. Mass data and formulas were imported into an Excel spreadsheet. The formulas were evaluated based on them making chemical sense and sorted to provide classes according to the degree of saturation (type) and the number of heteroatoms (class) present[8,9].

Results and Discussion

The methylation reaction presented here together with ESI selectively ionizes PASHs through conversion of the neutral sulfur atom into a sulfonium ion as shown in Figure 1:

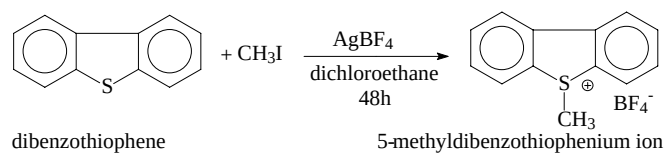

Figure 1. Methylation of PASH with dibenzothiophene as example.

Recalcitrant PASHs most probably are substituted by alkyl groups in the positions adjacent to the sulfur atoms[1] and thus it is likely that they exert a degree of steric hindrance to this reaction. To study this effect, five reference compounds were methylated using the described procedure. After the reaction time was increased from 2h as suggested in the literature to 16 h (necessary for quantitative reaction of 2,4,6,8-tetramethyldibenzothiophene), high yields of thiophenium salts were obtained as judged by matrix assisted laser desorption and ionization time of flight (MALDI-TOF) MS analysis. However, clusters of tetrafluoroborate and two sulfonium aromatic molecules could be observed to some extent.

To reduce the effect of this steric hindrance, which may be even larger in the PASHs in the vacuum residues, the reaction time for the samples was increased to 48 h. An example of the resulting mass spectra is shown in Figure 2. This method allows the selective investigation of complex solutions of sulfur containing heterocyclic compounds. It should be stressed here that without the methylation the atmospheric pressure chemical ionization (APCI) commonly used in LC/MS and MALDI ionization showed poor signal-to-noise ratio and no selectivity towards PASHs.

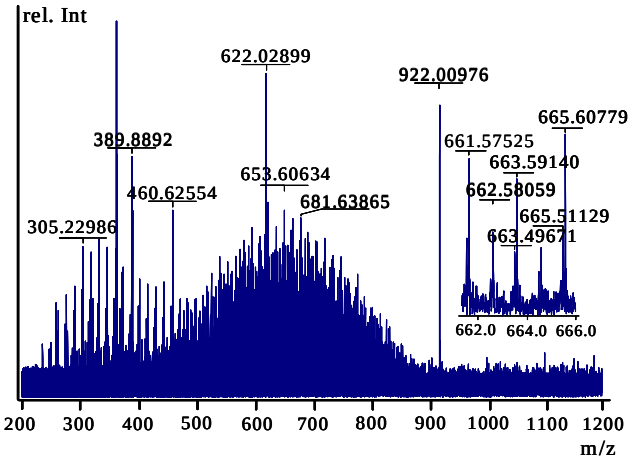

Figure 2. FT-ICR-mass spectrum of the aromatic effluent PASH fraction (only the mass range from m/z 200 to 1200 is shown). The insert shows the region from 662 to 666 m/z in more detail.

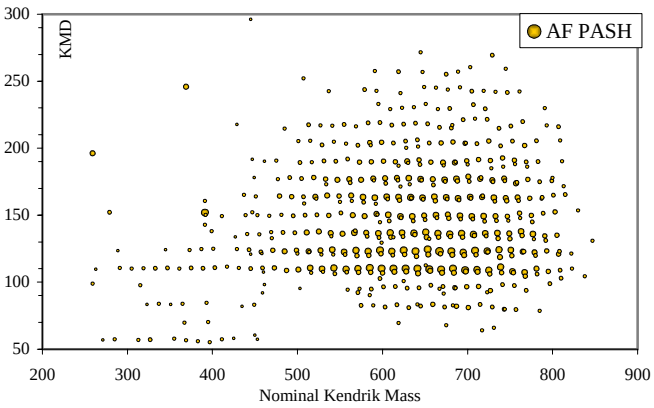

Figure 3. Kendrick mass defect (KMD) is plotted against Kendrick nominal mass. Series of PASH homologues of the aromatic fraction of the feed (AF PASH) appear in horizontal lines.

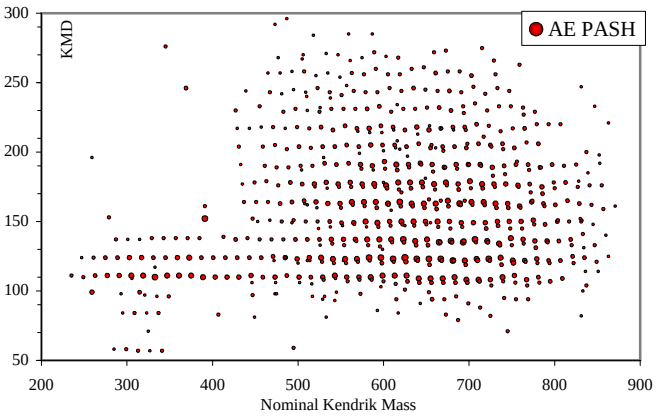

Figure 4. Kendrick mass defect (KMD) is plotted against Kendrick nominal mass. Series of PASH homologues of the aromatic fraction of the effluent (AE PASH) appear in horizontal lines.

Similar mass ranges as those shown in Figure 2 have been observed in previous experiments using different (APCI and MALDI) ionization techniques from nonderivatized samples, therefore the possibility of cluster formation does not seem to be serious. In contrast to these observations, about one third of the signals of samples of this study can only be explained by molecular clusters containing Ag^+ or BF_4^-. This however provides no problem as these clusters can be identified using the high accuracy data from FT-ICR-MS and treated separately.

Series of homologues can be identified visually as horizontal lines by plotting the Kendrick mass defect against Kendrick nominal mass. The Kendrick mass scale converts IUPAC masses by making CH_2 equal to 14.00000 as base of the scale. Kendrick mass defect (KMD) is the difference between nominal (Kendrick mass rounded to nearest integer) and accurate Kendrick mass. As a result members of homologous series feature the same KMD and are spaced at equal distances of 14 mass units. This is shown in Figures 3 and 4 for the PASHs of the aromatic fraction before and after HDS. The size of the dots reflects the intensity in the mass spectra.

The whole process of methylation reaction, ESI ionization, FT-ICR-MS data collection, and final data processing is highly selective towards PASHs. First results show that even in the two PAH fractions (feed and effluent), the large majority of the measured signals result from PASHs containing one (S1), two (S2) sulfur atoms. Compounds with three sulfur atoms (S3) are not as abundant but seem to be present in the sample. In Figure 5 the sum over the intensities of all identified molecules of the S class as well as the sum of intensities of all S2 class, S3 class, and PAH class compounds are given. This shows the tremendous selectivity towards PASHs over the much more abundant PAHs, as most compounds identified in all samples belong to the S and S2 class. Even in the PAH fractions which should consist of PAHs only, given the high selectivity of the Pd(II)-phase, very few masses were tentatively identified as belonging to PAH class compounds, again stressing the high selectivity of the methylation process.

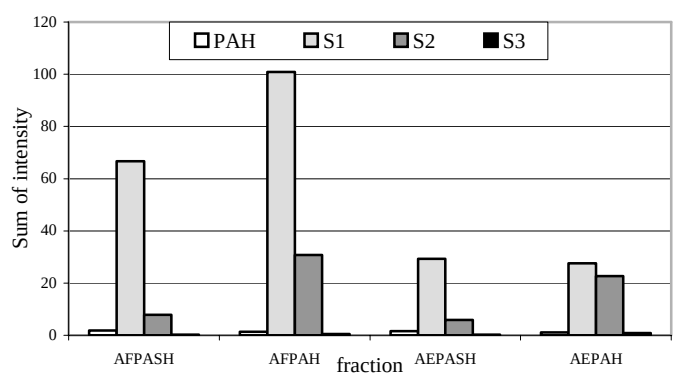

Figure 5. Sum over the intensities of mass signals of all members of one class for the dominant classes ("PAH", "S1", "S2" and "S3") present in sample vacuum residues.

Table 1 gives an overview of the distribution of compounds as a function of hydrogen deficiency in the four sample fractions. For the S1 class in both PAH fractions, more condensed material is present in comparison to both PASH fractions as can be seen from the higher Z number which is a measure for the hydrogen deficiency in the compounds. The same is true for the S2 class, but is not as distinct as for the monosulfur compounds.

	S1 class				**S2** class			
Z "type"	AF PASH	AFPAH	AE PASH	AE PAH	AF PASH	AFPAH	AE PASH	AE PAH
0	7	0	3	0	3	9	9	8
2	3	0	1	0	6	7	9	10
4	10	0	6	0	6	5	10	6
6	11	0	5	0	3	5	7	12
8	44	1	40	0	5	10	7	17
10	39	29	50	5	2	6	3	16
12	28	32	40	4	2	7	4	6
14	21	13	24	2	3	8	2	13
16	37	34	32	11	0	4	4	11
18	29	34	34	10	5	6	4	6
20	20	33	27	13	1	12	5	6
22	18	33	20	18	1	9	5	4
24	10	22	21	10	0	5	0	3
26	4	18	12	17	0	1	0	1
28	4	7	10	19	0	2	1	0
30	5	3	7	10	0	0	0	0
32	0	6	3	8	0	0	0	0
34	0	2	2	8	0	0	0	0
36	0	3	0	2	0	0	0	0
38	0	1	0	0	0	0	0	0

Table 1. Comparison of Compound Classes and Types of AE PASH Fraction and AE PAH Fraction; "Z" is the Value of Hydrogen Deficiency in Chemical Formulas $C_cH_{2c-\underline{Z}}O_oS_s$.

The data shown in Table 1 also demonstrate the effect of the hydrodesulfurization reaction. PASHs that survive the hydrotreatment show a trend towards higher hydrogen deficiency, possibly indicating a more condensed nature of those PASHs that do not react. However, by comparison of KMD plots of AF PASHs and AE PASHs (Fig. 3 and 4) a preferential loss of molecules with lower molecular mass during hydrodesulfurization is not observed.

Acknowledgement. Dr. Stephane Kressman and Dr. François Xavier, Institut français du pétrole, Vernaison, France, are thanked for preparing and supplying the aromatic fractions of the residue samples.

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