

Characterization of sulfur in asphaltenes by sulfur K- and L-edge XANES spectroscopy

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Bitumens exposed to atmospheric conditions undergo various types of weathering including evaporation, biodegradation, abiotic oxidation, and water washing. Sulfur present in bitumens is a good marker of oxidation processes as it is very sensitive to oxidation and exhibits a range of oxidation states from -2 to $+6$. Sulfur K- and L-edge XANES spectroscopy were applied to the asphaltene extracts of a series of recent geological and archeological bitumens from the Middle East. In all the samples, dibenzothiophene is the major sulfur moiety. In the least altered asphaltene, minor species include disulfide, alkyl sulfide and sulfoxide. The proportion of oxidized sulfur (sulfoxide, sulfone, sulfonate and sulfate) increases with the alteration of the samples, whereas the disulfide and alkyl sulfide content decreases. This work illustrates the interest of XANES spectroscopy as a selective probe for determining sulfur speciation in natural samples, and the complementarity of S K- and L- edge for identifying the oxidized and reduced forms of sulfur respectively.

Keywords: sulfur, speciation, oxidation, asphaltene, XANES.

1. Introduction

Determining the sulfur speciation in asphaltenes is important as it can be used as a marker of the alteration of oils in reservoirs. Classical techniques for chemical characterization of the sulfur include Raney nickel desulfurization, pyrolysis, and gas chromatography-mass spectroscopy (GC-MS) (Davidson, 1994). IR spectroscopy can also give very precise information on the overall oxidation state of the asphaltenes. XANES spectroscopy presents many advantages compared to these techniques: it does not require any sample pre-treatment, is non-destructive, element-specific, and sensitive to the electronic structure, oxidation state, and local symmetry of sulfur. In this paper, we investigate sulfur speciation in some asphaltenes isolated from a series of geological and archeological bitumens in Pakistan using S K- and L-edge spectroscopy.

2. Materials and Methods

2.1 Materials

Asphaltenes have been extracted from an oil seepage of the Gokhurt area (Gok330), a dry bitumen found near the seepage (Gok326), and an archeological bitumen (Meh335) originating

from the Gokhurt area. Previous study using δD isotopic analysis, IR, and GC-MS showed that the weathering state of the samples follows the order Gok330 < Gok326 < Meh335 (Lemoine, 1996).

2.2 Methods

XANES spectra at the S K-edge (2460–2520 eV) and L-edge (160–200 eV) were recorded at the Canadian Synchrotron Radiation Facility situated in the 1 GeV electron storage ring, Aladdin, University of Wisconsin. Both total electron yield (TEY) and fluorescence yield detection modes were used. The spectra shown are from TEY measurement. Data acquisition and treatment have been described previously (Kasrai *et al.*, 1994).

3. Background

S K-edge XANES spectroscopy has been recently applied to the study of sulfur speciation in various natural systems like coal (Kasrai *et al.*, 1996), asphaltenes (Waldo *et al.*, 1991; Gotte *et al.*, 1997), and humic substances (Morra *et al.*, 1997; Vairavamurthy *et al.*, 1997). The different forms of sulfur (disulfide, monosulfide, thiophene, sulfoxide, sulfone, sulfate) were quantified by a fingerprint approach, based on the fact that the energy of the S K-edge absorption peak (E_K) is linearly correlated to the oxidation state of S and to the white line peak area (PA).

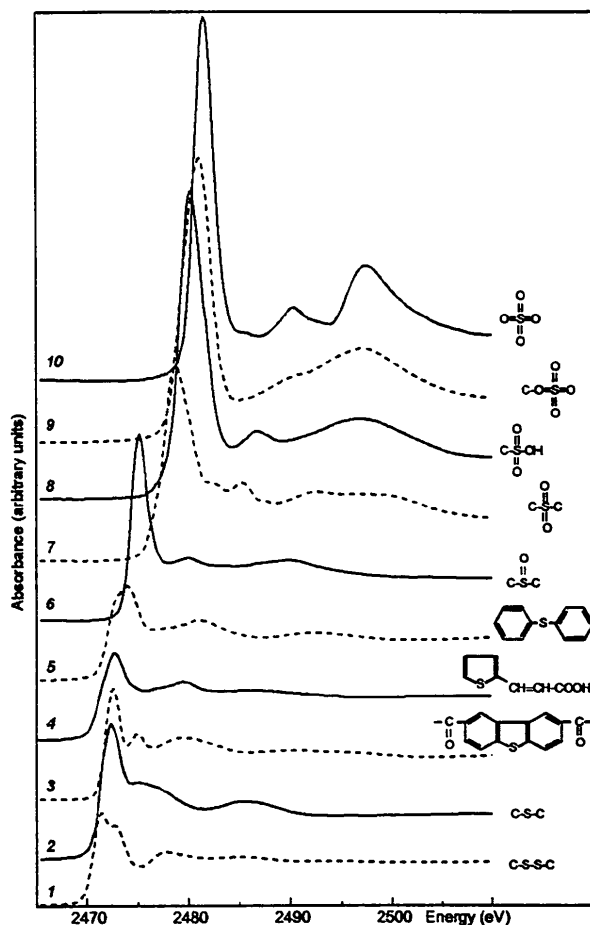


Figure 1
S K-edge XANES spectra for some reference compounds (1) DL-cystine, (2) methionine, (3) tilorone, (4) 3-(2-thienyl)-DL-acrylic acid, (5) poly(phenylene sulfide), (6) methionine sulfoxide, (7) dibenzothiophene sulfone, (8) anthraquinone-2-sulfonic acid, (9) dodecyl sulfate, (10) sodium sulfate.

Most of the studies used only a few model compounds. In order to evaluate the sensitivity of the technique to the atomic environment and local symmetry of sulfur, we recorded the S K- and L-edge XANES spectra of a large number of organic sulfur compounds. The S K-edge spectra for some of the reference compounds are presented in Fig. 1. We found a linear correlation between PA and E_K , as expected from previous studies (Fig. 2). However, for a given oxidation state, PA varies significantly depending on the local structure of S. Similar variation has been shown by Chauvistre *et al.* (1997) for some polysulfide compounds. This observation is important because it may lead to significant differences in the quantification of the different S species, depending on which model compounds are used. These differences can be estimated by the ratio $Q = SD_{PA}/PA_m$, SD_{PA} being the standard deviation of PA and PA_m the mean peak area for a given oxidation state. For the oxidized forms, Q varies between 3 and 14 %, which is an acceptable precision. For the reduced forms, Q is higher (9 - 26 %), and the gap of E_K between the different forms (monosulfide, disulfide, thiophene) is very narrow (0.1-0.8 eV). These characteristics lead to a large uncertainty on the identification and quantification of the reduced sulfur species. As a consequence, S K-edge analysis was used for quantifying the oxidized forms only.

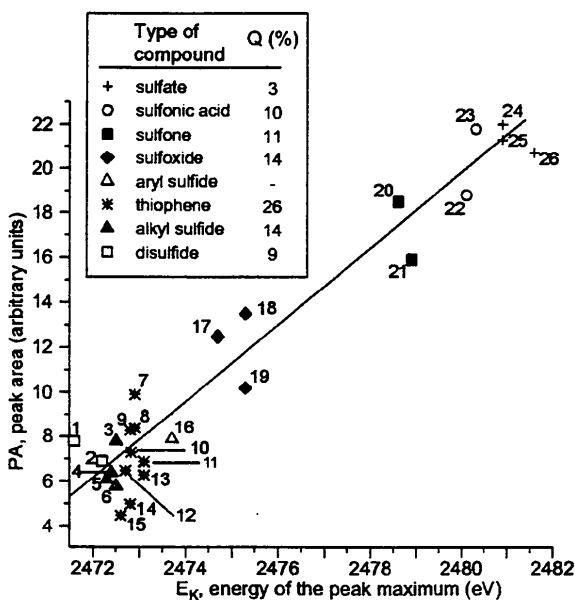


Figure 2

Plot of sulfur K-edge X-ray absorption white line peak area (PA) vs. energy of the maximum of the white line (E_K) for some organic sulfur model compounds. (1) DL-cystine, (2) dibenzyl disulfide, (3) methionine, thiosalicylic acid, (4) DL-cysteine, (5) S-benzyl-L-cysteine, (6) S-methyl-L-cysteine, (7) 2-(4-methoxy benzoyl) thiophene, (8) thioxanthene-9-one, (9) 3-thiophene malonic acid, (10) benzo-naphthothiophene, (11) 2,5-thiophene dicarboxylic acid, (12) 3-(2-thienyl)-DL-acrylic acid, (13) thianthrene, (14) 3-(2-thienyl)-DL-alanine, (15) tilorone analog, (16) poly(phenylene sulfide), (17) benzyl sulfoxide, (18) diphenyl sulfoxide, (19) DL-methionine sulfoxide, (20) L-methionine sulfone, (21) dibenzothiophene sulfone, (22) 5-sulfosalicylic acid dihydrate, (23) anthraquinone-2-sulfonic acid, (24) dodecyl sulfate, (25) gypsum, (26) sodium sulfate.

S L-edge XANES spectroscopy can also be used for studying sulfur speciation (Kasrai *et al.*, 1994; Kasrai *et al.*, 1996). Fig. 3a compares the S L-edge spectra for some reference compounds. They all exhibit three peaks labeled A, B, and C, whose energy position increases with the oxidation state of sulfur. As a consequence, peak positions can be used as a criterion to identify the different species in an unknown sample. However, L-edge spectra are more complicated than K-edge spectra because each peak arises from several electronic transitions (Hitchcock *et al.*, 1990). As a result, the simulation of the spectra by a linear combination of reference spectra did not provide satisfactory fits. For this reason, L-edge spectra were compared qualitatively to the reference spectra.

4. Results

4.1 Reduced sulfur species

The S L-edge spectra for the asphaltene samples are shown in Fig. 3a. The best match to peak positions for the oil seepage sample (Gok330) is found for dibenzothiophene (DBT, spectrum 4). However, the spectra are not exactly identical. This discrepancy may be due to the presence of additional minor species, including disulfide, alkyl sulfide, aryl sulfide, and other thiophenes. This hypothesis is supported by the presence of a shoulder at ~ 162.5 eV (arrow in Fig. 3a), which is interpreted as the presence of a small amount of disulfide (spectrum 1). A shift of the peaks towards higher energy is observed from the least oxidized (Gok330) to the most oxidized (Meh335) sample. This could indicate a replacement of DBT by single thiophene entities in this order, but this hypothesis has no chemical support. The energy shift is more likely due to a decrease in the amount of most reduced species (disulfide, alkyl and aryl sulfide) and an increase in the sulfoxide content (spectrum 6), whose peaks A and B align with peaks B and C of Gok326 and Meh335. This interpretation is supported by the absence of a disulfide shoulder in Gok326 and Meh335 spectra, as well as the decrease of peak A and increase of peak C intensities.

We conclude that reduced sulfur present in the asphaltenes is mostly in the form of DBT. Minor species including disulfide, alkyl and aryl sulfide are also present, but their proportion decreases as the samples are oxidized.

4.2 Oxidized sulfur species

The K-edge spectra for the asphaltenes samples are presented in Fig. 3b. The results and procedure of linear combinations of reference spectra to simulate the asphaltene spectra are summarized in Table 1. The amount of oxidized form increases in the order Gok330 < Gok326 < Meh335, which is in agreement with S L-edge results. The oil seepage (Gok330) contains 14% sulfoxide and 3% sulfone, indicating that the oil is moderately oxidized. The weathering phenomenon which affected Gok326 and Meh335 samples led to the formation of more oxidized forms, *i.e.*, sulfonate and sulfate (Gok326, Meh335). Sulfate has been identified in humic acids (Morra *et al.*, 1997; Vairavamurthy *et al.*, 1997). The extraction methods employed prevent inorganic sulfate contamination in the asphaltene and humic acid extracts. Thus sulfates are more probably present as ester-bonded sulfates, which are known to be produced by bacteria in high sulfur media (Paul & Clark, 1989). Therefore, the presence of sulfate may be a marker of bacterial activity.

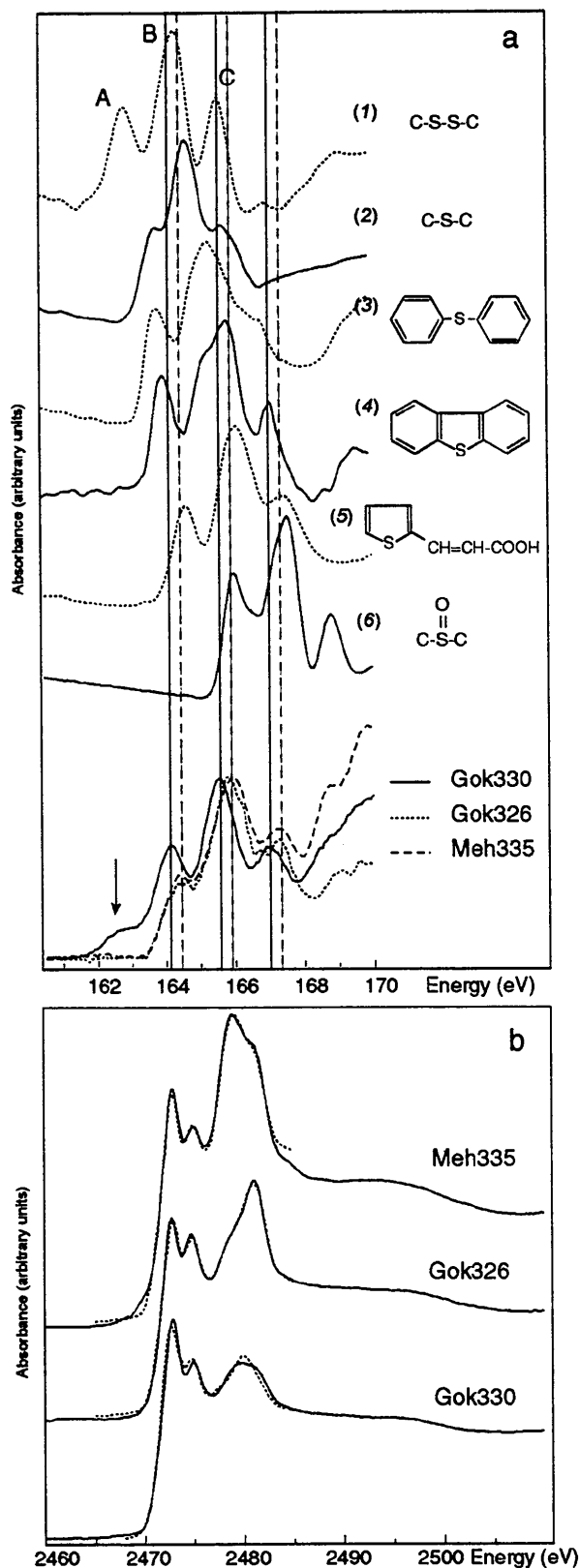


Figure 3
 (a) S L-edge XANES spectra for the asphaltenes and for some reference compounds: (1) DL-cystine, (2) methionine, (3) poly(phenylene sulfide), (4) dibenzothiophene, (5) 3-(2-thienyl)-DL-acrylic acid, (6) methionine sulfoxide. (b) S K-edge XANES spectra for the asphaltenes (solid lines) and simulations (dotted lines).

Table 1

Distribution of the oxidized forms of sulfur in the asphaltenes determined by fitting the K-edge spectra.

Sample	FM	reduced S	sulfoxide	sulfone	sulfonate	sulfate
Gok330	0.11	83	14	3	0	0
Gok326	0.09	70	17	2	2	9
Meh332	0.27	66	13	11	2	8

The asphaltene spectra were simulated by a linear combination of reference spectra. The figure of merit of the fit is defined as $FM = \sum (f_{\text{asphaltene}} - f_{\text{fit}})^2$ in the 2468 - 2485 eV range. Gok330 spectrum was simulated using the whole database of reduced and oxidized reference compound spectra (Fig. 2). Gok326 and Meh335 spectra were simulated using Gok330 spectrum as the reduced reference spectrum combined with the oxidized reference compound spectra. The percentages were then corrected for the sulfoxide and sulfone content of Gok330.

5. Conclusion

Sulfur speciation in some asphaltene samples was studied by S K- and L-edge XANES spectroscopy. The two edges proved very complementary. The former is sensitive to the oxidized forms of sulfur (sulfoxide, sulfone, sulfonic acid and sulfate), whereas the latter is sensitive to the reduced forms of sulfur (disulfide, alkyl sulfide, aryl sulfide, thiophene, DBT). In all the samples, DBT is the major sulfur moiety. In the least altered one, minor species include disulfide, alkyl sulfide and sulfoxide. The proportion of oxidized sulfur (sulfoxide, sulfone, sulfonate and sulfate) increases with the alteration of the samples, whereas the proportion of disulfide and alkyl sulfide decreases. Some sulfate species were detected in the most oxidized samples, and may be a marker of bacterial activity.

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