

Determining the Sulfur species in the dispersants Corexit 9500A and 9527A applying S K-edge XANES spectroscopy

Lisa Bovenkamp-Langlois¹ and Amitava Roy¹

¹J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, Baton Rouge, LA 70806. USA

Email: lbovenkamp@lsu.edu

Abstract: The dispersants Corexit 9500A and 9527A were used extensively during the Deepwater Horizon oil spill in the Gulf of Mexico. Sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to investigate the dispersants for the sulfur based components. The main sulfur containing component should be dioctyl sodium sulfosuccinate (DOSS). S K-edge XANES analysis shows that indeed the major sulfur species in both kinds of Corexit (9500A and 9527A) is sulfonic acid which is a part of DOSS. In addition some fraction of sulfone was detected.

1. Introduction

Following the April 20, 2010, explosion on the Deepwater Horizon oil rig in the Gulf of Mexico, approximately 5 million barrels (185 million gallons) of crude oil gushed out of the Macondo Canyon 252 (MC252) well for over four months [1]. The methods that were used to remediate the oil spill included direct collection of the crude oil from the riser pipe, collection by booms, and burning at the surface. Additionally, a significant fraction evaporated or dissolved. However, these methods were not rapid enough to collect all the oil. Therefore, dispersants, such as Corexit 9500A and 9527A (Nalco Environmental Solutions), were used at the wellhead (in ca. 5000 feet depth) and on the surface (about 2 million gallons altogether [1]) to disperse the oil more efficiently. This method presumably inhibits large volumes of oil from reaching the surface or being transported landward [2].

An oil spill dispersant breaks down the oil into very fine droplets and inhibits the formation of large volumes of emulsified oil. Smaller droplets also enhance biodegradation [3]. A dispersant typically consists of a surfactant in one or more solvents, used to deliver the surfactant to the oil-water interface. The surfactant reduces the surface tension of hydrophobic oil and disperses it into seawater as smaller droplets. Current dispersants, such as Corexit are considered less toxic than earlier mixtures [4]. However, their effects on marine life include acute toxicity of the dispersant itself and toxic oil components that have an increased solubility due to the dispersant [1]. The surfactant in Corexit (9500A and 9527A) is an organic sulfonic salt, dioctyl sodium sulfosuccinate (DOSS, other name: butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl, ester, sodium salt, cf. Figure 1). Additional compounds are TWEEN 80 (other name: Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives), SPAN 80 (other name: sorbitan mono-octadecanoate), di(propylene glycol) butyl ether, and some kind of kerosene (<http://www.nalcoesllc.com/nes/1602.htm>). The exact formulation of Corexit was divulged only after the Deepwater Horizon oil spill.



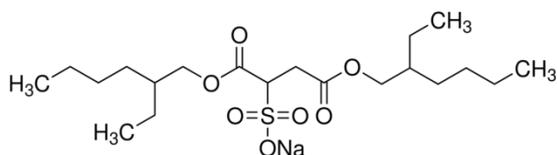


Figure 1: Structure of dioctyl sulfosuccinate sodium salt (DOSS)

Generally, sulfur species in crude oil and its derivatives are determined by some type chromatographic separation followed by elemental determination of sulfur, for example, by gas chromatography – inductively coupled plasma mass spectrometry [5]. Such techniques do not allow determination of all the chemical species at once and the preparation process itself may alter the speciation. X-ray absorption near edge structure (XANES) spectroscopy has been successfully used for sulfur speciation determination in crude oil and its derivatives for quite some time [6]. Since the toxicity and persistence of dispersants is of interest to a wide scientific community, the detection of DOSS without any chemical separation by XANES is important.

2. Materials and Methods

2.1 Materials

Corexit 9500A and 9527A were obtained from the Gulf of Mexico Research Initiative (GoMRI) consortium. They were stored in dark brown glass bottles at room temperature, exposed to fluorescent lighting. Reference compounds, such as Pentane-sulfonic acid sodium salt (PSSA), Diphenyl sulfone, and Zinc sulfate were purchased from Sigma Aldrich in high purity.

2.2 X-Ray-Absorption Near Edge Structure (XANES) Spectroscopy

S K-edge XANES measurements were performed at the electron storage ring J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD), Louisiana State University, Baton Rouge, Louisiana. The ring is operating at 1.3 GeV. Data were collected at the DCM beamline. The monochromator, of Lemonnier-type with design modifications made at Bonn University, Germany, was equipped with InSb(111) crystals and calibrated to the maximum of the white line peak of zinc sulfate to 2481.4 eV [7]. For low energy measurements in fluorescence mode a Si drift Vortex detector was used. The pressure inside the sample chamber was reduced to 10 Torr (fluorescence) and 42 Torr (transmission) to accommodate the shorter absorption length of photons in air. Corexit samples were measured in fluorescence mode and prepared as follows. About 50 μ l of the fluid was dropped on filter paper which was supported by Kapton tape. The samples were covered with mylar film. Reference compounds (Pentane-sulfonic acid sodium salt (PSSA), Diphenyl sulfone, Zinc sulfate) were measured in transmission mode. The parameters for the measurements were: 2440-2468 eV with 0.5 eV steps, 2468-2485 eV with 0.1 eV steps, and 2485-2520 with 0.3 eV steps. The integration time in all cases was 1 sec and each scan was repeated once to ensure reproducibility. The data were processed (background subtracted, normalized, averaged) and analyzed using the ATHENA software [8].

3. Results and Discussion

Sulfur K-edge XANES spectra of Corexit 9500A and 9527A together with reference compounds are shown in Figure 2. These samples were analyzed over a period of three years. The spectra of both samples of Corexit 9500A and 9527A are the same (apart from the variability in sample preparation). This indicates that DOSS is not unstable when exposed to light. Since the liquid was stored in brown bottles in fluorescent indoor lighting this is not contradictory to what was reported earlier [9]. The chemical shift due to the different oxidation states can be observed directly as energy shift in the S K-edge XANES spectra [10, 11]. Reference compounds that are adequate for this analysis of the chemical environment of sulfur in both types of Corexit are diphenyl sulfoxide, diphenyl sulfone, pentane

sulfonic acid sodium salt (PSSA), and zinc sulfate. These or similar reference spectra have been published previously in most cases with a different calibration scale [6, 10, 12-14]. Using this fingerprinting method the S species in Corexit (9500A and 9527A) easily can be identified as predominantly sulfonic acid because the White line maximum at 2480.7 eV and also the Shape resonances at \sim 2486 and \sim 2496 eV have the same shape and energy position. The shoulder at about 2478.9 is not part of the PSSA spectrum. This indicates that there is some contribution of sulfone. Since the local environment of sulfur in DOSS is just like in PSSA this shoulder must be a contribution from one of the other components. The only candidate is kerosene (one of petroleum distillates). It is known that petroleum products contain sulfur in different forms such as sulfides, thiophenes, sulfoxides, and sulfones [6].

The shoulder at 2478.9 eV is related to a sulfone which is evident from the literature [6, 12, 13]. However, for the present measurements only diphenol sulfone was available but the White Line (2479.4 eV) is not exactly at the same energetic position as the shoulder.

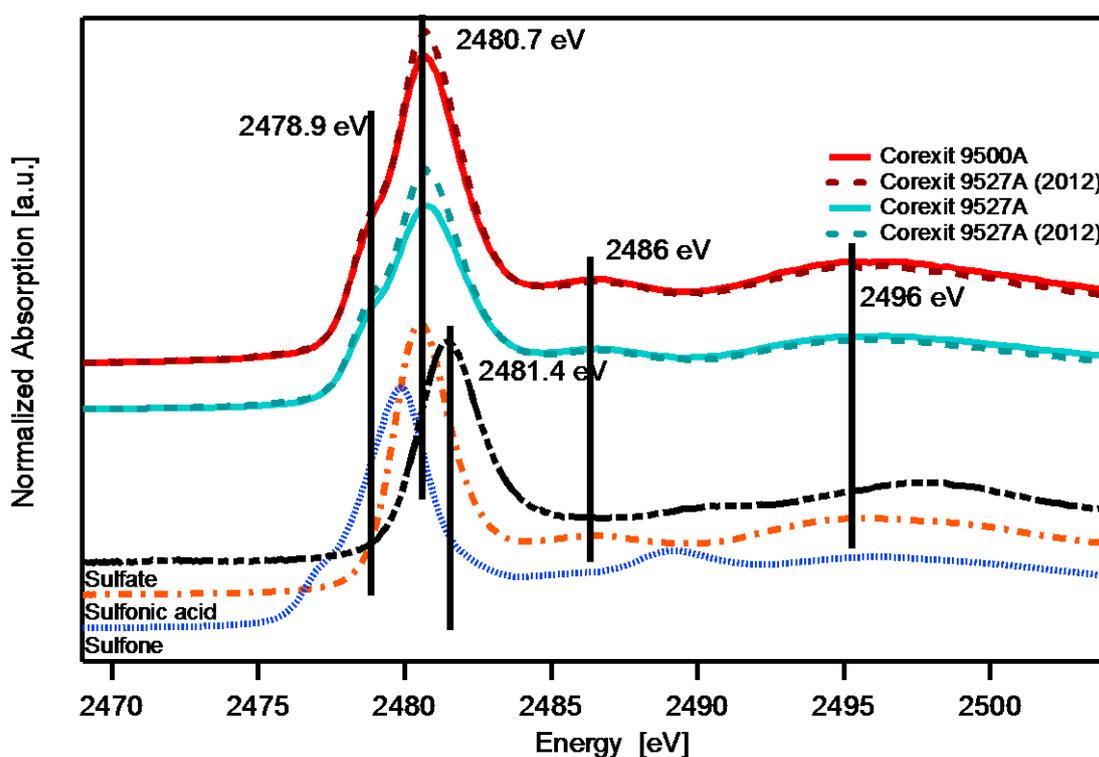


Figure 2: S K-edge XANES spectra of Corexit 9500A (red), 9527A (green) and the reference compounds: PSSA (orange), Diphenyl sulfone (blue), and Zinc sulfate (black)

Corexit 9500A and 9527A were used at an unprecedented scale during the Deepwater horizon spill, often deep in the subsurface. These dispersants have also been found to be toxic at certain levels to various organisms. S K-edge XANES of the dispersants confirm that sulfonic acid is indeed an important component. Small contributions from other sulfur containing compounds can be found as well. These are likely related to the petroleum distillates that make up the other components of the dispersants. The ultimate challenge will be the detection of Corexit in other oil spill related samples in the presence of the sulfur species from crude oil and seawater.

Acknowledgement

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