Structural Characterization of Deep Water Using Solid-State ^{13}C MAS NMR Techniques

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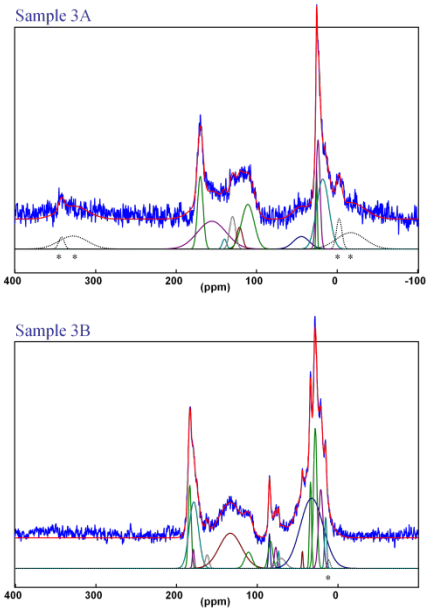
Deep water, such as that found in oil and gas formations or those found in certain subsurface water formations in the high plains, is extremely saline. Brackish groundwater exhibits salinity concentrations from 100.-400,000 mg/l depending on location. This water either needs to be disposed of or processed in an environmentally responsible manner. In general, this water is either injected back into deep wells, or desalinated for agricultural purposes, drinking, or supplementing river flow.[1] Not only does this water have salinity greater than seawater, it contains high concentrations of dissolved organic compounds (DOC), ten to 100 times higher than typical surface water. This DOC adsorbs to current desalination membrane technology, quickly ruining the membranes or acting as a source of food for microorganisms that can grow on the membrane surface also fouling them. The chemical structure of this organic carbon is largely unknown at the current time.

In conjunction with other characterization methods, we use Solid-State direct-polarization MAS ^{13}C NMR to characterize the organic carbon in produced water. The NMR techniques are similar to those used previously for soils and other natural organic matter.[2,3] Using variable, high spinning speeds, we can determine the carbon fraction in the produced water and compare them to standard humic acids previously studied. At the current time this is the first publication of ^{13}C NMR data on DOC from produced water

Sample Preparation: Samples were collected from two wells – one from the San Juan Basin in northwest New Mexico, and the other from the Permian Basin in southeast New Mexico. At the wellhead, ~80L of water were collected from the separator, 0.20 µm filtered to remove particles and microorganisms, and placed in 20L polyethylene carboys, immediately packed into coolers, and stored on ice until returned to the lab. At the lab, samples were stored in a 4°C cold room until analyzed. The water was isolated from its saltwater matrix on two columns of adsorption resin (Amberlite XAD-8 and XAD-4) in series.[4] The DOC was removed in several fractions — the first fraction removed with a NaOH solution, the second with an acetonitrile solution (CH_3CN). All of the fractions were then lyophilized.



NMR Spectroscopy: Experiments were performed on a Bruker Avance600, ^{13}C frequency of 150.903 MHz, usng a 2.5 mm broadband MAS probe and 26 kHz spinning speed (15KHz used to determine spinning sidebands). The pulse sequence used was direct polarization with a rotor synchronized Hahn echo, synchronized to 1 rotor cycle.

Conclusions: We demonstrate the first NMR characterization of water produced from oil and gas wells. Like aquatic humic acids, produced water contains high proportions of aliphatic, aromatic and carboxyl carbons, ~30%. Unlike aquatic DOC, the produced water samples do not contain much in the ketone/quinone, acetal/aromatic, or hetero-aliphatic regions. Acetal/aromatic signal is only found in the sample from the natural gas wellhead. The sp^2/sp^3 ratios for DOC from oil and gas wells are much higher (~2) than most surface aquatic samples (~1).[5] These samples need to be further characterized by gas chromatographic analysis, IR Spectroscopy, and HPLC analysis.

Figure 1: ^{13}C spectra of oil produced water. The two samples shown are from one well, both separations occurring on Amberlite XAD-8. Sample 3A was back eluted with acetonitrile, while Sample 3B was back eluted with NaOH. Blue lines indicate data, red lines the model using DMFit.[6] The other colored lines denote the Gaussian decomposition of the model. Those lines marked with * are spinning sidebands

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