First High-Field EPR Characterization of Tar Balls and Weathered Oils

V. Ramachandran, J. van Tol, A.M. McKenna, R.P. Rodgers (NHMFL); A.G. Marshall, N.S. Dalal (NHMFL & FSU, Chemistry)

Introduction

The 2010 colossal Deepwater Horizon Oil Spill in the Gulf of Mexico has necessitated an urgent need to characterize the chemical content and molecular structure of the material released in the Gulf and washed ashore. Over time and upon exposure to the marine and ambient atmosphere, this material weathers and may become potential environmental and ecological hazard due to the presence of toxic species such as catalytically active metal complexes and reactive organic free radicals in it. Thus a detailed knowledge of their concentrations and chemical identities is of vital importance [1]. In this study, we used high frequency EPR to obtain highly resolved spectra to better understand the various paramagnetic entities present in tar balls [2].

Experimental

Tar ball and weathered oil samples were collected from various locations in the Gulf of Mexico post DH Oil Spill incident. X band (9.4 GHz) and Q band (34 GHz) EPR spectra were measured using a Bruker Elexsys 500 spectrometer available at FSU Chemistry Department. HF-EPR spectra at 240 and 336 GHz were measured using a heterodyne spectrometer employing a 12.5 T superconducting magnet at NHMFL.

Results and Discussion

X band (Fig. 1a) and Q band EPR spectra of tar balls exhibited overlapping signals from two paramagnetic species, namely, a VO^{2+} porphyrin-type species (in contrast to findings in Ref 1) and an organic free radical (FR). The VO^{2+} species exhibited axial symmetry shown by two sets of octets (^{51}V-hyperfine) centered at g-values, $g_{\parallel} \sim 1.9620$ and $g_{\perp} \sim 1.9835$ (stick labels), whereas the FR signal (inset) was a sharp line centered at g ~ 2.0028. HF-EPR spectrum at 240 GHz (Fig. 1b) revealed well-separated features from the VO^{2+} and the FR species, and in addition a 6-line hyperfine structure due to the presence of Mn^{2+}. Another striking observation was the anisotropic FR spectrum at 240 and 336 GHz (Fig. 1c) showing the asymmetric nature of the molecule.

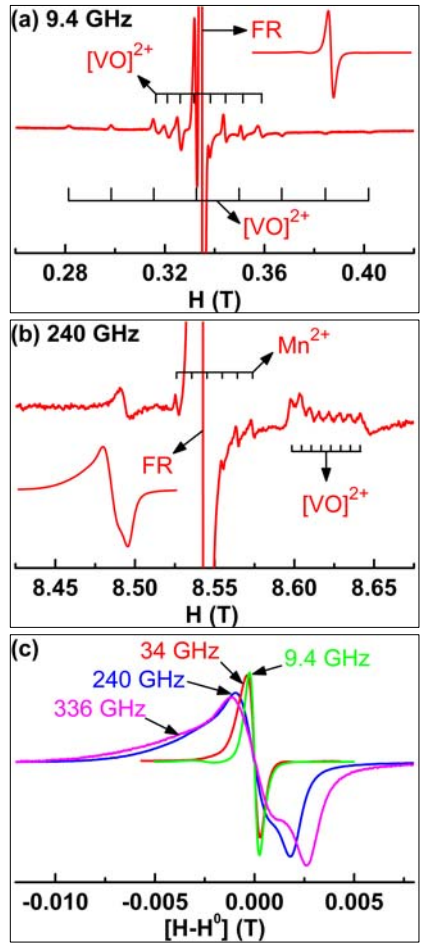

Fig. 1: Variable frequency, room temperature EPR spectra (See text) of a tar ball in its native state.

Conclusions

We have demonstrated the advantages of using HF-EPR spectroscopy for characterizing organic free radicals and paramagnetic metal complexes in tar balls and weathered oils from the DH Oil Spill. Fingerprints of V^{4+}, Mn^{2+} and an organic FR are detected. V^{4+} is complexed as VO^{2+} porphyrin; Mn^{2+} occurs in a relatively symmetric local environment; the organic FR is a large polycyclic hydrocarbon molecule shaped like a distorted disc. Two dimensional EPR studies on these samples using HYSCORE and pulsed ENDOR techniques are in progress.

Acknowledgements

This work is funded by the Future Fuels Institute.

References

[1] Kiruri, L.W., *et al.*, Environ. Sci. Technol., **47**, 4220-4226 (2013).
[2] Ramachandran, V., *et al.*, in preparation (2013).