[PS]Low Field NMR Evidence of Geo-Polymeric Behavior of Organic Matter in Shale and the Implications on Recovery*

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Abstract

The mechanism through which light oil is stored in organic matter and how it moves has implications on unconventional reservoir production scenarios. The traditional view is that this oil is found in sub-micron-sized pores observed in the organic matter of numerous shale reservoir rocks where phase behavior and flow properties are defined by established physics of confined spaces. An alternative view is that the organic matter behaves more like a plastic or polymer that can absorb certain solvents. The combination of NMR T_1 and T_2 measurements illustrate that a portion of the light oil in a hydrocarbon-bearing reservoir rock is dissolved in the solid organic matter. Differences in the relaxation mechanisms associated with T_1 and T_2 processes are the key in identifying the light oil that is captured in the organic matter. The restricted diffusion component of the T_2 mechanism for this captured oil generates a much faster T_2 relaxation component than observed in a T_1 measurement that lacks a diffusion mechanism. Distinct T_1 and T_2 measurements have greater resolution than the combined 2D T_1-T_2 maps that are often used in recent studies. NMR measurements on organic-rich shale and low-organic-content shale under dried and oil-saturated states illustrate the fast T_2 – slow T_1 component associated with light oil dissolved in the organic matter; this creates complex geo-polymer behavior. Thermogravimetric analysis of oil-saturated shales also shows that organic matter has geo-polymer characteristics. Comparisons made between TGA data of other polymers with sorbed solvents and organic matter with sorbed oil show similar trends. For organic-rich samples, oil evaporates at higher temperatures (200-350°C) compared with the bulk boiling point (174°C).

Reference Cited

Ritter, U., 2003, Solubility of petroleum compounds in kerogen: Implications for petroleum expulsion: Organic Geochemistry, v. 34/3, p. 319-326.

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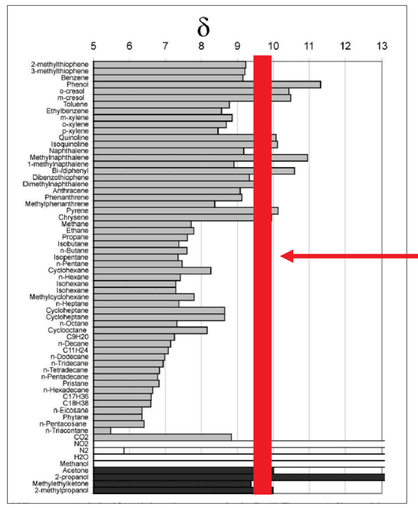
OBJECTIVES

- Investigate if polymer theory can explain some of the observations seen with hydrocarbon interacting with organic matter.
- Compare Low Field Nuclear Magnetic Resonance (NMR) and Differential Scanning Calorimetry (DSC) of absorbent polymers and highly organic shale.

THEORETICAL BACKGROUND

SOLUBILITY PARAMETERS

- The Hildebrand Solubility Parameter can be used to explain the relationship between organic matter and hydrocarbon:
- The Hildebrand solubility parameter comes from polymer science and is foundationally based on “like dissolves like”



$$\delta = \left[\frac{\Delta E - R * T}{V_m}\right]^{1/2}$$

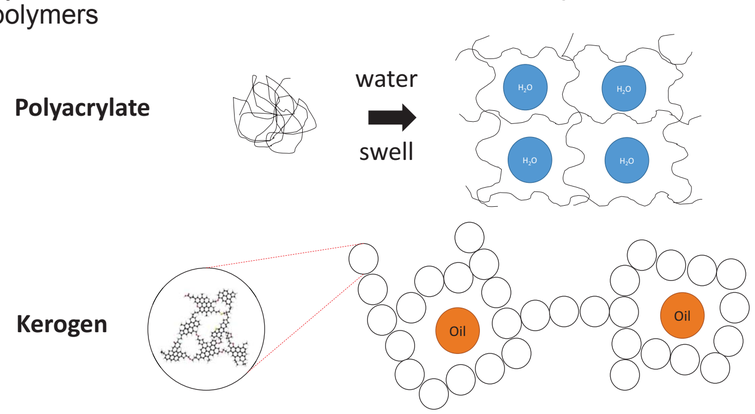
δ values determined by swell tests

kerogen “sweet spot” vs. various solvents

Ulrich Ritter, **Solubility of petroleum compounds in kerogen: implications for petroleum expulsion,** Organic Geochemistry, Volume 34, Issue 3, 2003, Pages 319-326, ISSN 0146-6380

ORGANIC MATTER POLYMER CONCEPT

- Conceptualize organic matter as a macro-molecule that absorbs hydrocarbon in a cross-linked structure a.k.a. superabsorbent polymers



MATERIALS AND METHODS

SAMPLES

- High molecular weight sodium polyacrylate water absorbent
- Envirobond™-403 hydrocarbon absorbent
- 20% T.O.C. Green River Oil Shale

NMR

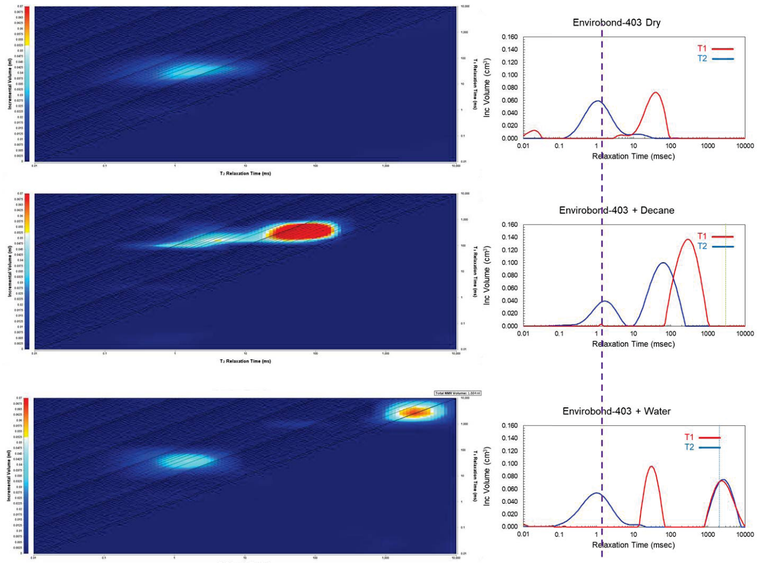
- Oxford Instruments 2MHz Geospec II
- T_1, T_2, & T_1 vs. T_1 map
- Dry, Oil Saturated, & Brine Saturated

DSC

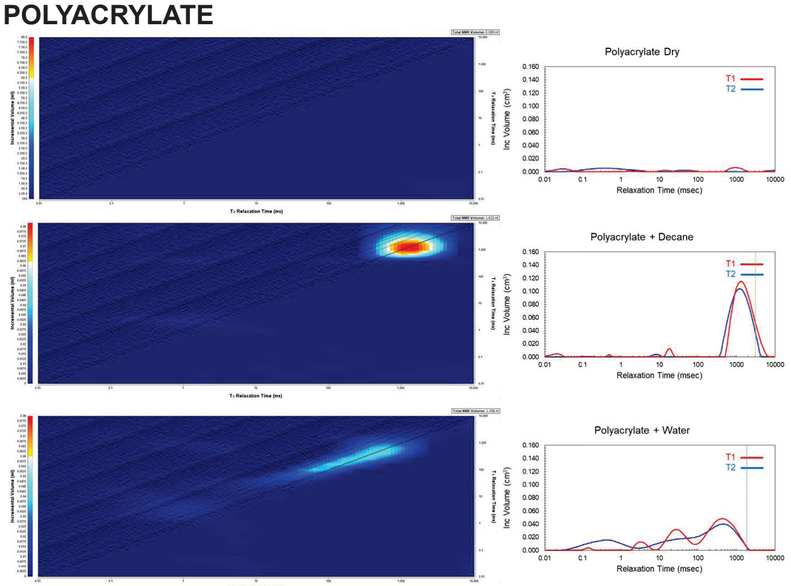
- Ambient-300°C
- Setaram SENSYS-Evo

RESULTS

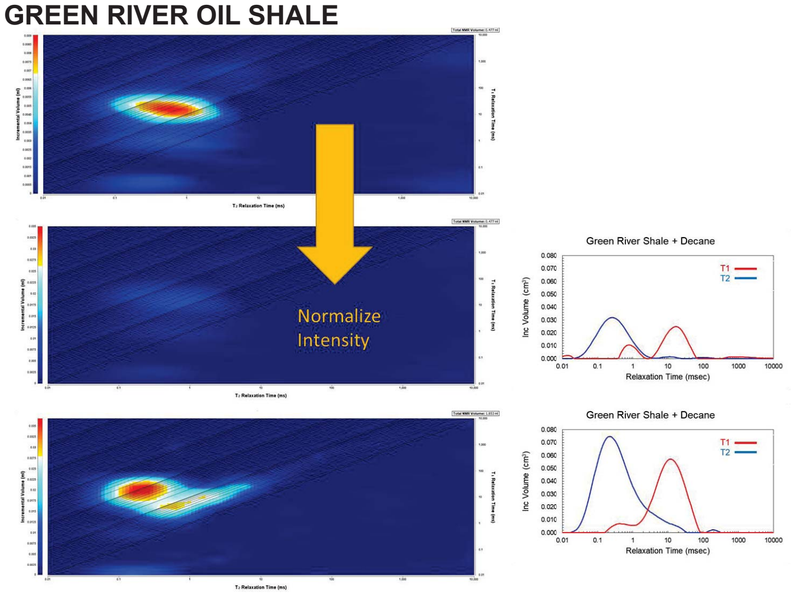
ENVIROBOND-403



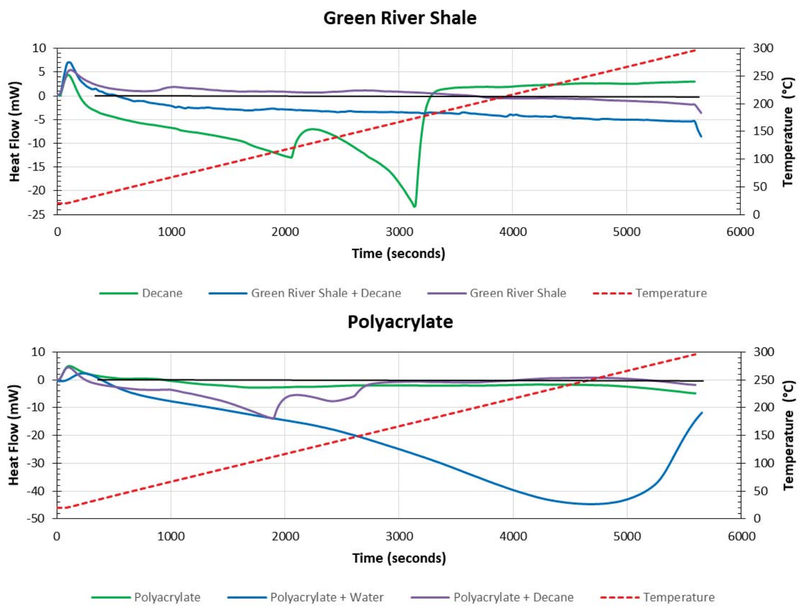
POLYACRYLATE



GREEN RIVER OIL SHALE



DIFFERENTIAL SCANNING CALORIMETRY



CONCLUSIONS

- Kerogen shows polymer-like NMR tendencies
  - T_1 and T_2 shifts of bulk fluids towards faster relaxation times
  - Misidentification of fluids due to relaxation overlay
  - Non-proportional NMR signal intensity increases when saturated with fluids
- DSC showed reduced volatility of bulk fluids due to association with absorbents
- Geo-polymer kerogen model explains some observations