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Alteration of oil by gas: experiments in fused silica capillary capsules to interpret natural petroleum inclusion pattern

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Reservoir case studies showed that the fluorescence of oil inclusion assemblages of current or palaeo-gas zone has patterns that are not seen in zones that have only been invaded by oil (Eadington *et al*., 2008; Bourdet *et al.*, 2010). It is suspected that a fraction of the oil is retained in the pores around grains when oil is drained by gas and that molecules from this residual oil partitioned in gas. To reproduce the alteration of oil by gas (gas-washing), we sealed small amounts of crude oil (59º, 42º or 33º API) and excess pure gas (methane, ethane, propane or CO_2) in fused silica capillary capsules (FSCCs, Chou *et al.*, 2008), with and without water. The UV-visible fluorescence spectra of oil phase(s) enclosed within the FSCCs were acquired using Hg lamp excitation with a narrow-band 365 nm filter at temperatures of 20 to 100 ºC. Raman and FT-IR spectra of the gas, oil and solid phases were measured at 20 ºC.

The 33° API oil (yellow fluorescence, Fig. 1 and Fig. 2) formed with ethane and propane a new immiscible fluorescent liquid phase with a blue fluorescence, a large amount of semi-solid residues with dark orange fluorescence while the oil fluorescence become whiter or the oil disappeared. Without water solid residues are not present in FSCC with ethane, while they are abundant in the capillary with ethane and water. The oil with methane kept the same fluorescence colour. Temperature has a small effect on the fluorescence spectra of liquids and solids. Temperature slightly increases the fluorescence intensity of the new immiscible liquids at low (400-450 nm) and high wavelength (500-700 nm) while the fluorescence of the residual oil is red-shifted. Experiments with 59°and 42° API oils (fluorescing blue, Fig. 3) do not show immiscible hydrocarbon liquids. The fluorescence of those crude oils displays red-shifts in the presence of gas that are accentuated with increasing temperatures. Solid residues are negligible. Methane has a similar or stronger effect compared to ethane and propane with those oils. Slight increases of the fluorescence spectrum at short wavelength occur for the 42º API crude oil with gas.

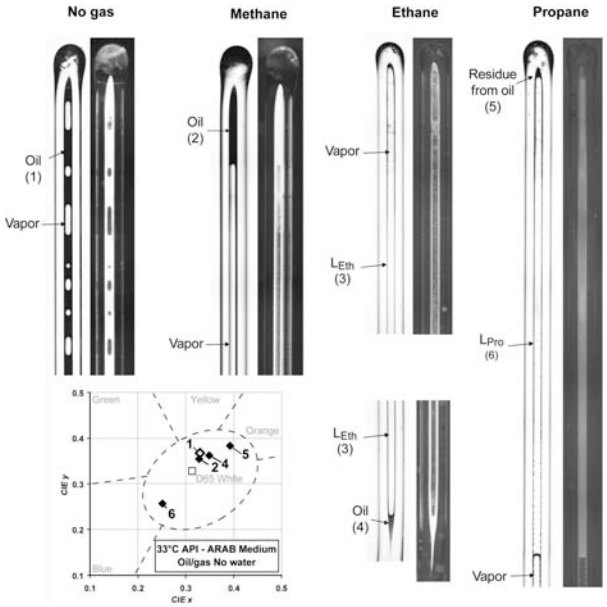

Fig. 1. *Paired photomicrographs (bright field and 365 nm illumination) of FSCCs enclosing Arab medium oil (33º API), or Arab medium oil mixed with methane, ethane or propane. The graph plot the CIE chromaticity indexes of oil or semi-solids observed in capsules.*

FT-IR and Raman spectra showed that at room temperature methane dissolves in the oil and concentrate in the vapour phase. The pressures estimated using the Raman methane peak position technique created for the system CH_4-H_2O (Lu et al., 2007) are between 95 and 200 bars. Ethane and propane dissolve in the oil, vaporise in the vapour phase and form a new immiscible liquid with heavy oil (33º API). Pressures are not measurable as yet for those gas, but the intensity

of the FT-IR and Raman scatter signals in the vapour phase were weaker for ethane than methane, and the propane peaks were very low. This suggests that their concentrations in the vapour phase are low at room temperature and the pressure is probably low. Vapour pressures for pure ethane and pure propane at 20 ºC are respectively at 34 bar and 10 bar (Danesh, 1998). Propane is the most effective gas to precipitate semi-solid residues; water band is always associated with the FT-IR signals of the semi-solid residues.

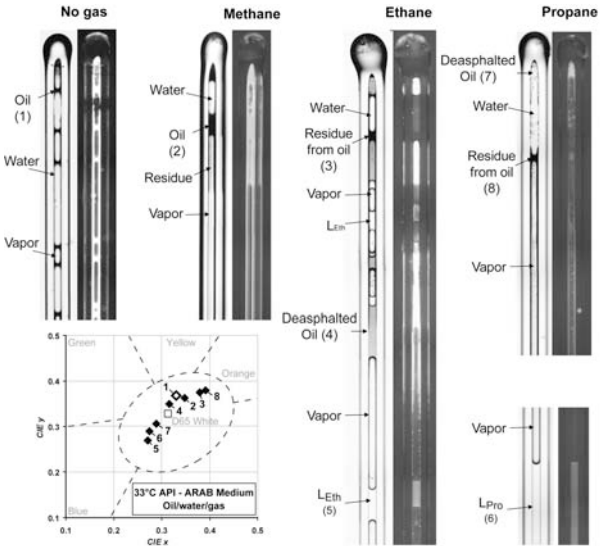

Fig. 2. *Paired photomicrographs (bright field and 365 nm illumination) of FSCCs enclosing Arab medium oil (33º API) with water mixed with methane, ethane or propane. The graph plot the CIE chromaticity indexes of oil or semi-solids observed in capsules.*

We interpret factors contributing to changes in the residual oil as: (1) decrease of fluorescence at short wavelengths (red-shift) is due to partitioning of low molecular weight aromatic molecules into the vapour phase or into the new immiscible liquid phase; (2) decrease of fluorescence response at long wavelengths (blue-shift) is due to loss of high molecular weight aromatics by precipitation of solid residues; (3) increase of fluorescence response at short wavelengths (blue-shift) is due to desorption of aromatics and resins from asphaltene. In the lowest API gravity oil, water has effects on precipitation of semi-solid residue and stability of oil phase.

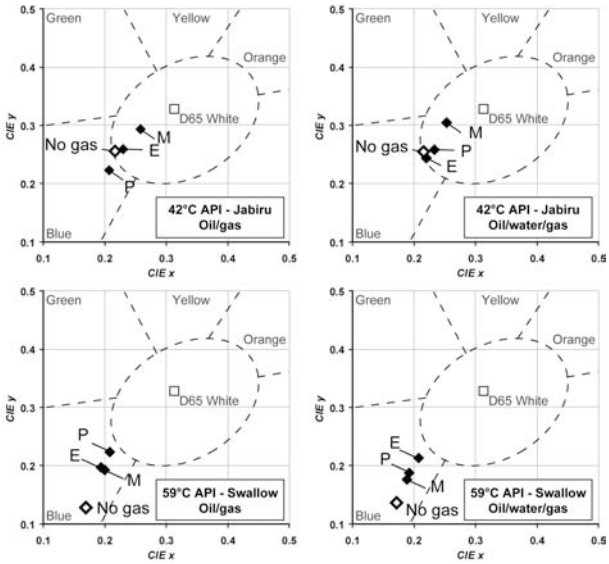

Fig 3. *CIE chromaticity indexes plots of the oil in capsules prepared with 42º and 59º API crude oils, with or without water, mixed with gas (M: methane, E: ethane, P: propane).*

The change of the fluorescence colour of the residual oil in presence of an excess of gas appears to be due to a combination of these phenomena. Their intensity depends on the initial composition of the oil. Pressure and nature of the gas present in the vapour phase has probably an impact on aromatic-bearing molecules solubility in vapour, however this assumption suggested by this study requires further experiments. These results are consistent with the variant attributes of oil inclusion assemblages trapped in palaeo-oil zones that were displaced by gas and support the concept of gas-washing of residual oil.

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