Fuel 220 (2018) 692–705

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Relaxation and relaxation exchange NMR to characterise asphaltene adsorption and wettability dynamics in siliceous systems

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ARTICLE INFO

Keywords:
Asphaltene adsorption
Clogging
Rock ageing
Wettability alteration rate
T2 relaxation
REXSY
v1

ABSTRACT

The fraction of asphaltenes in crude oils is among the major concerns in upstream and downstream petroleum engineering. At reservoir scale asphaltenes may cause compartmentalisation and at pore scale they may create barriers to flow, change wettability conditions and relative permeability; and as a result affect ultimate oil recovery. Rock core ageing in oil is a common step in laboratory core analysis. Where possible, crude oils relevant to the origin of cores are used, while the use of arbitrary oils, various hydrophobic chemicals and anti-wetting agents is not uncommon. Published ageing time and temperature vary broadly. This fact motivates us to evaluate the applicability of synthetic oils for studies requiring wettability alteration. We systematically study the precipitation kinetics of the heavy-end oil fraction and wettability alteration properties of mixtures comprised by various proportions of commercially available bitumen, aromatics and alkane components.

Low-field NMR relaxation measurements have been applied to characterise wettability of rocks by introducing an NMR wettability index. The latter requires multiple reference measurements at end-point saturation states similar to a standard Amott-Harvey workflow. Furthermore, petrophysical interpretation of T_2 relaxation data is prone to be affected by diffusional coupling effects. NMR correlation techniques have a higher prediction capacity, e.g. the T_2-store-T_2 (REXSY) experiment is naturally sensitive to the spatial variation of physical properties by detecting diffusion exchange between different relaxation environments. We applied a combination of relaxation and relaxation exchange techniques to study the effect of asphaltene deposition on pore-space morphology and wettability for two siliceous systems with different surface topology. The change of wettability over ageing time in different synthetic oils was tracked using T_2 relaxation measurements, providing estimates of ageing dynamics useful in designing wettability-related experiments.

Results show that the kinetics of asphaltene deposition and wettability alteration processes are strongly dependent on chemical composition of synthetic oils, asphaltene origin (light oil or bitumen) and solid phase morphology. Elements of the resulting deposition pattern and wetting state of the cores were inferred using the proposed approach, utilising low-field NMR T_2 relaxation and T_2-store-T_2 relaxation exchange experiments combined with numerical simulation of relaxation responses. The knowledge of deposition pattern and dynamics obtained mainly by the mean of combination of NMR relaxation techniques contributes to the improved design of core wettability alteration steps and potentially to enhanced petrophysical application of low-field NMR technology.

1. Introduction

1.1. Asphaltenes

Asphaltene dynamics in crude oils are among the major problems in petroleum engineering. The list of problems range from well completion using oil-based mud, pressure depletion and other situations leading to asphaltene precipitation onset conditions during production and transport in surface pipes. Wetting properties of natural rocks motivate studies of mechanisms governing wettability change and relationship to rock petrophysical properties; detection techniques and methods allowing to reproduce/control wettability change and associated chemical processes at reservoir conditions. Asphaltene is a heavy-end polar fraction of crude oils made of carbon, hydrogen, nitrogen, oxygen, sulfur and trace amounts of metals, operationally defined as the insoluble fraction of oil in light alkane and soluble in basic aromatic solvents [1]. Asphaltene dynamics represents complex processes considering their flocculation/aggregation behaviour,

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https://doi.org/10.1016/j.fuel.2018.02.059
Received 28 September 2017; Received in revised form 16 December 2017; Accepted 8 February 2018

interaction with other fluid components and various minerals. On the molecular level asphaltene dynamics can be described using the Yen-Mullins model [2], which assumes the basic structure of asphaltene molecule as a single moderately large polycyclic aromatic hydrocarbon with peripheral alkanes. The model postulates a two-step aggregation mechanism of basic asphaltene molecules: formation of small nano-aggregates and further clustering of these aggregates. In this work, however, we focus on scales far larger than molecular, i.e. on the effect of pore-scale asphaltene-to-solid interaction, and the deposit accumulation rate in rock void space depending on oil composition and the effect of deposits on wettability.

1.2. Wettability reversal/alteration in SCAL (ageing)

Wettability is a mutual solid-fluid property defined as the tendency of a fluid to spread over or adhere to a solid surface in the presence of other immiscible fluid(s). Wettability is one of the factors governing oil recovery since it controls initial fluid distribution, capillary pressure and relative permeability. It is a multi-scale phenomenon depending on mutual intermolecular interactions between the fluids and the solid, chemical potential of components, excess of free energy in solid (surface energy) and surface roughness (topology). The wetting properties of rocks in the context of petroleum engineering are considered qualitatively to be between strongly water-wet and strongly oil-wet states or a combination (mixed-wet). These states are quantified either through contact angle (which is a microscopic property) or through one of wettability indices, which relate observable change of saturation and saturation history to rock wetting capacity (macroscopic average property), such as the Amott method [3], the US Bereau of Mines (USBM) method and wettability index from pseudo work of imbibition w_R [4]. Among the alternative approaches is the direct measurement of zeta potential [5]. In this work we use a simplified approach to observe a wettability state of aged cores by measuring volume of self-imbibed heavy water into decane-saturated cores.

Core analysis in the context of evaluation of reservoir quality requires the restoration of a core's wettability state. This is typically performed by setting a core to strongly water-wet state using a variety of cleaning procedures and subsequent alteration of the core wettability to some degree of oil wetness. The latter can be achieved using special hydrophobic chemicals and anti-wetting agents (such as dimethyldichlorosilane) [6]. Alternatively, a so-called ageing process is used – exposure of the rock to crude oil at elevated temperature. Where possible, crude oils native to core samples are used. However, in many cases, the selection of oil is arbitrary, which complicates comparison of results. Furthermore, while the role of asphaltenes in wettability reversal is long known [7], the possible heterogeneous wettability as an outcome of ageing in crude oil has been previously reported by Graue et al. [8]. We study the effect of oil composition on precipitation kinetics of asphaltenes and relationship between NMR surface relaxivity and wettability alteration.

1.3. NMR applications to wettability

Low-field NMR relaxometry is a powerful tool for non-invasive studies of molecular dynamics in porous systems suitable to deal with paramagnetic environments such as natural rocks. Accordingly, it is commonly applied for the petrophysical characterisation of rocks. It has sensitivity to the wetting state of rock through the effect of surface relaxivity, which lead to the proposal of NMR indices correlating very well to standard USBM index [9,10] and to Amott index [11,12]. Further improvements were achieved with the aid of numerically modelled NMR response using simplified pores geometries [13]. These models assume homogeneity of surface relaxivity and wettability. However, the impact of wettability heterogeneity on relative permeability is long known, [14]. The effect of surface relaxivity heterogeneity was investigated numerically using simulated NMR relaxation experiments and 3D micro-CT representations of rock and various patterns of relaxivity distribution by Arns et al. [15], who demonstrated that heterogeneity of surface relaxivity affects NMR permeability cross-correlations by weakening correlation between porosity and log-mean relaxation time. Using an analytically derived model for rectangular pores, a framework to estimate the influence of spatially variable relaxivity on observed NMR responses in rocks has been proposed [16]. Systematic experimental studies of surface relaxivity heterogeneity on relaxation rates using sandpacks altered with ferrihydrite were conducted by Keating and Knight [17]. Clearly, the variations of wettability of a given mineral constituent of the rock correspond to variations of surface relaxivity. It is less obvious how the precipitation of asphaltenes following various scenarios (favouring pore topology or mineralogy or combination of both) would affect such interpretation. Low-field NMR relaxometry as employed in this study is not sensitive enough to provide direct insight into the molecular structure of asphaltenes nor reliably measure their quantity even at short echo-spacings of 80 μs. Nevertheless, it can be used to indirectly detect the presence and distribution of asphaltene floccules through the effect of their interaction with saturating fluid.

1.4. Distribution and rate of asphaltenes deposition

Asphaltene adsorption on solid surfaces in rocks is considered to be a major cause of wettability reversal inside oil reservoirs [18]. Another effect of asphaltene deposition is porosity and permeability reduction [19]. Asphaltenes are likely to precipitate on rock surfaces non-uniformly, depending on mineralogy, pore shape and surface roughness. Understanding of the influence of these factors would assist in improving multiphase flow models. In favourable conditions (low asphaltene concentration, strong aromatic solvent, surface with uniform and strong affinity) the sorption process follows a simple adsorption isotherm (Langmuir or type I according to IUPAC [20]), which corresponds to homogeneous monolayer formation. In less favourable conditions (high asphaltene concentration, poor solvent) multilayer formation is observed and various adsorption regimes may co-exist correlating to the degree of asphaltene aggregation, which can result in very high specific adsorption values q_a reported in units of $[mg/m^2]$. A variety of scenarios are covered by IUPAC type II to type V adsorption isotherms. No single analytical expression so far have been offered to cover all variants of sorption processes. The Fowler and Gugge140 nheim [21] model covers three types of isotherms: the mentioned type I, type III - pure multilayer formation without saturation limit and type V, which allows lateral interaction and includes capillary condensation effects. Characteristic qualitative difference of these scenarios result in either Γ-, *J*- or *S*-shape of an adsorption-equilibrium concentration trend (q_a vs C_{eq}) and also are expected to appear in deposition kinetics, whichever form is used: specific deposit mass per unit surface area $q_a(t)$, coverage $\theta_a(t)$ or occupied pore-space fraction, $d\phi_\delta(t)$.

Many techniques and their combinations have been applied to characterise asphaltene deposition. A study based on SEM and pressure drop in capillary allowed to conclude that submicron asphaltene aggregates are likely responsible for fouling [22]. A work based on optical microscopy/photomicrography techniques concluded that the deposition rate depends mainly on oil/n-alkane ratio and alkane carbon number [23]. 3D optical microscopy was used to investigate effects of carbon dioxide on asphaltene deposition at various pressures by detecting size of asphaltene aggregates and glass surface area covered by deposit [24]. It also was applied to measure a deposition rate in a glass microchannel as a function of pumped volume at a constant and variable flow rates [25]. It was established that the type of n-alkane and oil in the mixture governs the resulting thickness of a deposit. However, since experiments were carried out over limited time intervals (several hours), even qualitative predictions about the long-time dynamics are not possible. This signifies the importance of long time adsorption behaviour in asphaltene-solid systems.