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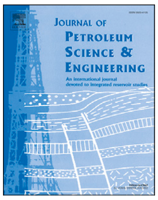

EPR study of spectra transformations of the intrinsic vanadyl-porphyrin complexes in heavy crude oils with temperature to probe the asphaltenes' aggregation

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ABSTRACT

Temperature dependencies of electron paramagnetic resonance spectra of intrinsic paramagnetic vanadyl complexes and dynamical viscosity for two heavy crude oils and asphalt samples are measured. Transitions between the different motional conditions (from the rigid to the fast motion regimes) are observed. The rotational correlation times (in the model of the isotropic diffusion) are extracted. It is shown that the characteristic temperatures for the motional regime transitions are mainly defined by the asphaltenes' content. From our analysis it follows that the thermal treatment leads to the destruction of the asphaltene complexes onto the 4–5 small pieces. The results indicate that paramagnetic vanadyl complexes are the sensitive intrinsic probes to study qualitatively and quantitatively structural transformations of aspahltenes of heavy crude oils in-situ.

1. Introduction

Asphaltene constituents of petroleum (defined as the heaviest fractions of crude oil insoluble in normal alkanes) impact all aspects of crude oil production and utilization (Trukhan et al., 2017; Speight, 2015; Ganeeva et al., 2011). The content of the high-molecular asphaltene components could reach the values of 45 wt % in native oils and up to 73 wt % in natural asphalts and bitumen. Undesirable asphaltene precipitation is a serious concern to the petroleum industry because asphaltenes can block catalyst active sites, plug up well bores and stop oil production, in addition to blocking pipelines (Ganeeva et al., 2011; Gawel et al., 2005; Yen and Chilingarian, 2000). As it is stressed anew in the recent review by Martyanov et al. (2017), a fundamental condition for the development of effective processes for heavy oil production and processing is the understanding of the key factors that determine the aggregative behaviour and stability of oil disperse systems (ODS), behaviour and chemical transformations of their components under various external conditions including elevated temperature.

Asphaltenes are known to form nanosized colloidal particles “nanocrystallites”, “nanocolloids”, or “nanoaggregates”. It is shown that asphaltenes aggregation begins already at their concentrations as high as 10 mg/L in some “good” organic solvents, as described by Evdokimov et al. (2016), Mullins et al. (2014) and by Shkalikov et al. (2010). The littlest aggregates contain 5–8 small asphaltene molecules. For example, in the well-known Yen-Mullins model (Mullins et al., 2014) the asphaltenes are defined as a central moderately-sized polycyclic aromatic hydrocarbon ring system linked with alkane chains on the exterior, with nanoaggregates up to six molecules and clusters of eight nanoaggregates on average (Lima et al., 2017).

However, after decades of intensive studies, the association and aggregation of asphaltenes are still not well characterized and are subjects of ongoing debate (Lima et al., 2017; Trukhan et al., 2017; Evdokimov et al., 2016; Ganeeva et al., 2011). Additionally, structural and molecular variability of asphaltenes do not allow to use an exact copy of one model which satisfactory describes a properties of one sort of ODS to other ODS. Therefore, the complex analytical study of each kind of ODS is in need both for the fundamental research and practical applications.

A significant factor influencing the asphaltene aggregation and

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