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Fluorine tracers for the identification of molecular interaction with porous asphaltene aggregates in crude oil



Siegfried Stapf^{a,*}, Amin Ordikhani-Seyedlar^a, Carlos Mattea^a, Ravinath Kausik^b, Denise E. Freed^b, Yi-Qiao Song^b, Martin D. Hürlimann^b

^a Dept. of Technical Physics II, TU Ilmenau, PO Box 100 565, 98684 Ilmenau, Germany

^b Schlumberger-Doll Research, One Hampshire Street, Cambridge, MA 02139, USA

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ABSTRACT

The frequency dependence of the proton longitudinal relaxation time $T_1(\omega)$, and the ratio of relaxation times at a given magnetic field strength T_1/T_2 , have been discussed as parameters to relate the molecular dynamics and the composition in crude oil. The broad distribution of both relaxation parameters as a consequence of the multitude of components in crude oil has been addressed by means of deriving suitable averaged parameters. In the presence of asphaltenes, however, this approach turns out to be problematic since the spread of, in particular, T_2 is increased, and the distribution of $T_1(\omega)$ varies with frequency. One possible reason for this observation is the suggested increased interaction strength of aromatic molecules with the polycyclic asphaltene cores since, in these oils, the signal is obtained solely from the mobile fraction of molecules (maltenes) while asphaltene aggregates themselves act as a relaxation agent due to their attached stable radicals.

In order to verify the notion of aromaticity as a decisive parameter of maltene relaxation, ^{19}F containing tracer molecules were added at low concentrations to natural oils of different asphaltene content, and their ratio T_1/T_2 and the field dependence $T_1(\omega)$ were measured. One main finding of this study is the significant increase of T_1/T_2 for aromatics in the presence of asphaltenes compared to alkanes. The results are interpreted in terms of selective maltene–asphaltene interaction based on frequency dependent relaxation results. The strong contrast of relaxation times allows for a simplified quantification of either asphaltene concentration or aromaticity of maltenes in natural oils.

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1. Introduction

Crude oil is a complex mixture of a large variety of hydrocarbons with different degrees of aliphatic and aromatic properties, as well as molecular size. Under equilibrium conditions, all components are dissolved, and a coarse distinction is made between material that is insoluble in a pure saturated hydrocarbon liquid – the so-called asphaltene – and those molecules that remain dissolved in such a paraffinic environment – the latter being called maltenes. In a simplified view, asphaltenes are non-volatile components that are dissolved in a mixture of maltenes, whereas asphaltenes show a tendency towards aggregation which frequently complicates the quantification of their molecular mass distribution. Here one needs to keep in mind that both classes constitute typically tens of thousands of individual components in any given oil reservoir, and that the precise distinction between

asphaltenes and maltenes depends on the experimental procedure used to separate them.

The presence of asphaltenes in crude oils is of considerable relevance in oil production from oil recovery via transport to refining. Change of external parameters such as pressure and temperature, but also composition drifts during transport or in the course of production from any given reservoir, may affect the economic potential of the crude oil. In addition, they can have dramatic effects on the feasibility of oil exploitation itself when aggregation of asphaltenes leads to fouling and clogging of pipes at a drilling site. Under reservoir conditions, asphaltenes form small aggregates of several molecules, which can, for instance, be detected by X-ray and neutron scattering techniques [1–3]. The transition towards larger agglomerates that lead to precipitation, and possibly blockage of boreholes or pipelines in the course of time, is less well understood, but appears to be affected by temperature changes, shear and addition of non-solvents. Indeed the very definition of asphaltenes via the SARA (Saturates/Aromatics/Resins/Asphaltenes) analysis is the fraction of molecules that precipitate following the

* Corresponding author. Tel.: +49 3677 693671; fax: +49 3677 693770.

E-mail address: Siegfried.stapf@tu-ilmenau.de (S. Stapf).

dilution of crude oil in n-heptane. Without the time-consuming and laboratory-based SARA analysis, the identification and quantification of asphaltenes is a difficult task. However, it would be desirable to provide an *in situ* technique for detecting asphaltenes, in order to be able to react in due time to a fluctuation of their concentration.

In low-viscosity oils, the distribution of molecular weights has been addressed successfully by combining downhole NMR measurements of T_1 , T_2 and the intra-diffusion coefficient (D) of these substances. The quantities are related to each other; they depend, in different ways, on the viscosity, i.e. on the composition of the crude oil. A detailed investigation of the dependence of ^1H relaxation and diffusion properties on molecular sizes has been discussed for linear alkanes [4,5]. In the more complicated situation of most crude oils, with many thousands of components, two-dimensional techniques that correlate two of the mentioned three parameters were employed as a means to assess oil composition [6]. In the presence of asphaltenes and resins, the relationship becomes more difficult to resolve since the interaction of soluble components (maltenes) with asphaltenes affects their relaxation, and possibly also their diffusion properties. If this interaction were understood well enough, a quantification of asphaltenes would be possible, since the latter remain invisible to conventional NMR methods as a consequence of their short T_2 .

There are at least two mechanisms that can affect the interaction of maltenes with asphaltenes in dependence of their size and shape. The first is purely geometric: asphaltene molecules aggregate with their polycyclic cores oriented in parallel sheets and the dangling ends of alkane sidechains constitute the outer regions of the aggregate. This geometry leaves voids that can be accessed by maltene molecules. Recently, the maltene content trapped in precipitated asphaltene has been described [7]. Even in the solution state, asphaltene aggregates can be considered as porous structures and the molecular dynamics of maltenes in confined spaces will be affected similarly to conventional, solid porous media [8], with maltenes being in exchange between the confinement and the free phase.

The second mechanism is related to the attracting force resulting from the delocalized electrons in aromatic π -bonds. It is known from experiment as well as DFT computations that mono- and polyaromatic rings interact strongly with each other and assume intermediate or even stable structures by a process called π -stacking. This process is responsible for asphaltene aggregation and precipitation [9–11], but also for the selective adsorption on ordered surfaces, and the generation of graphitic structures. Intermediate dimerization of benzene rings is another example of this interaction [12]. To this date, only a few numerical simulations are available that have investigated the interaction of maltenes and asphaltenes by density functional theory [13,14]. Related studies were carried out for modeling the interaction of aromatics with a graphene surface [15–18], where graphene can be considered as an idealized approximation of asphaltene. In an experimental low-magnetic field investigation comparing the ^1H relaxation properties of saturated-rich and aromatics-rich oils with those of asphaltene-rich oils [6], a tendency was found towards larger T_1/T_2 ratios in crude oils containing asphaltene, but with no obvious signature of aromatic maltenes.

These studies suggest that the interaction of aromatics with the polycyclic asphaltene molecules is stronger than that of alkanes, leading to preferential orientations and possibly extended lifetimes of the maltene in the vicinity of the asphaltene aggregate. As a consequence, the description of maltene–asphaltene interaction needs to take into account the specific geometry of the maltene.

Asphaltenes usually contain a significant amount of stable radicals and other sources of unpaired electrons such as vanadyl (VO^{2+}) ions [19,20]. Earlier studies have concluded that typically 1–3% of

all asphaltene molecules contain radicals [21]. This is sufficient to make the dipolar coupling between nuclear and electron spins a dominating effect for relaxation. Recently, an interpretation of crude oil ^1H relaxation dispersion was presented [22] that was in qualitative agreement with a reorientation mechanism on a two-dimensional topology where the small maltene molecules are considered having a particular interaction time τ_m on the surface of the large asphaltene aggregates, which needs to be compared with the characteristic time of residence in the proximity of the surface τ_s , a quantity that can be related to the interaction strength of maltenes with asphaltene surfaces. However, this interpretation was based on the assumption that all types of maltene species interact with asphaltene in a similar fashion. In particular, no difference between saturated (i.e. aliphatic) and aromatic maltenes was made.

In order to specifically investigate relaxation of individual species, we have used a number of perfluorinated and partially fluorinated compounds at small concentration in crude oil. We have employed an asphaltene-rich oil and compared it with two types of asphaltene-free oils, one of them containing significant amounts of resins. Frequency dependent relaxation times measurements (relaxation dispersion) were carried out for selected compounds, and are compared to other materials described in the literature. We attempt to identify an empirical relation of the commonly acquired parameter T_1/T_2 with the solvent/asphaltene interaction, with the aim of testing the feasibility of this type of tracer fluids and the possibilities for improving the available theoretical approaches for the description of maltene relaxation in the presence of asphaltenes.

2. Experimental

The composition and viscosities of the three reservoir oil samples used in this study are listed in Table 1. Oil A0 is a low-viscosity oil free of asphaltenes but with a significant amount of resins; this is to be contrasted with a waxy oil (W0) of similar viscosity but not containing any resins. The reference oil for asphaltene interaction contains 13 wt.% asphaltenes (A13) and is about one order of magnitude more viscous than the other two samples.

Tracer fluids were purchased from Sigma Aldrich and were used without further purification. Hexafluorobenzene (C_6F_6) and octafluorotoluene (C_7F_8) were chosen to represent typical aromatic molecules; perfluorooctane ($\text{n-C}_8\text{F}_{18}$) and –pentadecane ($\text{n-C}_{15}\text{F}_{32}$) correspond to the length distribution of saturated maltenes. In addition, 1,4-difluorobenzene ($\text{C}_6\text{F}_4\text{H}_2$) as well as tri- ($\text{C}_7\text{F}_3\text{H}_5$) and pentafluorotoluene ($\text{C}_7\text{F}_5\text{H}_3$) were selected in order to investigate whether the fluorinated compounds can be considered as suitable models for the protonated oil components, or if the large polarizability and the properties of the π -bond delocalization in fluorine nuclei is particularly affected by the interaction with asphaltenes.

Oil samples were stored in a dark place and were protected from light by filling them in non-transparent tubes. For all tracers with the exception of perfluoropentadecane, a defined amount of tracer fluid equivalent to 2 wt.% was added to the containers at ambient temperature, and these were gently shaken for several hours. The samples were then filled into NMR tubes of 10 and 5 mm outer diameter, respectively, and kept protected from light,

Table 1
Oil samples used in this study, and composition in wt.% obtained by SARA analysis.

Code	Saturates	Aromatics	Resins	Asphaltenes	Viscosity (cP)
A0	67	25	8	0	9
A13	38	32	18	13	73
W0	96	4	0	0	11

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