



Effects of paraffin chain size on the oil outflow investigated by a combination of thermal lens and laser-induced fluorescence spectrometries



Yuji Nascimento Watanabe^{a,b,*}, Ângelo Marcos Vieira Lima^c,
Cristina Maria Assis Lopes Tavares da Mata Hermida Quintella^b

^a Federal University of the Reconcavo of Bahia, Center for Teacher Formation, Av. Nestor de Melo Pita, 535, Centro, Amargosa, BA CEP: 45.300-000, Brazil

^b Institute of Chemistry, Federal University of Bahia, Rua Barão de Geremoabo, 147, Campus Universitário de Ondina, Salvador, BA CEP: 40.170-115, Brazil

^c Petróleo Brasileiro S.A. Rua Eteno, 2198 Complexo Petroquímico, Camaçari, BA CEP: 42.810-000, Brazil

HIGHLIGHTS

- TLS-LIF-FI coupling was sensitive to variations in fluid composition.
- LIF and TLS revealed different information, but complementary, about the sample.
- Paraffin molecules tend to increase the fluorescent quantum yield of natural oil probes.
- This increase is preferably in the vertically polarized fluorescence component.
- Higher paraffin molecules tend to move to the boundary layer during the flow.

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ABSTRACT

We investigated the influence of three different paraffin chain sizes (C22, C28, and C36) on the outflow profile of oil dissolved in mineral oil using thermal lens spectrometry (TLS) coupled with laser-induced fluorescence spectrometry (LIFS). The data show that the presence of paraffin molecules leads to an increase in the fluorescent quantum yield of natural oil probes, as observed by the reduction of the photo-thermal signal and the consequently increased fluorescent emission. We also observe that larger paraffin molecules such as C36 tend to move toward the bottom layer during the fluid outflow. This may be associated with the nucleation process and formation of paraffinic deposits in oil ducts.

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1. Introduction

The oil produced in the Reconcavo of Bahia Bay, Brazil, has a great commercial value owing to the presence of high levels of paraffin. The presence of large paraffin chains increases the oil value, because, when processed, other hydrocarbons can be obtained and sold to raw material industries for more attractive prices. However, what at first glance appears to be an economical

advantage becomes a problem for the oil industry, because, under specific temperature and pressure conditions, paraffinic deposits can form [1] both in the tabulation used for raw oil extraction, precluding the exploration of some mature fields, and in the transport ducts, obstructing the flow of the produced material.

In the past, several research groups dedicated time and effort to investigate the physicochemical mechanisms that lead to the formation of paraffinic deposits, as well as to develop methods to prevent the formation of these crystals and the consequent stagnation of oil production and transport [2–5]. Several techniques have been used to determine the properties such as thermal diffusivity, heat capacity, (paraffin) molecular diffusion coefficient, and kinematic viscosity, with the aim of developing alternative methods to characterize the types of oil [6–8]. Through a combination of these properties with different chemical compositions such as paraffin

Abbreviations: TLS, thermal lens spectrometry; LIFS, laser-induced fluorescence spectrometry; FI, flow injection; C22, C₂₂H₄₆; C28, C₂₈H₅₈; C36, C₃₆H₇₄; C, mechanical chopper; DF, dichroic filter.

* Corresponding author at: Federal University of the Reconcavo of Bahia, Center for Teacher Formation, Av. Nestor de Melo Pita, 535, Centro, Amargosa, BA CEP: 45.300-000, Brazil.

E-mail address: yuji@ufrb.edu.br (Y.N. Watanabe).

and asphaltene content [9–12], it is possible to establish reference criteria to determine the production conditions and the probability of paraffinic deposit formation. Such information may be useful in the management of the whole oil economical chain, favoring the development of technologies that enable real-time monitoring of the production and transport conditions.

Considering the economic and technological importance of a deeper understanding of paraffin formation, we report in this work the development of an experimental system that combines thermal lens spectrometry (TLS) and laser-induced fluorescence spectrometry (LIFS) in the study of molecular processes of microvolumes of flowing crude oil. The experimental system consists of an assembly of two detection lines: one for the molecular detection of fluorophores dispersed in the fluid, and the other to detect the photothermal signal generated by the nonradioactive deactivation of these species.

TLS was the first photothermal spectroscopic technique to be used for the investigation of chemical parameters [13], and, since it was first described by Gordon et al. in 1964, its applications have been constantly broadening, from the characterization of thermal properties of solvents [14] and high-sensitivity chemical analyses [15] to the measurements of protein-volume variations [16].

In the last years, TLS has been used for the evaluation of physicochemical properties of several fluids. Among the studies, the most relevant focused on the investigation of the influence of surfactants and nanoelectrolytes in water [17], monitoring of thermal parameters of different edible oils [18], indirect detection of minor compounds in complex mixtures [19], and evaluation of the influence of molecular interactions on the thermophysical properties of binary liquid mixtures [20,21].

More recent studies have proposed the use of TLS to evaluate fuels such as oil-biodiesel preparations [22], attesting the sensitivity of the technique to detect biodiesel levels in a certain amount of biodiesel [23], and enabling, for instance, the detection of nonconformities and biodiesel alterations. Silva et al. [21] described an attempt to establish a phenomenological correlation between the rheological and physicochemical properties of several biodiesel types. They utilized TLS to characterize different plant oils and their respective biodiesels, using values of thermal diffusivity. By relating this property to the viscosity of the samples, they proposed a classification of the produced biodiesel based on its ability to undergo atomization, i.e., to undergo combustion in automotive motors, which is directly correlated with the fuel quality.

In this work, TLS was coupled with LIFS to investigate distinct characteristics of the same sample under conditions typical of a flow injection (FI) system. Although this is not the first time that LIFS and TLS are coupled [24,25], this paper reports a novel experimental setup, in which the fluorescence emitted by the sample is resolved in its vertical and horizontal components. Using the principle of photoselection [26], this approach allows us to infer the intermolecular alignment, and, consequently, evaluate the liquid structure and its flow properties at the microscopic level. We expect this information to be complemented with the photothermal data obtained with TLS; the combination of these two different techniques enables us to obtain a more detailed view of the paraffin influence on the oil flow regime and the mechanisms that form paraffinic deposits.

2. Materials and methods

2.1. Materials

The sample consisted of oil from the Reconcavo of Bahia Bay dissolved in mineral oil, with a paraffin content of 14.7%, density of approximately 0.8 g mL^{-1} at $15 \text{ }^\circ\text{C}$, pour point at $39 \text{ }^\circ\text{C}$, and cloud

point at $49 \text{ }^\circ\text{C}$. The thermal conductivity of the sample is about $0.16 \text{ W m}^{-1} \text{ K}^{-1}$. The sample solvent was used as the carrier fluid. This fluid consisted of a mixture of liquid paraffin with chain sizes between 5 and 12 carbon atoms and density of approximately 0.85 g cm^{-3} at room temperature. Due to its low polarity, this represents an excellent solvent for the dead oil sample. In order to investigate the size of the paraffin chain on the dynamics of liquid outflow in the flow system, known amounts of paraffin $\text{C}_{22}\text{H}_{46}$ (C22), $\text{C}_{28}\text{H}_{58}$ (C28), and $\text{C}_{36}\text{H}_{74}$ (C36) were added to the sample.

2.2. Experimental methods

2.2.1. Signal generation

Fig. 1 shows a scheme of the experimental setup used in this work. The excitation source consists of an argon laser at 488 nm and 50 mW . The laser beam is focused on the sample (positioned at 40 cm) through a convergent lens, L_1 , modulated by a mechanical chopper (C), and deviated by a dichroic filter (DF), which reflects the excitation beam. A Glan–Thompson polarizer (Newport) is placed between the DF and the sample to assure 100% vertical polarization of the excitation photons. After absorbing the laser radiation, the sample undergoes both a nonradioactive decay, generating the TL signal, and a radioactive decay, evidenced by the emission of fluorescence.

The signal detection is divided in two different parts, simultaneously managed by our own computerized system for sample detection, control, and placement [27,28].

2.2.2. TLS

TLS is based on the absorption of light by a certain chemical species and on its subsequent nonradioactive decay, with release of thermal energy [13]. The heat released during the inactivation procedure in the excited state causes a punctual heating on the region exposed to the laser beam. When lasers with a Gaussian energy distribution profile are used, a temperature gradient proportional to the energy distribution in the laser beam is formed on the exposed region. This heat distribution in turn alters the medium density, causing a gradient in the refraction index (dn/dT) that modifies the direction of the photon propagation like conventional optical lens.

The amount of released heat is directly proportional to the absorbed energy, which depends on other factors; e.g., the molar absorptivity of the sample relative to the wavelength utilized (λ), laser-beam power, and concentration of the absorbing species; dn/dT in turn depends on the fluorescent quantum yield, thermal conductivity of the system (k), and calorific potential (C_p) [29,30].

The detection of the TL signal is performed using a double coaxial beam setup as shown in Fig. 1. The thermo-optical detection line comes from a Helium–Neon laser (with λ at 632.8 nm and

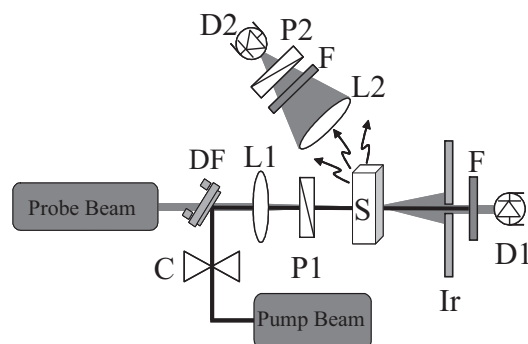


Fig. 1. Double coaxial beam TLS-LIFS system. C – Chopper; D – Detector; DF – Dichroic Filter; F – Filter; Ir – Iris; L – Lens; P – Polarizer; S – Sample.

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