Singlet Oxygen Production by a Crude Oil from the San Jorge Gulf Basin, Argentina[†]

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ABSTRACT

The quantum yields for singlet oxygen production by diluted solutions of an Argentine crude oil and its SARA (saturates, aromatics, resins and asphaltenes) fractions were obtained by direct detection of the characteristic phosphorescence following monochromatic excitation at 355 nm. The most efficient sensitizers of singlet oxygen in organic media are crude oil, maltenes and aromatics fractions (values of singlet oxygen quantum yield are around 0.7), and resins (values around 0.1) are the poorest. Also, the quenching of singlet oxygen by the crude oil and its fractions was investigated; the asphaltenes and the petroleum are relatively efficient quenchers of singlet oxygen.

INTRODUCTION

In Argentina, the petroleum industry began the first years of the XXth century with the discovery of petroleum in the city of Comodoro Rivadavia in 1907. The exploitation of oil fields in Patagonia has continued ever since without interruption with the concomitant damage to the environment mainly due to accidental discharges of crude oil into the soil or sea during extraction or transportation (1).

Petroleum is an extremely complex mixture of hydrocarbons, with minor amounts of compounds containing nitrogen, oxygen, sulfur and trace of metals. The composition and quality of petroleum vary as a result of its natural origin and to transport and storage conditions (2) and once it is released into the environment, on weathering processes (3).

When crude oil and related products are exposed to light, the formation of reactive oxygen species (ROS) is possible (4–6). Several studies have been published concerning the role played by the ROS singlet oxygen [O_2 ($^1\Delta_g$)], in the photooxidation of crude oil and petroleum products (4, 7–14). Due to the presence of many aromatic compounds, generation of singlet oxygen as a result of solar exposure of crude oil is expected. It is therefore worthwhile to explore the generation capability of a petroleum from a producing field in Argentina, especially since there are few reports in the literature concerning the capacity of crude oil to produce singlet oxygen. Corrêa et al. demonstrated the formation of singlet oxygen when crude oils from Brazil, Mexico, Arabia and Venezuela were exposed to sunlight and reported the corresponding singlet oxygen quantum yields (15). Lichtenthaler et al. estimated the singlet oxygen quantum yields for crude oils from Middle East, North Sea and Africa (4). Ray and Tarr employed crude oils from the Gulf of Mexico, including samples of the Deepwater Horizon spill, and reference materials from NIST to measure the total amount of singlet oxygen from crude oil films on water (6).

In this study, the quantum yields for singlet oxygen generation of an Argentine petroleum (*Escalante* crude oil, **EO**) and its saturates, aromatics, resins and asphaltenes (known collectively as SARA) fractions, not previously reported in the literature, are presented. Also, their properties as eventual quenchers of singlet oxygen were investigated. The information obtained can contribute to the interpretation of the photooxidation of a petroleum that can be considered one of the major sources of pollution in the central Patagonian coast (Argentina) (1, 16, 17). For comparison purposes, an Argentine light crude oil (*Medanito* crude oil, **MO**) was also investigated.

MATERIALS AND METHODS

Chemicals. Three crude oils from Argentina, two *Escalante* oils from the San Jorge Basin (**EO1**: from B-483 well of Cañadón Perdido Field and **EO2**: a blend of crude oils for shipping) and one *Medanito* blend from the Neuquina Basin (**MO**) were characterized according to the procedures described below. Chemicals obtained from commercial sources were used without further purification.

Crude oil characterization. The density of the oil was determined by means of the procedures described in ASTM methods D287 (18) and D1298 (19). A Brookfield LV viscometer was used for viscosity measurements.

SARA analysis. Conventional SARA analysis was carried out by precipitation and subsequent liquid-solid chromatography. Asphaltenes were extracted from crude oil in accordance with the procedure given in ASTM method D2007 (20). A solution of crude oil (10 g) in n-pentane (100 mL) was stirred for 1 h, with intermittent warming, and then allowed to stand in the dark for 24 h at room temperature. Afterward, the precipitated asphaltenes were collected by filtration and the filtrate was labeled as maltenes. The precipitate was washed with n-pentane until the solvent wash was colorless, then was dried at room temperature and weighted for determining asphaltenes content. Approximately 0.5 g of

maltenes suspended in n-pentane was further fractionated in a chromatographic column prepared with activated bauxite (21) and silica gel (20). The fractions were successively eluted with 50 mL of n-pentane, 50 mL of toluene and 50 mL of chloroform:methanol (1:1), and were labeled as saturates, aromatics and resins, respectively (22). Solvents were eliminated under vacuum at 40 °C in a rotary evaporator and the weight percentages (%) of each fraction were determined.

Sample preparation. Transparent solutions were prepared by dissolving appropriate amounts of crude oil and its fractions in different organic solvents: **EO1**, **EO2**, **MO**, maltenes and asphaltenes were dissolved in toluene, resins in chloroform and saturates in n-pentane. Solutions were prepared freshly prior to each measurement. Concentrations of asphaltenes were lower than 50.0 mg L^{-1} to avoid aggregation (23, 24).

UV–visible absorption spectroscopy. Absorption spectra were recorded on an Agilent 8453E diode array spectrophotometer. Measurements were made at room temperature using 1 cm path length quartz cells.

Time-resolved phosphorescence detection of singlet oxygen. Singlet oxygen generation and quenching were determined employing a system previously described (25). Briefly, a Nd:YAG laser (Spectron) operating at 355 or 532 nm was the excitation source and the emitted phosphorescence of singlet oxygen (mainly at 1270 nm) was detected at right angles after appropriate filtering, with an amplified germanium photodiode (Judson J16/8S). About ten shots were usually needed for averaging decay times, to get a good signal-to-noise ratio. Freshly prepared solutions were used for each measurement to avoid photodegradation of the samples.

The decay signals of singlet oxygen phosphorescence were obtained in air-saturated samples, in solutions bubbled with argon for 15 min, and in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO, 20 mM). The tail part of the decays (8 μs after the laser pulse) was fitted using a single exponential function and extrapolated to zero time, due to the signal distortion at short times by instrumental artifacts (e.g. the residual luminescence of the sensitizer or scattering of laser light).

Values of Φ_Δ were determined using optically matched solutions (A = 0.3 at 355 nm) of crude oil and its fractions (S) relative to a reference (R) solution of Zn-tetraphenyl porphyrin in DMF (ZnTPP, $\Phi_\Delta = 0.74$ (25)) employing Eq. (1) (26),

$$\Phi_{\Delta_S} = \Phi_{\Delta_R}(I_{\Delta_S}/I_{\Delta_R})(\tau_{\Delta_R}/\tau_{\Delta_S}) \quad (1)$$

where I_Δ, Φ_Δ and τ_Δ are the emission intensity, quantum yield and lifetime of singlet oxygen in each solvent, respectively. The plots of I (extrapolated to zero time) *versus* laser energy were fitted to straight lines, and the I_Δ values were obtained from the corresponding slopes. The laser energy (% E) was varied using a series of neutral density filters of varying transmittance.

For the singlet oxygen quenching measurements, the wavelength of the excitation laser beam was 532 nm. Rubrene (Rb, A = 0.5 at 532 nm) was chosen as sensitizer because of its high molar absorption coefficient at the available excitation wavelength and good solubility in the solvents employed. The absorbance of Rb was such as to assure that the incident light was predominantly absorbed by Rb. The rate constants (k_q) were estimated from the slopes of the linear plots obtained according to Eq. (2),

$$\tau_\Delta^0/\tau_\Delta = 1 + k_q\tau_\Delta^0(S) \quad (2)$$

where τ_Δ^0 is the singlet oxygen lifetime in the absence of S and (S) is the concentration of crude oil **EO1** and its maltenes, aromatics, resins and asphaltenes fractions in g L^{-1}. The values of τ_Δ^0 were obtained by extrapolation to zero concentration of linear plots of $1/\tau_\Delta$ *versus* (S). Unfortunately, at higher S concentrations, tails appear in the visible region of their spectra, limiting the range of (S).

Air-saturated solutions were used in all cases. The data were analyzed with Origin software.

RESULTS AND DISCUSSION

Crude oil characterization

To characterize the crude oils, their density and viscosity were measured and the American Petroleum Institute (API) gravity

was calculated (Table 1). A SARA procedure was performed to isolate the fractions of **EO1**, and a content of 43.4, 34.6, 17.4 and 4.6 wt % was obtained for saturates, aromatics, resins and asphaltenes, respectively. The saturates, aromatics, and resins fractions were liquids, colorless, yellow-orange and brown, respectively, whereas the asphaltenes were a black solid.

The saturates, aromatics and resins are the normal alkane soluble fractions collectively known as maltenes; meanwhile, the asphaltenes are the insoluble alkane fraction. As in most of the known crude oils, the saturated hydrocarbons are the predominant group of constituents for the *Escalante* crude oil, followed by the aromatic hydrocarbons (2). The total amount of resins and asphaltenes in a crude oil is highly dependent on oil generation processes. API gravity is one of the physical properties by which crude oils are generally classified, bought and sold. Based on the API value, the *Escalante* and *Medanito* crude oils can be classified as a conventional heavy oil and a light oil, respectively.

Generation of singlet oxygen

To estimate the role of **EO1**, **EO2**, **MO** and the fractions of **EO1** as sensitizers for generation of singlet oxygen, which is involved in photooxygenation reactions of petroleum, its phosphorescence signal was monitored. Independent control experiments were performed in the presence of argon and upon the addition of the known singlet oxygen quencher DABCO to the samples. Figure 1 shows the rise and decay of the 1270 nm emission produced after pulsed laser excitation at 355 nm in air-saturated, argon-bubbled and in the presence of DABCO of solutions of **EO1** in toluene.

To evaluate the involvement of singlet oxygen, the following aspects were considered: (i) the phosphorescence decay traces observed could be fitted with single exponential functions from which singlet oxygen lifetimes (τ_Δ) were derived and were found to be in agreement with the expected for the corresponding solvent, shortened by some quenching of singlet oxygen; (ii) the decay signal was reduced after bubbling argon to the solutions, most likely the signal was not further inhibited because oxygen was not completely removed from the air-saturated solutions; (iii) addition of DABCO, a known singlet oxygen quencher, resulted in a significantly decrease of the signal.

Unfortunately, for the asphaltenes fraction in toluene, the poor signal obtained, near the limit of detection, make it impossible to observe an effect on the singlet oxygen lifetime in the presence of argon or DABCO, suggesting that the deactivation of singlet oxygen by asphaltenes is the predominant process. Also, the signals likely include a contribution of the emission from low energy triplets of asphaltenes, which could show a red shift beyond that of the emission from some crude oils (27, 28), so the quantum yield was not calculated for asphaltenes.

The results suggest that the studied crude oils, and maltenes, saturates, aromatics and resins fractions of **EO1** can sensitize

Table 1. Properties of the crude oils.

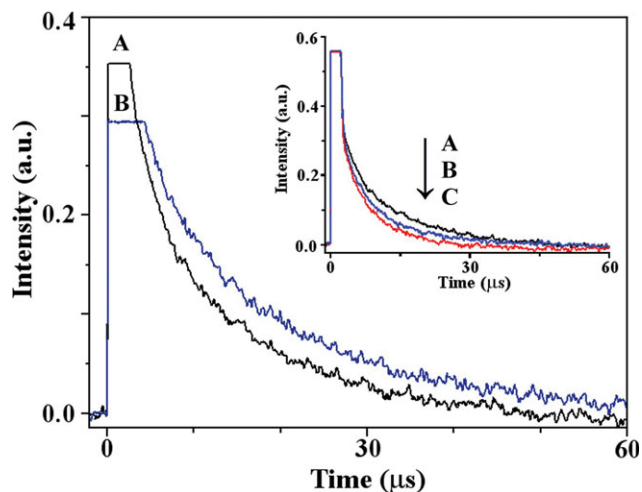| Crude oil	Density (g L^{-1})	API gravity	Viscosity (cP)
EO1	0.9307 ± 0.0001	20.5	1941 ± 24
EO2	0.9247 ± 0.0006	21.5	1766 ± 20
MO	0.8450 ± 0.0009	35.9	12.32 ± 0.17

Figure 1. Decay for the singlet oxygen phosphorescence emission monitored at 1270 nm generated upon excitation at 355 nm of *Escalante* crude oil (**EO1**) (A) and its aromatics fraction (B) in toluene. Insert: Decay for the singlet oxygen phosphorescence emission of a sample of **EO1** in toluene in air-saturated solutions (A), and in the presence of argon (B) and DABCO (20 mm) (C).

singlet oxygen in diluted solutions, then singlet oxygen generation quantum yields (Φ_Δ) were determined. When the phosphorescence intensities at zero time were plotted against laser energy, a flattening of the curve was observed at higher pulse energies, in accordance with the observations reported by Corrêa *et al.* (15), therefore, only low laser energies were considered. Straight lines were thus obtained when I_Δ is plotted against the laser pulse energy (Fig. 2), and Φ_Δ values were obtained from the corresponding slopes according to Eq. 1, the results are presented in Table 2.

The singlet oxygen quantum yields of Table 2 are similar to the values reported by Lichtenthalert *et al.* (4) for a series of crude oils and higher than those reported by Corrêa *et al.* (15). However, due to the differences in the crude oil properties studied in each case and methods for obtaining the quantum yields, a direct comparison, as already mentioned by Corrêa *et al.* (15), is difficult. However, some general observations can be made as follows: (i) clearly, all crude oils in dilute solutions generate singlet oxygen with appreciable quantum yields (values between 0.15 and 0.8 are reported) despite their geographical origin; (ii) crude oils with lower densities are expected to have higher quantum yields; (iii) the maltenes are the responsible of the most of singlet oxygen generation, which can be related to the content of aromatics; (iv) similar observations regarding singlet oxygen generation and the dependence with density were made by Ray and Tarr in crude oil films on water (6), which is valuable information to understand the processes that impact crude oil spilled and exposed to sunlight. Interestingly, the ability to produce singlet oxygen by the fraction labeled as saturates was observed. This fraction of the crude oil is not absorbed on the chromatographic column and is the first eluted fraction of the maltenes (21), is composed mainly by linear, branched and cyclic alkanes; however, aromatics with long side chains could be present (29, 30) which probably are responsible of the generation of singlet oxygen.

It is expected that when such a complex mixture of compounds like crude oil is exposed to light, not only singlet oxygen
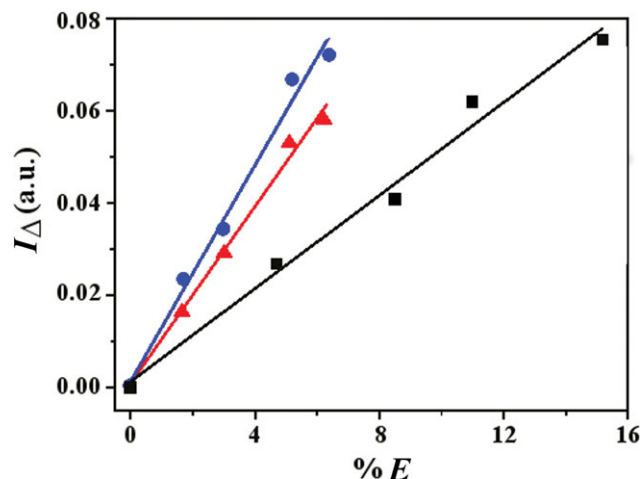

Figure 2. Plots for singlet oxygen phosphorescence emission at 1270 nm *versus* laser energy for solutions of the reference ZnTPP in DMF (black squares) and Medanito crude oil (**MO**, blue circles) and Escalante crude oil (**EO2**, red triangles) in toluene. Excitation wavelength 355 nm.

Table 2. Singlet oxygen quantum yields (Φ_Δ) at 355 nm and quenching rates constants (k_q) of crude oils and its fractions in different solvents.

Sample	Solvent	Relative Φ_Δ *,[†]	k_q ($\times 10^5$ L g^{-1} s^{-1})*,[‡]
EO1	Toluene	1	1.49
EO2	Toluene	0.94	–
MO	Toluene	1.14	–
Saturates	Pentane	0.32	–
Aromatics	Toluene	0.88	0.49
Resins	Chloroform	0.15	0.32
Asphaltenes	Toluene	–	5.65
Maltenes	Toluene	0.97	0.28

*Estimated error ± 10%. [†]Relative to the value of Φ_Δ for **EO1**. [‡]Sensitizer: Rb.

can be produced, also some components could be efficient quenchers of singlet oxygen. To study the deactivation of singlet oxygen, solutions of a sensitizer in the presence of crude oil and its fractions were irradiated. Rb, which sensitizes its own photooxidation, was chosen as sensitizer due to its solubility in organic solvents, and its absorption at 532 nm, the wavelength emitted by the available laser. In the present case, the bimolecular rate constant of the quenching of singlet oxygen by Rb (k_q in Eq. 2), the concentration of Rb and first-order rate constant of singlet oxygen deactivation in the solvent ($1/\tau_\Delta^0$ in Eq. 2) were in the order of 10^7 M^{-1} s^{-1}, 10^{-5} M and 10^4 s^{-1} (31), respectively, so the effect of singlet oxygen quenching by Rb is considered to be within the uncertainty of the values of k_q reported. In the presence of **EO1** and its fractions, the lifetime of singlet oxygen produced by Rb after pulsed laser excitation at 532 nm is reduced. To evaluate the magnitude of the interaction of singlet oxygen with crude oil and its fractions, the rate constants (k_q) were obtained according to Eq. 2 from the Stern–Volmer plots (Fig. 3).

An inspection of the values of k_q in Table 2 shows that **EO1** and its fractions are single oxygen quenchers. Although the variations due to differences in techniques and crude oils, the quenching rate constants show a similar trend to that reported by Corrêa *et al.* (15), with the highest values for the asphaltenes,
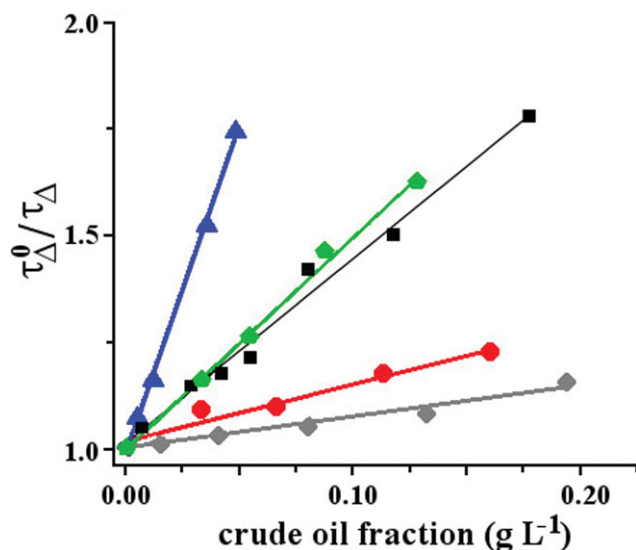
Figure 3. Stern–Volmer plots of the quenching of singlet oxygen by Escalante crude oil (EO1, black squares), maltenes (gray diamonds), asphaltenes (blue triangles), aromatics (red circles) and resins (green pentagons). Sensitizer Rb, excitation wavelength 532 nm.

followed by crude oil. The extreme complex structure of asphaltenes (containing isolated molecules with one aromatic ring system of about seven fused ring PAHs according to the Yen-Mullins model (27), long chain aliphatic groups, heteroatoms like sulfur, nitrogen and oxygen, and trace quantities of heavy metals, like V and Ni) and the presence of triplets of lower energy (28) could explain the observation that asphaltenes are the most efficient quenchers of singlet oxygen.

Due to instrumental limitations, only the generation of singlet oxygen was studied at 355 nm, further studies using different wavelengths should be performed to support the potential generation of singlet oxygen by crude oil and its fractions when exposed to natural sunlight. Also, studies in different media are required for further development of prediction models applicable to the photodegradation of crude oil and derivatives in environmental conditions. Nevertheless, the results presented here provide evidence that the crude oil from San Jorge Basin can both produce efficiently and deactivate singlet oxygen in dilute solutions. The singlet oxygen generation is related mainly to the maltene fraction, especially the aromatics, and the quenching ability to the asphaltene content of the crude oil. This information can contribute to understand the processes occurring in oil systems when exposed to light.

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