

PHOTOCHEMISTRY OF PETROLEUM

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ABSTRACT

The current knowledge of photochemical weathering of petroleum and its fractions in the environment is reviewed, mostly in relation to petroleum films over water. Literature results are compared with the authors' work. The effects of photochemical oxidation of petroleum on the physical and biological properties of petroleum are examined as well as suggested mechanisms for the observed transformations.

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INTRODUCTION

The nature of petroleum

The composition of the fossil liquid hydrocarbon mixture called petroleum can vary greatly according to the location and type of petroleum and can often change with time from a single oil well [1]. The composition of even a well characterized and consistent petroleum such as light arabic crude is only partially known due to the large number of individual components present [2]. Due to this complexity, complete characterization is impossible or at least impracticable, and petrochemists characterize petroleum through its physical characteristics and general chemical composition [3].

Petroleum is usually divided into fractions according to solubility, boiling point, and chromatographic properties on silica gel. In chemical terms, it is divided into an aliphatic fraction, an aromatic fraction, a polar fraction, and asphaltenes [3].

The aliphatic fraction, which is almost invariably the largest fraction, contains a predominate series of linear saturated hydrocarbons in which the even numbered and odd numbered members of the carbon series are of equal concentration. It also contains branched hydrocarbons and many cyclic and polycyclic hydrocarbons (naphthenes). It does not contain alkenes.

The aromatic fraction contains alkylated aromatic hydrocarbons with one to five conjugated aromatic rings. Compounds such as partially aromatic steranes and hopanes are also present. Thiophenes are also included in this fraction as they elute from silica jointly with the carbocyclic aromatics. The degree of alkylation of the aromatic nucleus varies with the mode of formation and maturity of the petroleum [4] but the unalkylated nucleus is usually present in low concentration compared with alkylated derivatives [5].

The polar fraction is complex but contains many heterocyclic aromatics which can include porphyrin derivatives and aliphatic components containing nitrogen and sulfur. Polar oxygen containing groups such as phenols, alcohols, ketones, and carboxylic acids are usually present only in trace amounts.

The asphaltine fraction is defined as that fraction insoluble in pentane or heptane. Its composition can vary greatly from one petroleum to another or may even be absent. Although the asphaltene fraction is usually small, its quantity is a very important factor in petroleum extraction, transportation, and refining. It also affects petroleum rheology when there is an oil spill on water. The “asphaltenes” are usually of higher molecular weight than the other fractions, and contain polycyclic aromatics and polar functional groups. They have a tendency toward association, forming complexes or aggregates of high molecular weight. The asphaltene fraction is also the most strongly absorbing fraction of UV and visible light followed by the polar fraction.

All petroleum fluoresces, at least weakly [6], because they all contain at least a small quantity of aromatics. The aromatic, polar, and asphaltene fractions are all fluorescent, and fluorescence has been widely used in prospecting to discover petroleum deposits, and in environmental monitoring when a spill has occurred.

Petroleum oil spills

Natural seeps where petroleum finds its way to the surface have been and continue to be used as indicators of underground or underwater oil fields. The California and Gulf of Mexico fields were discovered in this way. In these natural seeps, small amounts of oil are continuously discharged over long periods and the environment can process this oil readily. Catastrophic discharges provoked by human activities, on the other hand, have caused major ecological disasters.

When oil is spilled on water, the first and most rapid processes are physical. The oil spreads, drifts, the lower boiling components evaporate into the air and more soluble components dissolve in the water. The overall solubility of petroleum in water is very low, and the components with the highest water solubility are of low molecular weight. These components have a tendency to equilibrate with the atmosphere and to be lost from the water column. Depending on weather and water conditions, dispersion into the water column may also occur. Oil-in-water dispersions are not stable, but water-in-oil dispersions can be very stable and can incorporate as much as 90% water [7]. This dispersion is called "Chocolate mousse" or just "mousse", because of its appearance. It is highly detrimental to cleanup efforts. Its formation is aided by the presence of asphaltenes in the original crude and by weathering.

Weathering consists of the physical, biological, and chemical transformations undergone by petroleum in the environment. Although the physical processes are rapid, they lead to a viscous, nonvolatile residue that is assimilated by the environment with difficulty.

Biological degradation has been extensively studied [8], and is slow because petroleum is toxic and contains many poorly metabolizable components. Weathered petroleum presents a small interface between hydrophobic petroleum globules or film and the aqueous medium needed by microorganisms. Although petroleum provides a carbon source for microorganisms, it does not supply other nutrients such as nitrogen and phosphorus which are also needed. In tropical nutrient depleted seawater this lack of secondary nutrients can severely reduce the rate of biological degradation [9].

Chemical transformations are also known to occur [10]. Although some of these transformations may be thermal, the major processes are photochemical in nature. Photochemical transformations in petroleum have received much less attention than have biological transformations as they were not initially considered

important [11]. It is now known that photochemical transformations are important [12,13] and in tropical environments can be as important as biological processes [9].

Synergies have been observed between biological and photochemical degradation, in which photochemical transformations oxidize recalcitrant organic components into derivatives which are biologically metabolized [14–17]. Polar oxidized components are generated upon irradiation, even under arctic conditions [18] and these components are more water soluble. As a result, the “solubility” of petroleum in water increases and a heightened toxic effect is observed [10,19–24] due to the higher concentration of organics in the water. The specific toxicity may, however, be about the same [25].

PHOTOCHEMICAL WEATHERING

Published environmental and laboratory studies often do not or cannot separate biological from chemical transformations, and while they report the oil transformation, it is impossible to know what part is photochemical. Controlled laboratory studies have mainly been concerned with distilled fractions of petroleum or model compounds and while valuable, may not represent real environmental transformations. The number of publications in which crude oil films are irradiated with solar or simulated solar light under conditions such that biological transformations are not occurring is very limited.

Water column

Much of the best work has been done on aqueous phase reactions of the water soluble fraction of petroleum, distilled or refined fractions, and model compounds [26]. Although petroleum components have very limited solubility in water, and this work does not directly address oil phase processes which occur in a floating film, it does provide important insights concerning the photochemical processes that transform hydrocarbon contaminants in water. It has been found that natural bodies of water rapidly remove hydrocarbon impurities [27], and this process is partly photochemical [28–29]. Although it has been shown that these soluble components do undergo photochemical oxidation, there is still fragmentary knowledge of the chemical pathways [30].

Since the dissolved hydrocarbon fraction in water (*e.g.* seawater) is essentially transparent to solar light [31], most of these studies have used sensitizers, of which the most used is 9,10-anthraquinone. This compound has been found as

a component in contaminated seawater [32–33], and is thought to be formed by oxidation of anthracene. Studies of saturated hydrocarbon substrates have recently been reviewed [26] and will not be commented here.

It has been found that the irradiation of alkylbenzenes in the presence of anthraquinone gives 1-phenylalkanones, alcohols, and benzaldehyde [34,35]. These same compounds have been isolated from contaminated seawater and a photochemical origin suggested [28,29,33]. Controlled photooxidation of the water soluble fraction of gasoline in the presence of anthraquinone yielded the same reaction products [32]. Irradiation of alkylnaphthalenes in the presence of oil or a singlet oxygen sensitizer also gave polar oxidation products including alcohols, aldehydes, acids, and quinones [36]. When no sensitizer was added, oxidation was slower but still observed. Anthracene absorbs solar light and is photooxidized to the 9,10-endoperoxide [37] and anthraquinone [17,37]. Interestingly, the anthraquinone is more readily biodegraded than is anthracene [17]. It has been found that a series of other polyaromatic hydrocarbons, including benzo(*a*)pyrene, are also photochemically oxidized [38,39]. It has also been shown that benzothiophene is rapidly photooxidized in seawater [40], and the observed products indicate that the initially formed products are also photo-reactive [40]. The benzothiophene and dibenzothiophene fractions of petroleum are rapidly oxidized following an oil spill [41–43], and the products are more water soluble and toxic than the original thiophenes [41,44]. In this case photochemical reactions may be responsible for the initial loss [41–43] and further reaction in the water phase.

Oil film photochemistry

Most of the published work on the photochemistry of oil films has been concerned with the observation of physical and chemical alterations in the oil. Although there is some speculation as to the photochemical processes involved, little mechanistic work has been done.

Analysis of the existing results is complicated because different studies have employed crude oils with varying compositions, and have used differing irradiation conditions and analytical methods. As a result, the conclusions are often divergent. Considering this state of affairs and the need for more information on the photochemical transformations in petroleum, we decided to study a single well-characterized crude petroleum under tropical solar conditions so that data from different experiments could be compared. The study would then be

expanded to compare these results with those from other crudes under the same experimental conditions. The following sections indicate what is known and compare our results with those of the literature.

PHYSICAL AND CHEMICAL TRANSFORMATIONS

Bulk composition

It is generally observed that oil weathering leads to the formation of more polar oxygenated functions such as alcohols, ketones and acids. These changes could be caused by photochemical and biological processes. As an example, weathered oil from the Ixtoc 1 oil spill (78 days environmental exposure) caused an increase in the polar fraction from an initial 8% to 20–30% in the weathered samples [45].

In controlled laboratory experiments [46], no increase in polar components in the floating oil could be detected using Prudhoe Bay crude even after four months. Here biological processes could not be excluded. In an experiment using Ekofisk Crude and a dispersing detergent, the oil film did not accumulate polar components [47], whereas a two-week exposure without dispersant did result in increased oxygen content [18]. A 70-day exposure of light Arabian crude generated measurable changes in the floating oil including the formation of IR absorbing polar components [48]. Here again biological effects could not be discounted. A 20-day exposure of membrane absorbed oil in a tropical sea environment also produced easily measurable oxidation of the oil [49]. Here biological and photochemical processes occur simultaneously.

Irradiation of oil films under unnatural conditions also produced an increase in the IR absorption due to the incorporation of oxygen [50] (carbonyl and ether linkages) although the change varied greatly with the oil used. Irradiation of different crude oils under artificial sunlight caused a reduction in the aromatic fraction and an increase in the polar and asphaltenic fractions in each case [51].

Experiments done in our labs, using an intermediate Brazilian crude, demonstrate the dependance on the method of analysis. Irradiation for up to 100 hours (18 days) under natural conditions and the exclusion of biological processes did not show measurable transformations in oil composition as measured by CHN, NMR, or GC–MS analysis [52]. Analysis by IR showed small but measurable formation of carbonyl and ether groups [52]. On the other hand, separation of irradiated oil into its fractions (Table 1) showed that there were easily measurable changes in the composition even after seven days of irradiation. The aliphatic fraction decreased, and the polar and asphaltenic fractions increased [53].

Table 1 Brazilian Crude oil composition initially, after 64 hour weathering without irradiation, and after 64 hour weathering in a solar simulator (64 hours corresponds to 7 days solar exposure)

Sample	Composition (%)		
	Crude oil	Non-irradiated 64 h	Irradiated 64 h
Aliphatics	43	42	33
Aromatics	38	36	33
Polar	14	17	25
Asphaltenes	5	5	9

An increase in the quantity of higher molecular weight polar material had previously been seen when an aromatic rich crude was irradiated for 500 hours with a UV lamp [54]. This paper also reported the loss of low molecular weight components [54]. Carbon dioxide formation [55] and the formation of volatile aldehydes and ketones have also been observed [56], and photochemical processes may be involved in the observed long term weight loss.

Analysis of oil spilled with carbon 14 enriched phenanthrene and hexadecane showed that these compounds were oxidized and incorporated in the asphaltene fraction [57]. Phenanthroic acids are formed when petroleum is weathered by both biological and photochemical processes [58]. Sulfonated carboxylic acids with surfactant activity are also observed when oil is photooxidized [59].

Following an oil spill, it is known that the thiophenes are rapidly oxidized to sulfoxides [41–43] and that irradiation rapidly produces this transformation, although it may not be the only cause [43].

Photochemical transformations most certainly oxidize crude oil. The main questions now are how important is this process in overall oil weathering, and how does it depend on oil composition and environmental conditions.

Water solubility

Irradiation of oil can increase the water soluble material [18,20,25,60] and this water is toxic to many aquatic organisms [18–23,25,41]. This increased toxicity is mainly due to the higher concentration of material, with specific toxicities being about the same as for the non-irradiated soluble fraction of petroleum [18,25]. The most toxic components are hydroperoxides [19,23]. In addition to the hydroperoxides [18,19,23], acids [18,21,23,62], phenols [21,23], ketones [21,46,61], alcohols [18,61], lactones [61], and sulfoxides are found [41,43]. Although some of these compounds are quite toxic, it is unlikely that high enough

concentrations would be formed in the open sea or large bodies of water to cause any effect [55,58]. In salt marches, mangrove swamps, or other shallow bodies of water with limited water movement, the organic concentration in the water could reach a toxic concentration.

We have found that solar irradiation of the intermediate Brazilian crude over seawater rapidly causes a large increase in both absorption and emission [62]. The synchronous excitation/emission spectra (Figure 1) show that with irradiation, emitting components with emission at longer wavelengths are seen, indicating that higher molecular weight species with water solubility are being formed.

Emmulscibility

Mousse formation is an important process in petroleum weathering because the water-in-oil emulsion is of high viscosity, the mousse has a high adherence to

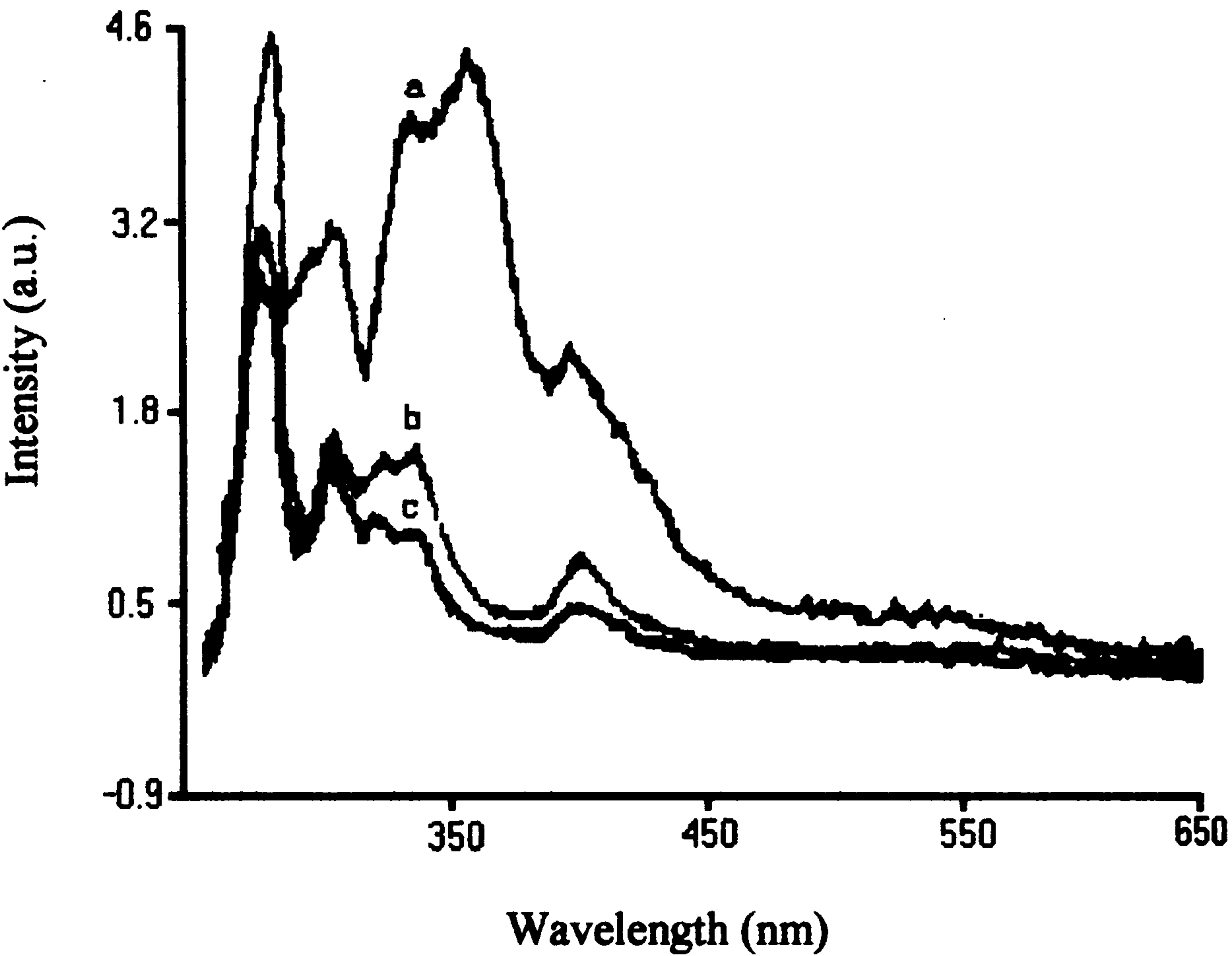


Figure 1 Synchronous fluorescence spectra of the aqueous phase of a film of Brazilian petroleum irradiated with sunlight for 8 hours: (a) irradiated; (b) in contact for 8 hours but not irradiated; and (c) in contact for 30 min, not irradiated.

sand and rock, and it is very difficult to treat or remove from the water [7,63]. It is generally understood that mousse formation is related to asphaltene content since these components are most effective in lowering the inter-facial tension and stabilizing the emulsion [10]. It has been found that irradiation of petroleum films causes a rapid decrease in the interfacial tension [35,48,51], and that sometimes mousse formation is only possible following irradiation [7]. It is thought that irradiation generates tenso-active compounds such as carboxylic acids [59] which act to stabilize the emulsion, and increase the concentration of "asphaltenes" [53–54].

With the Brazilian petroleum, 8 hours was sufficient to lower the interfacial tension by half from 25 to 12 mN m⁻¹ (Figure 2) [62]. This oil did not form

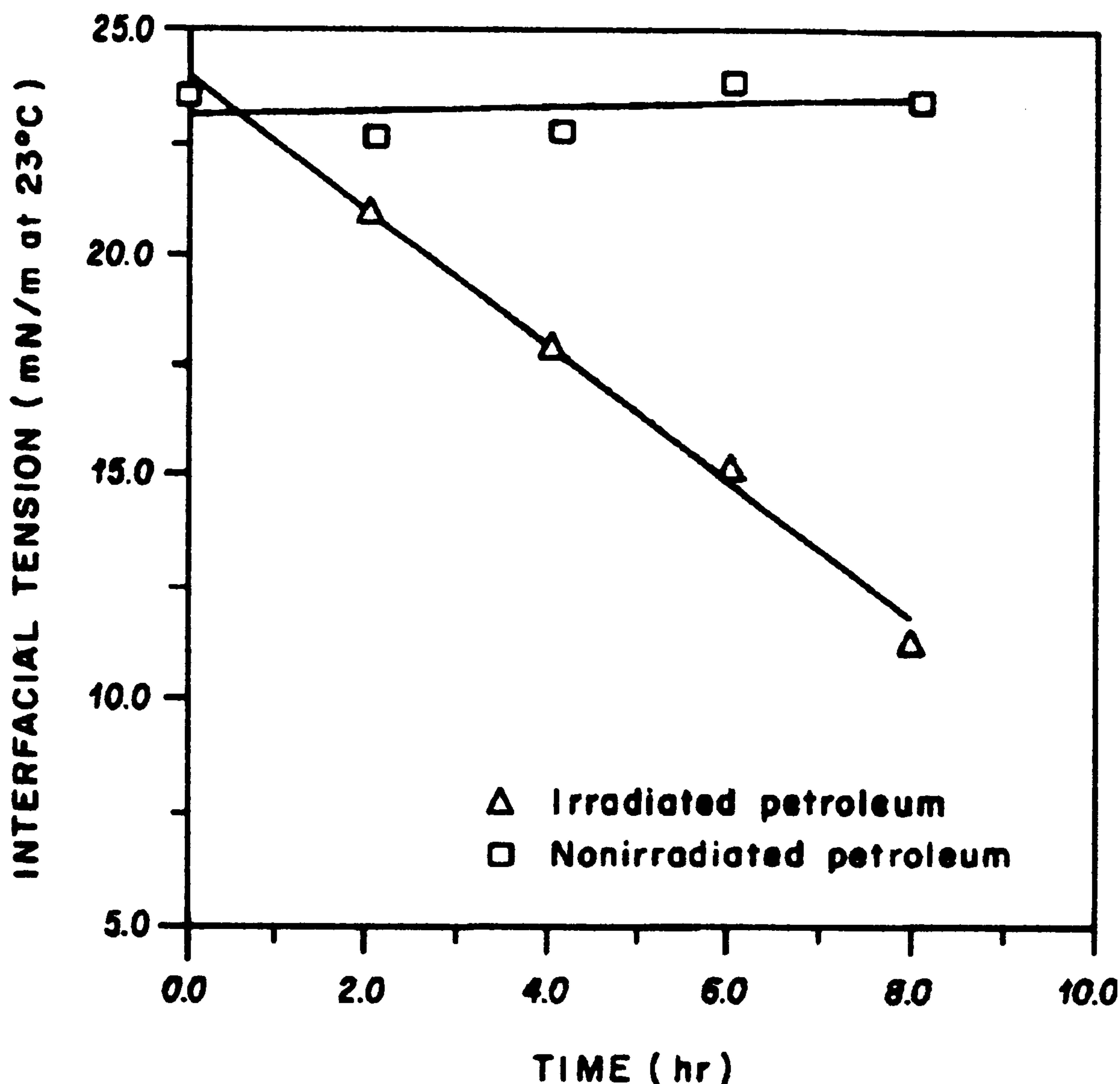


Figure 2 Interfacial tension of a film of Brazilian petroleum as a function of irradiation time using sunlight.

stable oil-in-water emulsions either before or after irradiation. It also did not form a stable water-in-oil emulsion before irradiation but did after only 8 hours of solar exposure.

Viscosity

As oil weathers the viscosity increases. Initially this is due to the evaporation of lower molecular weight low viscosity components. The effect of photochemical transformations on viscosity is still in doubt [12,13]. It has been reported that irradiation increases the viscosity [35] for a light crude. It is also indicated that the mean molecular weight decreases [10] which would decrease the viscosity. It has also been reported that the lens diameter of oil on water films can either increase or decrease with irradiation [60]. Lens diameter depends on viscosity and interfacial tension. Since interfacial tension invariably decreases, the observed effect may be caused by changes in viscosity.

In our experiments with the Brazilian crude, short term solar irradiation (8 hours) produced a slight increase in viscosity [62] in relation to an unirradiated blank. This effect was, however, small compared with that due to evaporation.

Fluorescence

All petroleum is fluorescent [6]. This fluorescence is used in prospecting to identify and characterize oil in rock [64] or over water [65]. It is also widely used to locate and follow oil spills [66] and to measure oil pollution in contaminated water [55,67,68]. Due to the large number of fluorescent chromophores, energy transfer, and quenching processes within the petroleum matrix, petroleum fluorescence is dependent on the wavelength of excitation and the concentration [69]. To reduce the complexity of the analysis synchronous excitation – emission fluorescence is often used [70].

Although fluorescence is widely used for petroleum analysis, it has been little used in photochemical studies [15]. In a study of oil dispersed in seawater, it was found that the synchronous fluorescence decreased with irradiation [15].

We have found that, for the petroleum studied, fluorescence is a sensitive indicator of photochemical transformation. A measurable decrease in the synchronous fluorescence is observed after only 2 hours of solar irradiation [62], and the total intensity decreases by more than 60% in 100 hours [52]. We have found

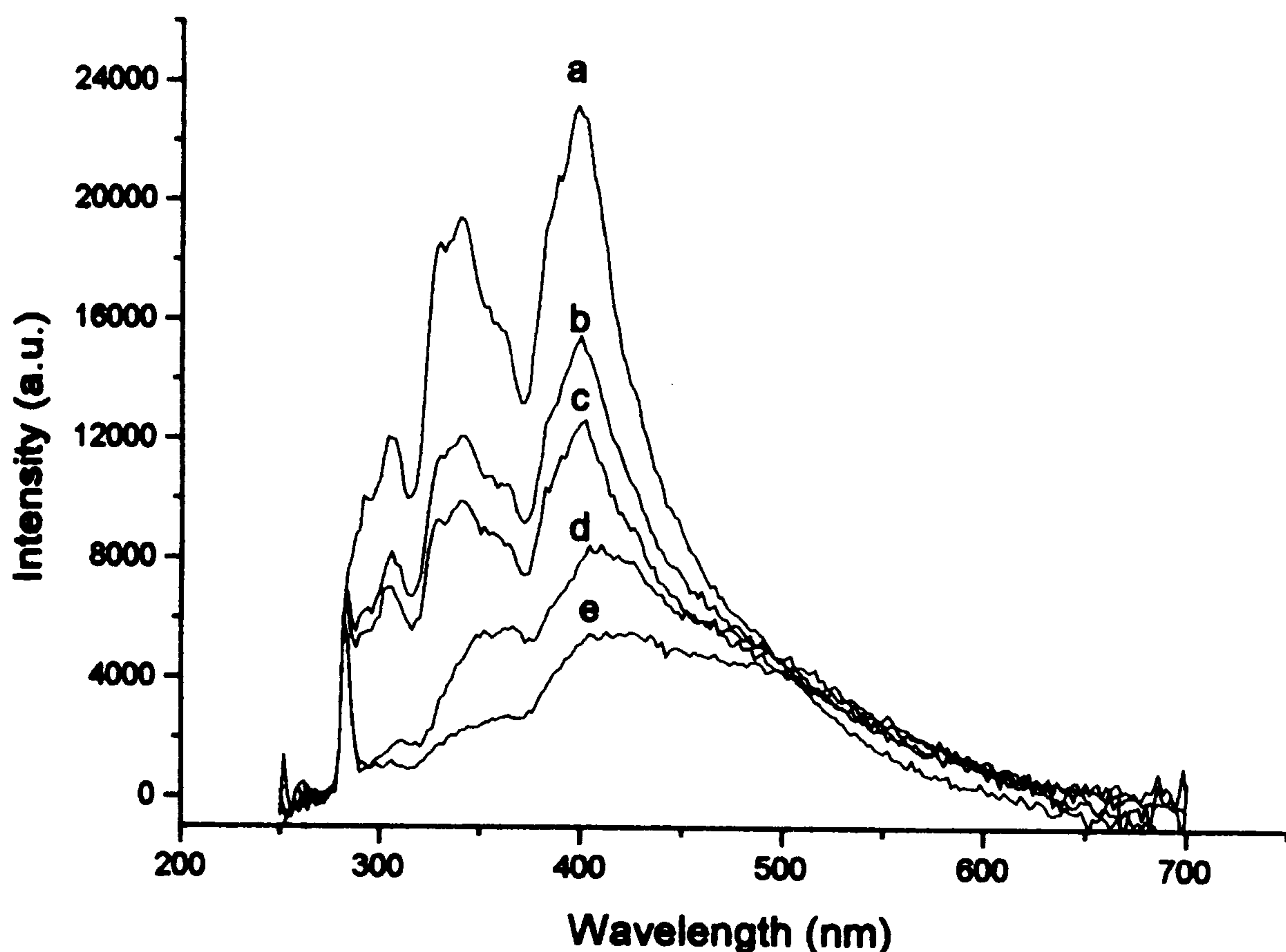


Figure 3 Synchronous fluorescence spectra of a Brazilian petroleum and its fractions: (a) petroleum; (b) maltene; (c) aromatic; (d) polar; and (e) asphaltene.

that the aromatic, polar, and asphaltic fractions are all fluorescent [53] Figure 3. Although the fluorescence intensity decreases proportionately at all wavelengths [52], analysis of fluorescence quantum yields following irradiation for 4 days [71] shows that at short wavelengths (UV) there is a slight reduction in emission intensity. In the 400–500 nm region the quantum yield of emission does not change, and in the red there is a slight increase in the quantum yield. The aromatic fraction absorbs and emits mainly in the UV, the polar fraction has a stronger absorption tail into the visible and more emission in the visible, and the asphaltene fraction is black with absorption into the near IR.

It is now known that for this petroleum there is a photochemical consumption of aromatics and the formation of polars and asphaltenes. If the products of photochemical oxidation are polar and show a larger Stokes shift between absorption and emission, they will give a weak signal when synchronous fluorescence is used, even if the products are still fluorescent. Synchronous fluorescence then “sees” the loss of the relatively non polar components even when the total fluorescence has changed very little.

CAUSES

Although photochemical processes can be important in weathering, the mechanisms by which oil is photochemically transformed are poorly understood. Two basic processes have been proposed [10,12,13,26] in which light absorption initially generates singlet oxygen or free radicals.

Light dependance

It might be expected that the importances of the singlet oxygen and/or free radical mechanisms would depend on the wavelength of absorbed light as longer wavelength visible light photons do not generate excited states with enough energy to break single bonds homolytically and generate free radicals. It has been found that only UV (below 350 nm) light is effective in photodegrading a Libyan Crude distillate [72], but since only the fraction boiling to 310°C was used, most of the components absorbing in the visible would have been removed. In other studies both UV and visible light were effective [42,55].

We found that fluorescence detected photodegradation was induced by either UV or visible light and that when the entire spectrum was present the reaction was faster than with either alone [62].

Free radical oxidations

Free radical reactions involving hydrogen abstraction and the formation of hydroperoxy radicals are commonly used to explain the observed transformations. Irradiation of petroleum results in the oxidation of saturated hydrocarbons with highest reactivity at tertiary carbons [72,73]. The resulting products, alcohols, ketones, aldehydes, acids, and alkenes are also readily explained by invoking hydroperoxide chemistry [26]. It has been found that free radical inhibitors reduce the rate of photochemical degradation [50] and free radical generators such as aromatic ketones [74], quinones [34,56], and naththols [60,75] accelerate it.

We have found that a free radical generating quinone, 9,10-phenanthrenequinone, markedly increases the rate of formation of water soluble products but does not change the rate of fluorescence of the oil film [62]. Depending on which phenomenon is being analyzed, one could conclude that free radical processes are important or not.

The major difficulty with the free radical process is that petroleum does not contain components capable of photochemically generating free radicals. Petroleum and its derivatives are notably lacking in ketones or quinones, further-

more naphthols are poor absorbers of sunlight and present in very low concentration. Although all these are produced by photochemical degradation [17,46,61] of petroleum, they are not initially present.

Free radicals can be generated in water by photochemical electron transfer [37,76] and this mechanism may be important at the oil–water interface, but is unlikely to be operative in the bulk oil or the oil–air interface where most of the light is absorbed due to the low polarity of petroleum. Dibenzothiophenes are normal components of petroleum and are known to be rapidly photooxidized to the corresponding oxides [41,42]. It is known that dibenzothiophene oxide loses oxygen on irradiation [77]. The reaction is suggested to proceed through the formation of atomic oxygen which then abstracts hydrogen from the solvent generating free radicals. It is possible that this mechanism is operating in petroleum films. The dibenzothiophene oxides could then be radical initiators generating alkoxy and peroxy radicals. Once started, free radical processes could then generate other initiators.

Singlet oxygen

Petroleum contains aromatic hydrocarbons known to generate singlet oxygen which is a logical intermediate for the photooxidation of petroleum. It has indeed been found, using indirect methods, that a light diluted maltene fraction of petroleum is a good generator of singlet oxygen [78]. Neat films of maltene were however, very poor singlet oxygen generators [78]. It has also been found that the photooxidation of a refined fuel oil could be retarded by beta-carotene and accelerated by tetraphenylcyclopentadienone, respectively a quencher and sensitizer of singlet oxygen [79].

Experiments using crude have shown that mousse formation can be inhibited by beta-carotene [7]. On the other hand, it was concluded that the photooxidation of crude oil films on glass was caused by free radical mechanisms and that singlet oxygen was not involved [50].

We have found, using direct observation of singlet oxygen emission at 1.27 μm , that dilute samples of various crude oils are good singlet oxygen generators [80]. The quantum yield is wavelength dependant (it is higher at 355 than 532nm) but still appreciable when green light is used. The aromatic fraction is the best sensitizer, the polar fraction is intermediate, and the asphaltene fraction is the worst, but even the asphaltene fraction generates significant singlet oxygen [80]. Some representative quantum yields are shown in Table 2.

Table 2 Quantum yields of singlet oxygen formation (excitation at 355nm) for diluted samples of a Brazilian crude oil and its fractions

Sample	Singlet oxygen quantum yield
Crude oil	0.20
Maltenes	0.28
Aromatics	0.40
Polar	0.31
Asphaltenes	0.19

Undiluted petroleum is a poorer generator, but detection of singlet oxygen emission is still possible, indicating that the quantum yield is not more than an order of magnitude lower [81].

Addition of tetraphenylporphorin, as a singlet oxygen sensitizer, to crude oil films accelerated the sunlight induced loss of fluorescence of the oil film but did not increase the quantity of water soluble material [81].

CONCLUSIONS

It is now known that photochemical processes are important contributors to the environmental weathering of petroleum and its derivatives. These processes can affect oil properties after even short exposure times and have important implications for oil recovery and environmental damage.

The mechanisms involved in the photochemical weathering are still largely speculative. Although free radical processes have been implicated, the nature of the initiator is unknown. Singlet oxygen has also been suggested and is formed when petroleum films are irradiated. The principal components of petroleum are, however, poor chemical quenchers of singlet oxygen and known products of singlet oxygen are not observed. Singlet oxygen is quenched by the aromatic and polar fractions of petroleum at rates indicative of physical quenching with little chemical quenching [82] (table III). The asphaltene fraction is, however, a strong singlet oxygen quencher and some of this may be chemical (Table 3).

The results presented until now show: (1) Obtaining useful and relevant data is possible even when studying such a complex and varying substrate as petroleum. (2) Petroleum photochemical studies are important toward an understanding of petroleum weathering in the environment. (3) There is much to be learned. It is the hope of the authors that this review will stimulate more research in this area.

Table 3 Rate constants for the quenching of singlet oxygen by the fractions of a Brazilian crude petroleum

Fraction	$kq(g^{-1} l s^{-1})/10^2$
Aliphatic	1.5
Aromatic	7.2
Polar	86.6
asphaltene	721.0

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