Effect of the Media on the Quantum Yield of Singlet Oxygen ($O_2(^1\Delta_g)$) Production by 9*H*-Fluoren-9-one: Microheterogeneous Systems

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The quantum yield (Φ_Δ) of singlet oxygen ($O_2(^1\Delta_g)$) production by 9*H*-fluoren-9-one (FLU) is very sensitive to the nature of the solvent (0.02 in a highly polar and protic solvent, such as MeOH, to 1.0 in apolar solvents). This high sensitivity has been used for probing the interaction of FLU with micellar media and microemulsions based on anionic (sodium dodecyl sulfate, SDS; bis-(2-ethylhexyl)sodium sulfosuccinate, AOT), cationic (cetyltrimethylammonium chloride, CTAC) and nonionic (*Triton X-100*, TX) surfactants. Values of Φ_Δ of FLU vary in a wide range (0.05 – 1.0) in both microheterogeneous media and neat solvent, and provide information on the microenvironment of FLU, *i.e.*, on its localization within organized media. In ionic and nonionic micellar media, as well as in four-component microemulsions, FLU is, to various extents, exposed to solvation by the polar and protic components of the microheterogeneous systems (water and/or butan-1-ol) in the micellar interfacial region ($\Phi_\Delta = 0.05 - 0.30$). In contrast, in AOT reverse micelles (consisting of AOT as surfactant, cyclohexane as hydrophobic component, and water), FLU is located in the hydrophobic continuous pseudophase, and is totally separated from the micellar water pools ($\Phi_\Delta \approx 1.0$).

1. Introduction. – Molecular oxygen in its lowest-energy excited singlet state ($O_2(^1\Delta_g)$) has attracted considerable interest during the last decades due to its importance as an oxidizing intermediate in chemistry, biology, medicine, and the environment [1]. Singlet oxygen (denoted as $^1O_2$ below) is most often produced by photosensitization, which implies energy transfer (ET) from the triplet excited state of a light-absorbing molecule (sensitizer, Sens) to dissolved molecular oxygen (*Eqns. 1* and *2*).

$$\text{Sens} \xrightarrow{h\nu} {}^1\text{Sens}^* \xrightarrow{\text{ISC}} {}^3\text{Sens}^* \tag{1}$$

$$^3\text{Sens}^* + {}^3O_2 \xrightarrow{\text{ET}} \text{Sens} + {}^1O_2 \tag{2}$$

Here, the quantum yield of $^1O_2$ production (Φ_Δ) depends on the quantum yield of the triplet-state formation, *i.e.*, of intersystem crossing (ISC; *Eqn. 1*), and on the efficiency of the ET process (*Eqn. 2*). A large variety of substances (*e.g.*, aromatic hydrocarbons and ketones, xanthene dyes, or pigments such as porphyrins, chlorophylls, flavins, and metal complexes) can act as sensitizers in the formation of $^1O_2$ [2]. The efficiency of this process depends on the photophysical properties of the sensitizer, but may also be considerably affected by the nature of the reaction medium. Among aromatic ketones, 1*H*-phenalen-1-one (PN) exhibits a high Φ_Δ value in a variety of solvents and, therefore, is widely used as a reference $^1O_2$ sensitizer [3]. In contrast, previous studies have shown that Φ_Δ of 9*H*-fluoren-9-one (FLU) is considerably influenced by the nature of the solvent, and shows a wide range of variation (<0.1 in highly polar and protic solvents, *e.g.*, MeOH, to 1.0 in alkanes) [4]. Regular trends have been observed in the variation of Φ_Δ of FLU as a function of polarity and proticity of different media. Values of Φ_Δ decrease with increasing solvent polarity and protic character as a consequence of the decrease of the quantum yield of intersystem crossing (Φ_{ISC}) [4][5a–5c]. Values of Φ_{ISC} and Φ_Δ close to unity have been found in apolar solvents (*e.g.*, alkanes), S_1 deactivation to the triplet state being the dominant pathway. In nonprotic solvents of increasing polarity, Φ_{ISC} and, therefore, Φ_Δ decrease due to solvent-induced changes in the energy levels of singlet- and triplet-excited states of FLU [5d][5e]. In polar solvents, S_1 has a dominant π/π^* configuration, and the $T_2(n/\pi^*)$ state has a higher energy than S_1; therefore, ISC to the triplet manifold is not favored[1]). FLU is a poor $^1O_2$ sensitizer in protic solvents because H-bonding considerably increases the rate of internal conversion from S_1, thus lowering both Φ_{ISC} and Φ_Δ to values much smaller than those in nonprotic solvents of similar polarity. A protic solvent quenches the S_1 state of FLU at rates that roughly follow its H-bonding power [5a–5c]. In binary mixtures of alkanes and alcohols, preferential solvation of FLU by the protic solvent *via* H-bonding leads to a fast decrease of Φ_Δ with increasing amounts of alcohol [4]. Nevertheless, the effect of the polarity (nonspecific interactions) is still noticeable: a decreasing trend is observed for both Φ_{ISC} and Φ_Δ when the polarity of the alcohol increases [4][5a–5c].

In this work, we have used the strong solvent sensitivity of Φ_Δ of FLU for probing its interaction with organized media such as micellar systems and microemulsions, which are often used as simple models that mimick cellular environments (*e.g.*, membranes) [6]. Driven by hydrophobic and hydrophilic interactions, surfactants, *i.e.*, amphiphilic molecules composed of a polar or charged head group bound to a long hydrophobic hydrocarbon chain, form micellar aggregates in aqueous solutions when the surfactant concentration exceeds the critical micellar concentration (cmc) [7a]. As a result, hydrophobic compartments (dispersed pseudo-phase) immersed in a continuous aqueous pseudo-phase are created (*Fig. 1,a*). Microemulsions [7b][7c] are transparent isotropic fluids of low viscosity. They spontaneously form by mixing two nonmiscible liquids ('oil', usually a hydrocarbon, and water), a surfactant (ionic or nonionic), and, most frequently, a co-surfactant (typically an alcohol of medium chain length). Depending on the oil/water ratio, microemulsions may consist of oil-rich microdroplets dispersed in a continuous aqueous phase at high water content (so-called *oil-in-water* (O/W) microemulsions) or of microdroplets of water dispersed in an oil-rich continuous phase at high oil content (*water-in-oil* (W/O) microemulsions, also called *reverse* micelles; *Fig. 1,b*). At intermediate ratios of water to oil, bicontinuous structures, consisting of H_2O and oil channels, separated by a flexible monolayer of amphiphile molecules, may form [7c][7d] (*Fig. 1,d*). Three-component (oil, water, surfactant) W/O microemulsions may also be prepared (*Fig. 1,c*). Such microheterogeneous systems represent highly dynamic fluid structures that are capable of dissolving both hydrophobic and hydrophilic organic substances in their different pseudo-phases. This compartmentalization may lead to concentration, polarity, and orientation effects, which have been shown to influence a variety of processes, including

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[1]) The energetically lower-lying T_1 state has a π/π^* configuration.

$^1O_2$ production and reactivity [8]. For investigating the effects of microheterogeneous media on the Φ_Δ of FLU and obtaining information on its location in these systems, we have chosen various types of micellar media and microemulsions based on anionic (sodium dodecyl sulfate, SDS; bis-(2-ethylhexyl)sodium sulfosuccinate, AOT), cationic (cetyltrimethylammonium chloride, CTAC), or nonionic (*Triton X-100*, TX) surfactants (see *Exper. Part*).

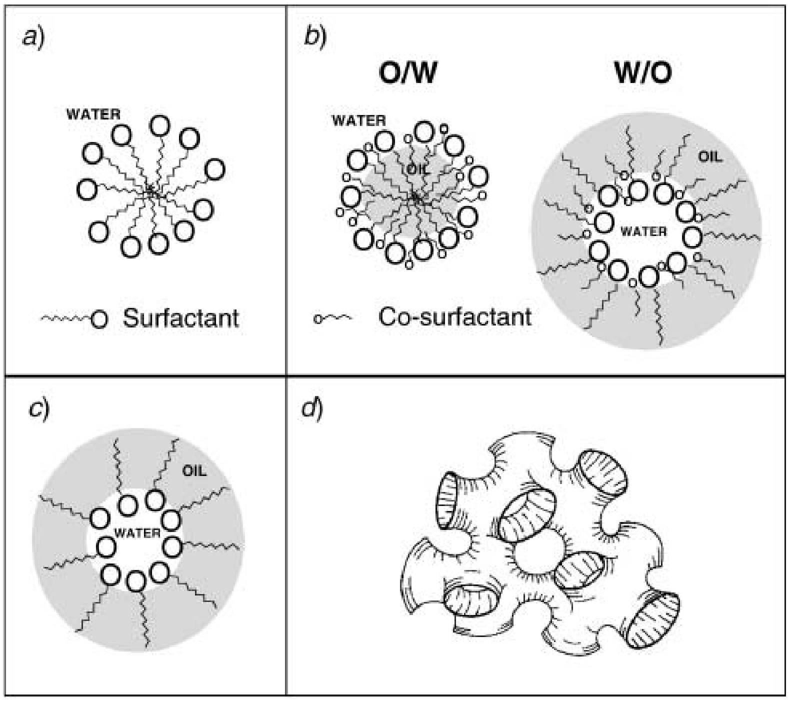


Fig. 1. *Schematic representations of* a) *an ionic micelle*; b) *oil-in-water* (O/W) *and water-in-oil* (W/O) *microemulsions*; c) *a reverse micelle* (may also form in the absence of H_2O); d) *a bicontinuous microemulsion* (ionic surfactant plus oil (hydrocarbon, *e.g.*, cyclohexane). *Figs. 1,a–c* have been taken from [8b], *Fig. 1,d* from [7d]. Nonionic micelles are not represented.

2. Results and Discussion. – 2.1. *Determination of the Quantum Yields of $^1O_2$ Production by Fluorenone in Microheterogeneous Media.*

The determination of the quantum yields of $^1O_2$ production (Φ_Δ) was based on the detection of the near-IR phosphorescence at 1270 nm of $^1O_2$ produced upon continuous excitation of the sensitizer (see *Exper. Part*). The intensity of the $^1O_2$ luminescence signal (S_e) observed during steady-state irradiation of the sensitizer is given by *Eqn. 3*.

$$S_e = CP_a\Phi_\Delta k_e\tau_\Delta \tag{3}$$

C: Proportionality factor, including geometric and electronic characteristics of the detection system, as well as specific parameters of the medium (refractive index, near-IR absorbance); P_a ($= P_0(1-10^{-A})$): rate of absorption of photons by the sensitizer (P_0 and A are the incident photonic rate and the absorbance of the sensitizer at the irradiation wavelength, resp.); k_e: rate constant of $^1O_2$ emission; τ_Δ: $^1O_2$ lifetime in the corresponding medium (the parameters k_e and τ both depend on the nature of the medium [8c][9]).

Quantum-yield determinations based on the above method provide only relative measurements and require the use of a reference sensitizer (R) of known $\Phi_{\Delta,R}$. For determining Φ_Δ of the probe sensitizer, *Eqn. 4* (derived from *Eqn. 3*) may be used [8d][10]:

$$\Phi_\Delta/\Phi_{\Delta,R} = (S_e/S_{e,R})(P_{0,R}/P_0) \tag{4}$$

Eqn. 4 holds only when the following conditions are met: *1*) the luminescence signals produced by the probe (S_e) and by the reference ($S_{e,R}$) are measured in the same medium; *2*) solutions of probe and reference are optically matched at the wavelength(s) of irradiation (λ and λ_R), so that the absorption factor ($1-10^{-A}$) remains unchanged ($P_{a,R}/P_a = P_{0,R}/P_0$) and the factor C remains constant; *3*) the $^1O_2$ lifetime τ_Δ is not affected by the nature or the concentration of the sensitizer. The $^1O_2$ lifetime τ_Δ in a sensitizer solution may be expressed by *Eqn. 5:*

$$\tau_\Delta = 1/(k_d + k_e + k_{sens}\,[\text{Sens}]) \tag{5}$$

k_d: Pseudo-monomolecular rate constant (s^{-1}) of $^1O_2$ deactivation by the medium; $k_e \ll k_d$ in the investigated media [8c]; k_{sens}: bimolecular rate constant (l mol^{-1} s^{-1}) of $^1O_2$ quenching by the sensitizer.

Eqn. 4 is valid only under conditions where $^1O_2$ quenching by the probe, as well as by the reference, is negligible compared with $^1O_2$ deactivation by the medium ($k_{sens}[\text{Sens}] \ll k_d$, and $\tau_\Delta = 1/k_d$ (*Eqn. 5*)). In this work, ^{1}H-phenalen-1-one (PN) and rose bengal (RB) were used as standards for determining the Φ_Δ values of FLU in the selected media. As shown previously [8a–d], quenching of $^1O_2$ by RB or PN in micellar media and microemulsions is negligible compared to $^1O_2$ deactivation by the media. Similarly, no significant $^1O_2$ quenching by FLU occurred under the experimental conditions used in this work. Within experimental error, the value of τ_Δ in a given microheterogeneous system (measured by time-resolved $^1O_2$ phosphorescence) remained constant in the range of FLU concentrations (2–4 mM), and, as in neat solvents [4], no differences were observed between FLU, PN, or RB solutions.

Absorption spectra recorded for RB and PN in micellar media and microemulsions have shown that these sensitizers are predominantly located in interfacial regions [8d]. The absorption spectrum of FLU is only slightly affected by solvent polarity [4], and does not give a clear indication of its location in microheterogeneous systems. Note that τ_Δ values in the organized media investigated ($\tau_\Delta = 12-43$ μs [8c]) are independent of the location where $^1O_2$ is generated, since equilibration of $^1O_2$ between the pseudophases is very fast in comparison to $^1O_2$ decay.

The value of Φ_Δ of RB shows little variation in polar protic solvents, where the probe is readily soluble, and we have shown that the value in MeOH (0.76) is retained in micellar media and microemulsions [8d]. PN has a Φ_Δ value close to unity in the solvents used for the preparation of the microheterogeneous systems (*e.g.*, 0.97, 1.0, and 0.98 in water, BuOH, and cyclohexane, resp.). An average value of $\Phi_\Delta = 0.98$ was used in this work [3][8d]. Both FLU and PN were irradiated at 367 nm. Under these conditions, the $^1O_2$ luminescence signals are directly proportional to the Φ_Δ values of the sensitizers ($S_e/S_{e,R} = \Phi_\Delta/\Phi_{\Delta,R}$; *Eqn. 4*), and the experimental error is minimized. When RB was employed as a reference ($\lambda_R = 547$ nm), corrections for the different incident photonic rates at 367 and 547 nm had to be made (see *Exper. Part*). Values of Φ_Δ for FLU, determined in the selected microheterogeneous systems and in the solvents used for their formulation, are listed in *Table 1*.

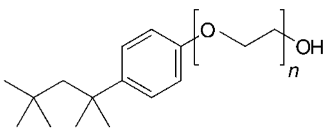
Table 1. *Quantum Yields of* $^1O_2$ *Production* (Φ_Δ) *by* 9H-*Fluoeren-9-one* (FLU) *in Different Types of Media*. Abbreviations: SDS, sodium dodecyl sulfate; CTAC, cetyltrimethylammonium chloride; TX, *Triton X-100* (see chemical formula below). Microheterogeneous systems prepared with H_2O unless indicated otherwise.

Medium Type	Conditions	Φ_Δ[a])
Micellar solution[b])	SDS (0.47M)	0.05
	CTAC (0.34M)	0.07
	TX (0.47M)	0.19
SDS Microemulsions[b])[c])	*A:* 23% D_2O	0.22
	B: 39% D_2O	0.13
	C: 55% D_2O	0.11
AOT Reverse Micelle	$\omega = [H_2O]/[AOT]$	
	0	0.99
	1	0.96
	4	0.98
	15	0.97
O/W Microemulsions[b])[c])	SDS	0.08
	CTAC	0.10
	TX	0.17
W/O Microemulsions[c])	SDS	0.27
	CTAC	0.30
	TX	0.25
Solvent	H_2O/D_2O	[d])
	BuOH	0.08[e])
	Cyclohexane	1.00[e])
	TX (neat)	0.48

[a]) Reference sensitizers: both rose bengal (RB; $\Phi_\Delta = 0.76$) and 1*H*-phenalen-1-one (PN; $\Phi_\Delta = 0.98$), except in AOT reverse micellles (PN; $\omega \leq 4$); error: ±0.04. [b]) Prepared with D_2O. [c]) With H_2O; for preparation, see *Table 2* and *Fig. 4*. [d]) Not determined, since FLU is not soluble enough in H_2O/D_2O. [e]) Determined in previous work [4].

2.2. *Comparison of Quantum Yields of* $^1O_2$ *Production*. As shown in *Table 1*, values of Φ_Δ of FLU in organized media vary strongly (from 0.05 up to 1.0). FLU is nearly insoluble in water. Its solubility is limited in ionic micellar media, where the volume fraction of the dispersed pseudo-phase (surfactant hydrophobic tails; *Fig. 1,a*) is relatively small (*ca.* 12%, calculated from the partial molar volumes for SDS and CTAC micelles of 246.7 and 365.4 ml/mol, resp, [11]). The local concentration of FLU in the hydrophobic micellar cores is, therefore, more than eight-times higher than its overall concentration. Values of Φ_Δ in ionic micelles are comparable to those in polar alcohols (≤ 0.07) [4]. These results may be rationalized by the efficient formation of H(D)-bonds between FLU and $H_2O(D_2O)$ molecules at the charged micellar interface. As indicated in the *Introduction*, H-bonding induces an important decrease of Φ_Δ, and efficient solvation of FLU by H_2O was observed previously in MeCN/H_2O mixtures [4]. In the micelles, the polar carbonyl group of FLU is most probably oriented towards the ionic heads of the surfactant in the interfacial *Stern* region, as observed for other ketones [12].

FLU is readily dissolved in nonionic TX micelles that have a larger micellar volume fraction (27.5% at a concentration of 0.47M of TX) than *ionic* micelles.



TX molecule(s): $n = 9$ or 10

The TX molecule consists of a hydrophobic tail (Ph group with an octyl chain) and an extended hydrophilic ethyleneglycol part, with the OH end group being in contact with the aqueous continuous pseudo-phase upon micelle formation. The value of Φ_Δ (0.19; *Table 1*) for FLU in TX micelles is much higher than in ionic micelles, which indicates that the contribution of solvation by H-bonding is less-pronounced in the former system. However, a Φ_Δ value of 0.19 shows that FLU is not predominantly located in the hydrophobic inner core of the TX micelles, but interacts with the hydrophilic part of the surfactant in the vicinity of the interfacial region. It should be noted that TX is a viscous liquid in which FLU is soluble, and that Φ_Δ of FLU in neat TX reaches a value of 0.48. Therefore, FLU is, on average, more exposed to the hydrophilic part of the surfactant in the more-restricted volume of the TX micelles than in neat TX.

In O/W four-component microemulsions, values of Φ_Δ were similar to those found in micellar media based on the same surfactant (*Table 1*), although the volume fraction of the dispersed hydrophobic phase was larger due to the presence of cyclohexane in the 'swollen micelles' (*Fig. 1,b*). However, these systems contain BuOH as a co-surfactant, which decreases the interfacial tension between the hydrophilic (water) and hydrophobic (cyclohexane) pseudo-phases, and is mainly located in the micellar interfacial region, its OH group being oriented towards the surfactant polar heads [7c][13]. FLU is soluble in alcohols, and, therefore, interacts with BuOH *via* H-bonds, leading to values of Φ_Δ practically equal to those in BuOH (0.08 and 0.10 in anionic and cationic O/W microemulsions, resp., see *Table 1*). As observed in micellar media, FLU exhibits a higher Φ_Δ value (0.17) in the TX-O/W microemulsion than in the ionic ones, which confirms that FLU is (on average) distributed in a less polar/protic microenvironment in TX systems.

In W/O four-component microemulsions, where the continuous bulk pseudo-phase is hydrophobic (surfactant tails in cyclohexane), Φ_Δ values (0.25–0.30) are higher than in O/W microemulsions. However, FLU is still located in a microenvironment where the interactions with the polar and protic components of the organized media occur (*e.g.*, interfacial region), albeit to a lesser extent. In fact, Φ_Δ values are similar to those observed in mixtures of 20–25% of BuOH in cyclohexane [4], independently of the nature of the surfactant. Since these two solvents are miscible, some BuOH may also be present in the continuous pseudo-phase. Therefore, in W/O microemulsions, FLU is probably distributed between the continuous organic pseudo-phase and the interfacial region (where BuOH is mainly located). Moreover, interactions of FLU with H_2O molecules cannot be excluded: when the amount of H_2O is increased (*Table 2*), Φ_Δ values decrease significantly (*Table 1*).

Table 2. *Composition of Microemulsions.* All values are given in weight-%; see also *Figs. 1* and *4*.

Microemulsion	Surfactant	BuOH	Water[a])	Cyclohexane
W/O	8[b])	16	7	69
O/W	8[c])	16	72	4
O/W	28[d])	7	62	3
A: SDS (23% D_2O)	10	20	23	47
B: SDS (29% D_2O)	10	20	39	31
C: SDS (55% D_2O)	10	20	55	15

[a]) H_2O or D_2O. [b]) SDS, CTAC, or TX. [c]) SDS or CTAC. [d]) TX only.

Interestingly, in AOT reverse micelles (three-component W/O microemulsions; *Fig. 1, c*) that do not contain BuOH, Φ_Δ values were close to unity (*Table 1*). Within experimental error, Φ_Δ did not depend on the amount of water encapsulated in the inner polar core of the micelles, at least not in the range investigated ($\omega = [H_2O]/[AOT] = 0, 1, 4, 15$). Therefore, this is the only system investigated where FLU is dissolved in the hydrophobic continuous pseudo-phase (cyclohexane), and is separated and protected from the micellar water pools, independently of the water content.

2.3. *Polarity Parameter and Quantum Yields of $^1O_2$ Production by FLU in Micellar Media.* The empirical parameter $E_T(30)$ is a spectrophotometric measure of solvent polarity based on the excitation energy (kcal mol^{-1}) of the negative-solvatochromic indicator '2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenoxide (PBD) [14]. The normalized parameter E_T^N has been used previously to investigate the effects of solvent polarity and proticity on $^1O_2$ production by FLU [4]. In the solvents of interest for this work, E_T^N values are 0.006, 0.494, 0.586, and 1.0 for cyclohexane, TX, BuOH, and water, respectively [4][14b]. PBD may also be used in micellar media to probe the polarity of the microenvironment of the dye in these media [15]. It is shown that PBD is invariably bound to the polar micellar interface and 'senses' changes in polarity resulting from salt addition, counterions, temperature, and surfactant chain length and concentration. The E_T^N values determined in this work as a function of the concentration of CTAC (*Fig. 2*), TX, and SDS are in agreement with literature data reported for cationic (dodecyltriethylammonium bromide, CTAB), nonionic (TX), and ionic (SDS) surfactants [15]. E_T^N values decrease with increasing CTAC (see *Fig. 2*) and TX concentrations (not shown) above their cmc values, the decrease slowing down significantly at higher concentrations[2]).

These changes have been explained by a decrease in the 'hydration' of the interface and, therefore, in the polarity of the probe surroundings when the size of the micelle increases. With the surfactant concentrations used in this work (*Table 1*), the polarity of the probe microenvironment increases from nonionic to cationic to anionic micelles ($E_T^N = 0.656$, 0.689, and 0.831, resp.). It should be noted that the polarity of the

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[2]) These changes are much smaller in the case of SDS.

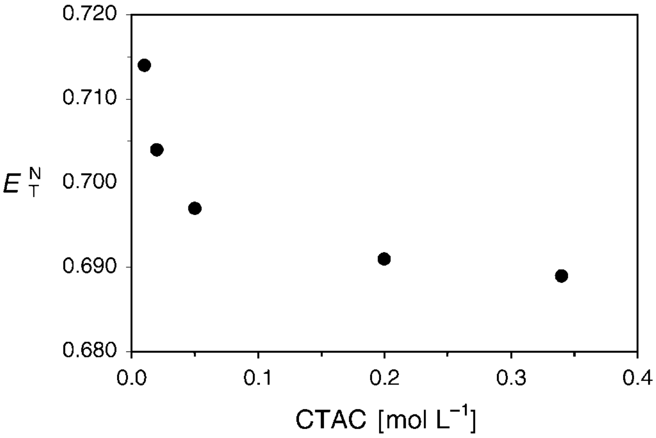

Fig. 2. *Variation of* E_T^N *values measured in a micellar solution as a function of the concentration of the CTAC* (cetyltrimethylammonium chloride) *surfactant*. The solvent polarity values were determined with *Reichardt*'s dye (PBD; see *Exper. Part*) [14a,b].

interfacial region is always higher than that of BuOH ($E_T^N = 0.586$) and lower than that of H_2O ($E_T^N = 1$). No such values could be determined in the four-component microemulsions because PBD is colorless (protonated form) in these media. *Zachariasse et al.* [15a] reported that the polarity of the probe environment measured with PBD in O/W microemulsions at a bulk pH of 9.5 is similar to that of the micelles, in spite of the presence of BuOH as a co-surfactant in the former systems [15a]. However, the microemulsions prepared in this work could not be brought to a pH high enough to favoring the colored PBD form, without breaking down (formation of turbid or biphasic mixtures).

For comparison, *Fig. 3* shows the variation of Φ_Δ of FLU in micellar media and in neat solvents as a function of E_T^N determined in the same media. The solubilization site of FLU may be discussed in comparison with that of the polarity probe PBD. In SDS micelles, the very low value of Φ_Δ of FLU (0.05; *Table 1*) and the high E_T^N value (0.831) measured with PBD indicate that the two probes are in contact with water in the interfacial region. In CTAC micelles, this interaction is less pronounced, both probes being located in a polar, alcohol-like environment, with Φ_Δ (0.07; *Table 1*) and E_T^N (0.689), which is characteristic for polar alcohols [4]. In TX micelles, E_T^N (0.656) is only slightly lower than in CTAC micelles, indicating again a polar alcohol-like microenvironment of PBD (*Fig. 3*). However, Φ_Δ of FLU (0.19; *Table 1*) is almost three-times higher than in CTAC micelles, surprisingly high for such an environment. Therefore, FLU must be located in a less polar and protic microenvironment than PBD in TX micelles, *i.e.*, FLU penetrates deeper into the TX micelle than PBD. It is interesting to note that the Φ_Δ value of FLU (0.48) in neat TX is unexpectedly high, considering that the TX molecule is a primary alcohol. The corresponding data point in *Fig. 3* is situated on the trend line of nonspecific polarity effects, between DMA (dimethylacetamide) and AN (acetonitrile). It appears, therefore, that specific solvation by H-bonding does not dominate the FLU/TX interaction in neat TX.

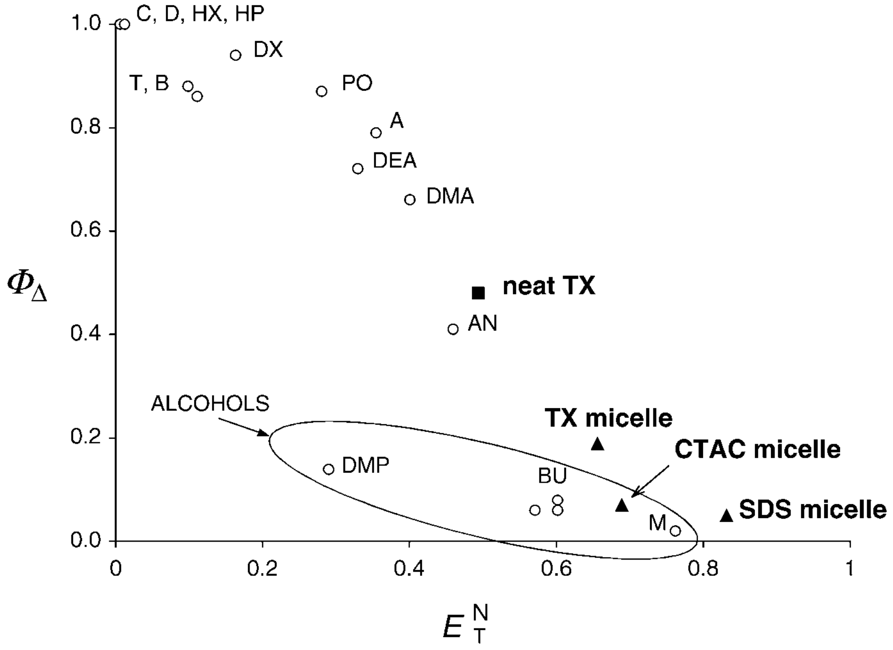

Fig. 3. *Quantum yields of* $^1O_2$ *production* (Φ_Δ) *by 9 H-fluoren-9-one* (FLU) *in solvents of varying polarity* (E_T^N), *as well as in nonionic* (TX), *cationic (CTAC), and anionic* (SDS) *micelles* (triangles). Solvent data were taken from [4]. Abbreviations (left to right): C, cyclohexane; D, dodecane; HX, hexadecane; HP, heptane; B, benzene; T, toluene; DX, 1,4-dioxane; PO, propylene oxide; A, acetone; DMA, *N,N*-dimethylacetamide, DEA, *N,N*-diethylacetamide; AN, acetonitrile; DMP, 2,4-dimethylpentan-3-ol; BU, butan-1-ol; M, methanol; TX, *Triton-X-100.*

3. Conclusions. – The quantum yields of singlet-oxygen production (Φ_Δ) by 9-*H*-fluoren-9-one (FLU) in neat solvents, mixtures of solvents [4], and in microheterogeneous media (this work) are highly dependent on the nature of the media and cover a wide range of values. In this work, we have shown that the high sensitivity of Φ_Δ of FLU to its environment (0.02 in a highly polar, protic solvent to 1.0 in apolar solvents [4]) may be used for probing main solubilization sites in organized media such as micelles and microemulsions. Although FLU is not water-soluble, it is exposed to water molecules in ionic micellar systems (based on SDS and CTAC), as shown by the very low values of Φ_Δ in these media (0.05–0.07). H-Bond formation between FLU and water probably occurs at the interface, where the carbonyl group of FLU is oriented towards the polar heads of the surfactant. In nonionic TX micelles, FLU is exposed to a less polar/protic microenvironment ($\Phi_\Delta = 0.19$) than in ionic systems; nevertheless, the most probable solubilization site of FLU remains the interfacial region formed by the hydrophilic part of the micelle (ethyleneglycol chains of the surfactant), where interactions of FLU with the OH group of TX (and with $H_2O(D_2O)$) may occur. In microemulsions containing BuOH as a co-surfactant, values of Φ_Δ depend largely on the water content. Here, FLU is mainly located in the interfacial region, where most of the co-surfactant (BuOH) is present, and exposure to water increases with increasing water content. Only in AOT reverse micelles (that do not contain BuOH) is FLU dissolved in the hydrophobic continuous pseudo-phase (cyclohexane), and is totally separated from the micellar water pools, which leads to Φ_Δ values of unity within experimental error.

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Experimental Part

General. 9*H*-fluoren-9-one (*Fluka*, *puriss.*) and the reference sensitizers, 1*H*-phenalen-1-one ('perinaphthenone', *Merck*) and rose bengal (*Aldrich*, 97%), were purified as described in [4]. *Reichardt*'s dye, '2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide' (PBD) was purchased from *Fluka*. D_2O with an isotopic enrichment of 99.9% was supplied by *Euriso-Top*, *Groupe CEA*, France. H_2O was of triply-distilled quality (*USF Purelab*). The surfactants – sodium dodecyl sulfate (SDS), cetyltrimethylammonium chloride (CTAC), *Triton X-100* (TX) and bis-(2-ethylhexyl)sodium sulfosuccinate (AOT) (*Fluka*, highest purity available) – were used as received for the preparation of the micellar media and the microemulsions. Note that, whereas the ionic surfactants are solids, the nonionic surfactant (TX) is a viscous liquid at r.t. Cyclohexane (*Merck*) and BuOH (*Roth*) for the preparation of the microheterogeneous media were of the highest purity available and not further treated.

Preparation of Micellar Media and Microemulsions. Surfactant solns. contained 0.34 or 0.47M of SDS, CTAC, or TX (cmc: 8.3, 1.4, and 0.26 mM, resp. [6a]): Microemulsions were prepared by mixing the four components – cyclohexane; H_2O or D_2O; SDS, CTAC or TX (as surfactant); and BuOH (co-surfactant) – under continuous stirring at r.t. The microemulsions were stable for several months [16]. The pseudoternary phase diagram, showing the domain of existence of four-component microemulsions based on SDS as surfactant, is depicted in *Fig. 4* [16]. The compositions (in weight-%) of the microemulsions used in this work are given in *Table 2*. Unless indicated otherwise (see below), microemulsions contained the same weight-ratio of surfactant (SDS, CTAC, or TX) to co-surfactant (BuOH) of 1:2, with 8% and 16% of the total weight of surfactant and BuOH, resp. Oil-in-water (O/W) microemulsions contained the highest amount of water (72%) and a low amount of cyclohexane (4%), whereas water-in-oil (W/O) microemulsions had a high content of cyclohexane (69%) and a low content of water (7%). O/W microemulsions formulated with TX [17] could only be obtained with a much higher surfactant/co-surfactant ratio (4:1) [8c]. Bicontinuous anionic SDS microemulsions of various compositions were also prepared for determining the effect of the relative amounts of water and oil on the Φ_Δ value of FLU (microemulsions *A* to *C*, *Table 2*; *Figs. 1,d* and *4*).

In apolar solvents, the AOT surfactant aggregates into reverse micelles (W/O) capable of encapsulating relatively large quantities of water in their inner polar cores and form highly monodisperse solutions. The size of the micelles depends on the molar H_2O/AOT ratio ($\omega = [H_2O]/[AOT]$) [18]. Values of $\omega = 0$, 1, 4, and 15 were used in this work ($[AOT] = 0.1M$), with cyclohexane as the hydrocarbon (oil) phase, as in the four-component microemulsions. All the solns. were clear in the range of the water-to-surfactant ratio used ($1 < \omega < 15$). A schematic representation of micelles and microemulsions is given in *Fig. 1*.

Steady-State $^1O_2$-Phosphorescence Measurements. Quantum yields of $^1O_2$ production (Φ_Δ) were determined by monitoring the weak $^1O_2$ phosphorescence at $\lambda = 1270$ nm upon continuous irradiation of the sensitizer. The home-built equipment used has already been described in detail [10]. Briefly, the sample soln. in a quartz cuvette (1 × 1 cm) was irradiated with a Xe/Hg lamp (1 kW) through a H_2O filter, focusing optics, and a monochromator. The $^1O_2$ luminescence was collected with a mirror, chopped, and, after passing through a focusing lens, a cut-off filter (1000 nm), and an interference filter (1271 nm), was detected at 90° with respect to the incident beam using a cooled (– 78°) Ge photodiode. Since the $^1O_2$ lifetime is higher in D_2O (*ca.* 63 μs) than in H_2O (*ca.* 4 μs) [19], O/W microemulsions and micellar media were prepared with D_2O instead of H_2O to obtain signals of appropriate intensity. All solns. were air-equilibrated, and experiments were performed at 22 ± 1°.

Values of Φ_Δ for FLU in various media were determined rel. to reference sensitizers (R) of known quantum yield ($\Phi_{\Delta,R}$), and calc. according to *Eqn. 4*. In this work, rose bengal (RB) and 1*H*-phenalen-1-one (PN) were employed, with $\Phi_{\Delta,R}$ values of 0.76 and 0.98, resp., in all media investigated. The $^1O_2$ luminescence intensities (S_e) were recorded alternately for solns. of FLU and R at matched absorbances (*ca.* 0.5 and 1.0) at the corresponding irradiation wavelength(s) (367 nm for FLU and PN, 547 nm for RB). Signals were stable during

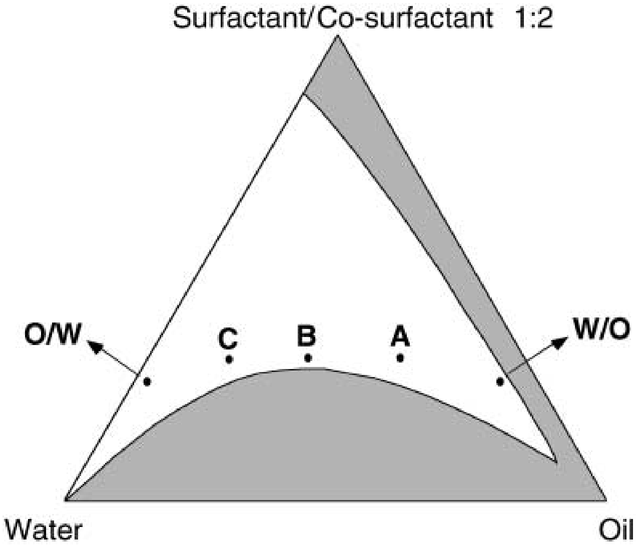

Fig. 4. *Pseudoternary phase diagram* (in weight-%) *of four-component microemulsions based on SDS as surfactant* (co-surfactant: butan-1-ol; oil: cyclohexane) [16]. The apexes correspond to 100% of the component or pseudo-component indicated; microemulsions formulated for this work (O/W, W/O, SDS (*A* – *C*; see *Table 2*) are marked; mixtures in the dark area are either turbid or biphasic.

irradiation time (*ca.* 3 min). The baseline was recorded before and after each irradiation period. The incident radiant power W [mW] on the sample cell was measured with a thermopile and used to calculate rel. incident photonic rates ($P_0/P_{0,R} = (W\lambda)/(W_R\lambda_R)$), where λ and λ_R are the wavelengths of irradiation of the sample and reference solns., resp. Values of incident radiant powers varied from 7.3 ($\pm$0.2) to 8.0 ($\pm$0.2) mW at 367 nm, and from 3.6 ($\pm$0.1) to 4.0 ($\pm$0.1) mW at 547 nm. The exper. results are the average of at least two independent series of measurements. The absorption spectra were recorded on a *Varian Cary 50* spectrophotometer. No change was observed in the spectra of FLU, PN, and RB after irradiation.

Solvent-Polarity Parameters. The $E_T(30)$ parameter, defined as the excitation energy (kcal mol^{-1}) of the solvatochromic indicator '2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenoxide' (PBD) in a particular solvent [14], can be calculated from λ_{max}, corresponding to the intramolecular π/π^* charge-transfer transition (absorption band at the longest wavelength): $E_T(30) = N_A hc/4.18\ \lambda_{max}) = 2.862 \times 10^{-5}/\lambda_{max}$, where N_A is the *Avogadro* number, *h Planck*'s constant (6.6256×10^{-34} J s photon^{-1}), c the speed of light (2.9979×10^8 m s^{-1}), and λ_{max} the maximum absorption wavelength (in nm). The ground and excited states of PBD have a large difference in dipole moments, therefore, the π/π^* transition energy is highly sensitive to solvent polarity. A high $E_T(30)$ value corresponds to a high solvent polarity. $E_T(30)$ values may be normalized to E_T^N values by reference to SiMe$_4$ ($E_T^N = 0$; $E_T(30) = 30.7$ kcal mol^{-1}) and H$_2$O ($E_T^N = 1$; $E_T(30) = 63.1$ kcal mol^{-1}) to avoid the dimension kcal mol^{-1} [14]. In this work, E_T^N values were measured at r.t. in SDS, CTAC, and TX micelles as a function of the conc. of the surfactant.

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