

## PORPHYRIN-QUINONE EXCITED STATE INTERACTIONS IN REVERSED MICELLES†

SÍLVIA M. B. COSTA, M. R. AIRES DE BARROS and J. P. CONDE

*Complexo Interdisciplinar, Centro de Química Estrutural, Instituto Superior Técnico, Avenida Rovisco Pais, 1096 Lisboa-Codex (Portugal)*

(Received August 21, 1984)

### Summary

Excited state charge transfer interactions between zinc tetraphenylporphyrin and anthraquinone 2-sulphonate or duroquinone were studied in reversed micelles of dodecylammonium propionate and benzyldimethyl-*n*-hexadecylammonium chloride (BHDC) as a function of the water content.

The contribution of two spectroscopically different porphyrin species detected in BHDC is discussed in the analysis of the steady state fluorescence quenching kinetics.

---

### 1. Introduction

Molecular aggregates (micelles, vesicles and monolayers) have been used as model systems in view of their chemical potential to mimic some functions of biological organizates [1, 2].

Inverted micelles formed in apolar solvents constitute an alternative approximation to the study of selective compartmentalization effects which can drastically affect the spectroscopic and redox behaviour of solubilized probes [3, 4]. Furthermore, the properties of reversed micelles depend critically on the water content below the maximum hydration number [5].

In this paper we report a study of static and dynamic interactions between a fluorescence probe (zinc tetraphenylporphyrin (ZnTPP)) and quenchers (quinones) in reversed micelles with a variable molar ratio of water to surfactant.

### 2. Experimental details

#### 2.1. Materials

ZnTPP from Hambright, Washington, DC, the sodium salt of anthraquinone 2-sulphonate (AQS) from BDH Chemicals and duroquinone (DQ) from Aldrich Chemicals were used without further purification. Benzyl-

---

†Paper presented at the Xth IUPAC Symposium on Photochemistry, Interlaken, Switzerland, July 22 - 27, 1984.

dimethyl-*n*-hexadecylammonium chloride (BHDC) from BDH Chemicals was dried over  $P_2O_5$  and stored in a vacuum. Dodecylammonium propionate (DAP) was prepared by the method of Kitahara [6] and dried in a vacuum over  $P_2O_5$ . Triton-X-100 (Scintillation grade) from BDH Chemicals was used as received. Sodium diiso-octylsulphosuccinate (Aerosol OT (AOT)) from Fluka and cetyltrimethylammonium bromide (CTAB) from Merck were recrystallized and dried in a vacuum over  $P_2O_5$ .

The solvents heptane and benzene were dried and distilled over sodium wire. Stock solutions of reversed micelles were prepared by adding dropwise the calculated amount of water to the appropriate solutions of BHDC, DAP or AOT in benzene and stirring until the solution became transparent.

## 2.2. Apparatus

The absorption spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer in 1 cm quartz cells. The emission spectra were recorded with an MPF-3 Hitachi Perkin-Elmer spectrofluorometer also in 1 cm quartz cells.

## 3. Results and discussion

### 3.1. Absorption and emission

The absorption and emission properties of ZnTPP in several homogeneous and heterogeneous solvents were studied since the porphyrin can probe the polarity of its microvicinity. In Table 1 are shown the values of  $\lambda_{max}$  corresponding to the  $S_1 \rightarrow S_0$  transitions generally referred to as Q(0,0) and Q(0,1) and values of the emission maxima [7].

In solvents such as heptane, benzene and ethanol, the expected shifts are observed both in the absorption and in the emission maxima in agreement with the polarity and polarizability of these solvents. In anionic reversed micelles of AOT no shift is detected for the homogeneous solvent, indicating that the probe is located in the apolar phase even in the absence of water. However, in cationic reversed micelles of BHDC and DAP pronounced red shifts are detected in the absence of water; these persist in DAP on addition of water but disappear in BHDC.

The data can be interpreted as the consequence of a strong and specific interaction of ZnTPP with the surfactant molecule head groups analogous to those reported by Vogel and coworkers [8, 9] involving the Lewis acid-base-type interactions between metalloporphyrins and nitrogen. The surfactant in benzene may form cylindrical aggregates [10] in which the porphyrin can be stacked, assisted by the benzyl moieties of the surfactant in BHDC.

Indeed in the absence of water the porphyrin emission intensity changes when the surfactant concentration is increased, until it reaches a constant value  $((1.7 - 3) \times 10^{-3} \text{ M})$  which suggests a well-defined critical micellar concentration  $C_{cmc}$  above which pre-micellar aggregates are formed with a characteristic structure and aggregation number. However, the interaction with DAP seems to be effective at very low surfactant concentra-

TABLE 1

Absorption maxima  $\lambda_{\max}(Q(0,0))$  and  $\lambda_{\max}(Q(0,1))$  and emission maxima  $\lambda(I_{f_1})$  and  $\lambda(I_{f_2})$  of zinc tetraphenylporphyrin in different media

Solvent	Absorption		Emission		
	$\lambda_{\max}(Q(0,0))$ (nm)	$\lambda_{\max}(Q(0,1))$ (nm)	$\lambda(I_{f_1})$ (nm)	$\lambda(I_{f_2})$ (nm)	$\lambda(I_{f_1})/\lambda(I_{f_2})$
Heptane	582	544	638	595	1.74
Benzene	588	549	646	597	1.11
Ethanol	596	555	657	601	0.74
Triton-X-100	596	555	655	601	0.65
CTAB	600	560	660	610	0.61
DAP-benzene	603	563	662	610	0.54
DAP-benzene-1 vol.%H <sub>2</sub> O	603	563	662	610	0.54
BHDC-benzene	610	570	668	620	0.46
BHDC-benzene-1 vol.%H <sub>2</sub> O	588	549	646	597	1.11
AOT-benzene	588	549	646	597	1.11
AOT-benzene-1 vol.%H <sub>2</sub> O	588	549	646	597	1.11

tion, implying that it exists before the formation of a molecular aggregate and that the absorption and emission spectra are not sensitive to its formation, whereas in BHDC it is only possible to detect spectral changes on formation of the premicellar aggregate and these are most probably due to its formation.

On addition of water no changes are observed in the absorption and emission spectra of ZnTPP in DAP possibly owing to the fact that the water molecules bind with the three available hydrogen atoms in the ammonium group and therefore the interaction with the polar group is still strong in the presence of water. The situation might be different in BHDC since, whereas in the absence of water the structure of the aggregate may be such that it allows an access of the polar groups near the porphyrin, in the presence of water there is a competition for the surfactant polar groups between the water (bound) and the porphyrin which renders the binding of the porphyrin weaker with a consequent migration of the probe to the non-polar solvent.

Indeed the absorption spectrum obtained in the absence of water changes drastically with the addition of water and in the limit it is identical with that obtained in a homogeneous solution of benzene (Fig. 1). Identical spectral changes are observed when the surfactant concentration is changed from  $10^{-4}$  to  $10^{-1}$  M.

The observation of an isosbestic point implies the existence of two different species of porphyrin, one associated with the interface emitting at  $\lambda = 620$  nm and  $\lambda = 668$  nm and the other corresponding to the free porphyrin in benzene emitting at  $\lambda = 597$  nm and  $\lambda = 646$  nm. Therefore at different molar ratios  $w_0$  of water to BHDC it is possible to follow the displacement of the associated porphyrin by the number of molecules of water per micelle, resulting in a quenching of its emission (Fig. 2).

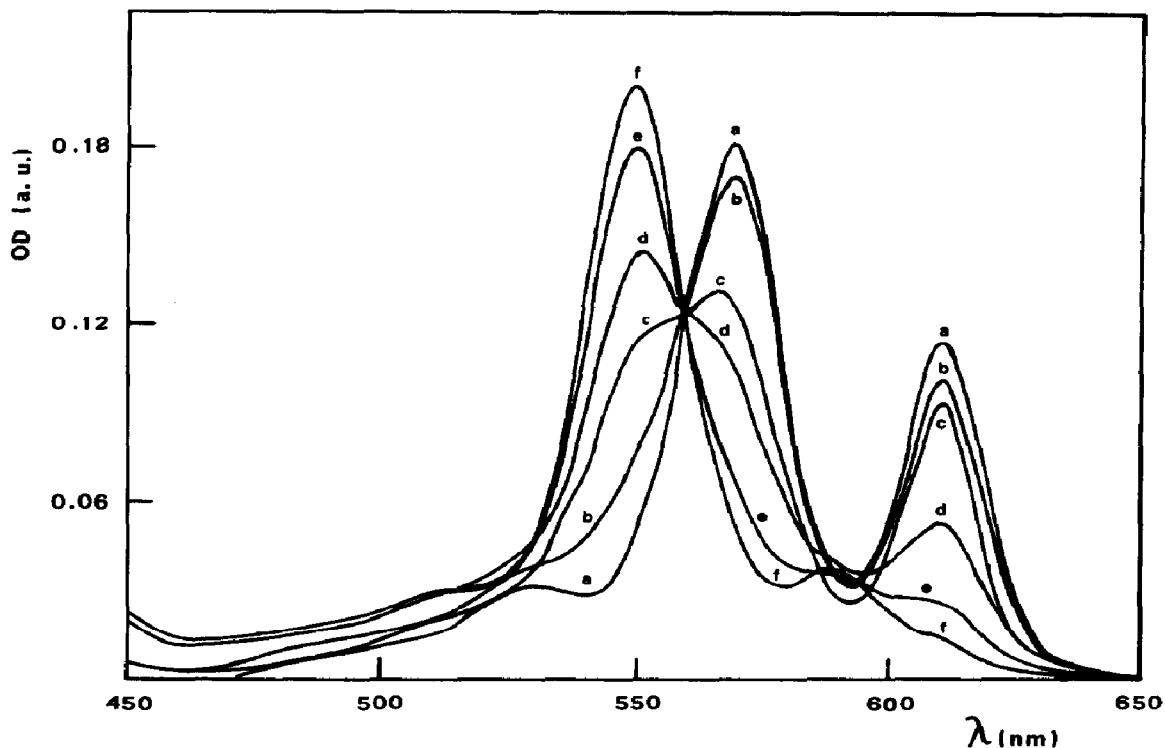


Fig. 1. Absorption spectra of ZnTPP in reversed micelles of BHDC ( $[S] = 0.1$  M) at various  $w_0 = [H_2O]/[S]$  values: curve a,  $w_0 = 0$ ; curve b,  $w_0 = 1$ ; curve c,  $w_0 = 2$ ; curve d,  $w_0 = 3$ ; curve e,  $w_0 = 5$ ; curve f,  $w_0 = 10$ .

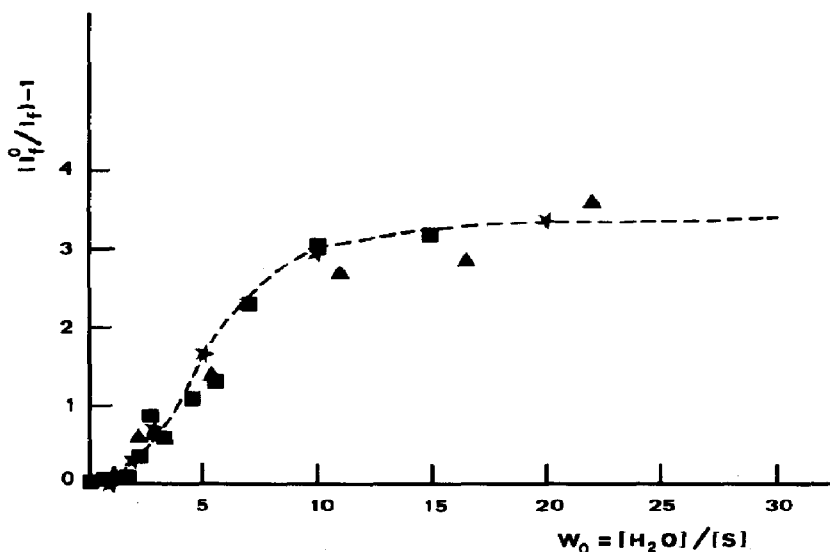
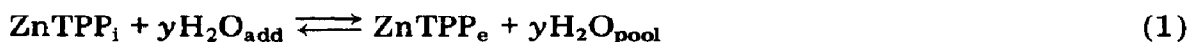


Fig. 2. Effect of the water content  $w_0$  on the fluorescence emission of ZnTPP at 620 nm: ---, calculated curve;  $\star$ ,  $\blacksquare$ ,  $\blacktriangle$ , experimental data ( $\star$ ,  $[S] = 10^{-1}$  M;  $\blacksquare$ ,  $[S] = 5 \times 10^{-2}$  M;  $\blacktriangle$ ,  $[S] = 10^{-2}$  M).

Three regions can be distinguished. At  $w_0 < 2$ , where premicellar aggregates are thermodynamically favourable, the probe and water molecules have a Poisson distribution and the water is bound between the aggregates. A second region at  $2 < w_0 < 10$ , where the content of water is such that the thermodynamically favourable situation is that of reversed micelles of BHDC, is stabilized by the formation of hydrogen bridges between the bound water and the polar surfactant head groups. The addition of water favours the coalescence of premicellar aggregates and hence a change in the porphyrin microenvironment. The water is distributed amongst the aggregates with a Poisson distribution corresponding to that of aggregates with a larger radii. As a result of the additional effect of coalescence there is a clear change in the distribution of the porphyrin towards the organic homogeneous phase.

A third region corresponds to  $w_0 > 10$  where the water added to the interior of micelles forms a pseudophase with bulk microemulsion properties. Here the coalescence of premicellar aggregates is complete and the porphyrin is totally in the organic phase.

Therefore the equilibrium



can be assumed, with an equilibrium constant  $K$  given by

$$K = \frac{[\text{ZnTPP}_e]}{[\text{ZnTPP}_i][\text{H}_2\text{O}]^y} \quad (2)$$

and where the subscripts e and i denote the organic phase and the micelles respectively.

The fraction  $p$  of aggregates given by

$$p = \frac{[\text{ZnTPP}_i]}{[\text{ZnTPP}_t]} = \frac{1}{K[\text{H}_2\text{O}]^y + 1} \quad (3)$$

correlates with  $K$  and  $[\text{H}_2\text{O}]^y$ , where the subscript t denotes the total of organic phase and micelles.

For a given surfactant concentration  $[\text{S}] = 0.1 \text{ M}$  and for  $K = 0.376 \text{ M}^{-1}$ , an empirical distribution function  $p$  of aggregates of ZnTPP with the water content  $w_0$  is obtained with

$$p = \frac{1}{0.0376w_0^3 + 1} \quad w_0 = \frac{[\text{H}_2\text{O}]}{[\text{S}]} \quad (4)$$

which gives an excellent fit to the experimental data shown in Fig. 2, since these data can be adjusted to

$$\begin{aligned} \frac{I_t^0}{I_t} - 1 &= f\{p(w_0)\} \\ &= \frac{I_{t_1}}{I_{t_2} + p(w_0)(I_{t_1} - I_{t_2})} - 1 \end{aligned} \quad (5)$$

where  $I_{f_1}$  and  $I_{f_2}$  are the fluorescence emission intensities at  $\lambda_{em} = 620$  nm ( $\lambda_{exc} = 570$  nm) and at  $\lambda_{em} = 600$  nm ( $\lambda_{exc} = 570$  nm).

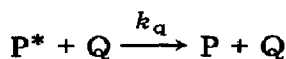
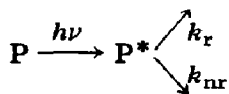
### 3.2. Steady state kinetics

The detection of two species of porphyrin in reversed micelles of BHDC enabled the study of charge transfer interactions with two quinones preferentially located in different environments, such as DQ which is mainly in the apolar organic phase and AQS which, because of its negative charge and solubility, should reside at the interface.

#### 3.2.1. Quenching by duroquinone

The fluorescence emission of ZnTPP is quenched as shown in Fig. 3 for several  $w_0$  values. The results seem to indicate essentially dynamic quenching although there is also a static component due to the quencher molecules which enter the micellar region.

The data can be accounted for using the kinetics scheme



where P represents porphyrin chromophore.

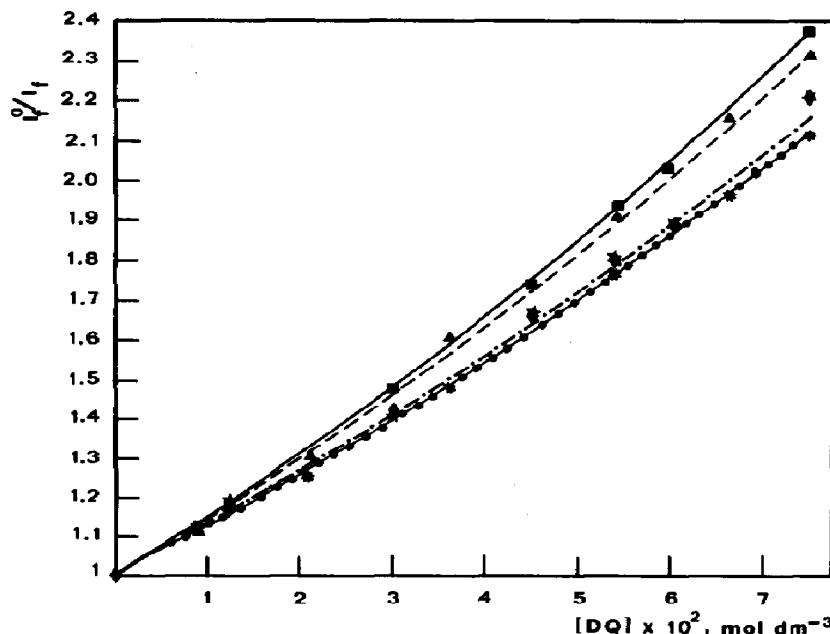
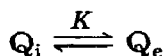


Fig. 3. Fluorescence quenching of ZnTPP by DQ in reversed micelles of BHDC ( $[S] = 5 \times 10^{-2}$  M) at various  $w_0$  values:  $w_0 = 0$  (■, experimental; —, calculated);  $w_0 = 2$  (▲, experimental; ---, calculated);  $w_0 = 5$  (★, experimental; - · -, calculated);  $w_0 = 10$  (◆, experimental; —●—, calculated);  $w_0 = 15$  (\*, experimental; —●—, calculated).



where  $Q_e$  represents the quencher molecules in the organic phase and  $Q_i$  denotes the quencher molecules in the micelle.

This kinetics scheme leads to [11]

$$\frac{I_f^0}{I_f} = (1 + k_q \tau_0 [Q_e]) \exp(\langle q \rangle) \quad (6)$$

where  $\langle q \rangle$  is the average number of quenchers per micelle  $M$ .

Equation (6) can be reduced to

$$\frac{I_f^0}{I_f} = (1 + k_q \tau_0 [Q_i]) \exp(K [Q_i]) \quad (7)$$

since  $K[M] \ll 1$  and  $[Q_e] \approx [Q_i]$ .

The range of  $w_0$  values used covers the three micellar regions referred to above and as shown in Fig. 3 a good fit of the experimental data can be obtained using

$$\frac{I_f^0}{I_f}(w_0) = \left\{ \frac{I_f^0}{I_f}(w_0 = 0) \right\} p(w_0) + \left\{ \frac{I_0}{I_f}(w_0 = 10) \right\} [1 - p(w_0)] \quad (8)$$

where the distribution function  $p$  is taken into account.

The parameters obtained with the quenching data are shown in Table 2. As expected, larger values of  $w_0$  render the interface more hydrophilic thereby reducing the approach of the quencher to the interface. Consequently,  $K$  increases and  $k_q \tau_0$  decreases. It is interesting to note that the quenching data obtained in DAP also show, in contrast with the absorption and emission spectra, the effect of the water content on the Stern-Volmer constant  $K_{SV}$  (Fig. 4). However, as can be seen in Table 3, an inverse trend is observed so that an increase in  $w_0$  decreases the equilibrium constant, which may indicate that the quencher DQ is incorporated into the micelle and  $k_q \tau_0$  increases.

TABLE 2

Effect of water on the Stern-Volmer constant  $K_{SV}$  and the equilibrium constant  $K$  in the system zinc tetraphenylporphyrin- duroquinone in reversed micelles of benzyldimethyl-*n*-hexadecylammonium chloride

$w_0$	$K_{SV}(k_q \tau_0)$ ( $M^{-1}$ )	$K$ ( $M^{-1}$ )
0	11	3.5
2	10.2	3.9
5	9.1	3.6
10	7.8	4.4
15	8.1	4.1

$$w_0 = [H_2O]/[S]; [S] = 5 \times 10^{-2} M.$$

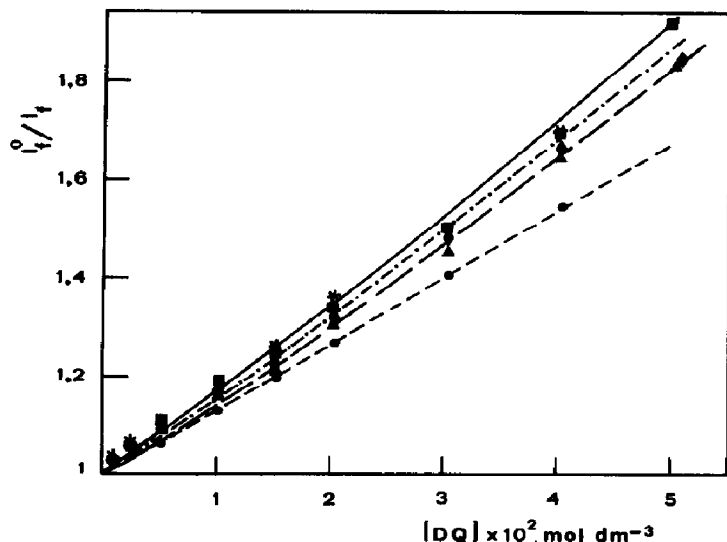


Fig. 4. Fluorescence quenching of ZnTPP by DQ in reversed micelles of DAP ( $[S] = 0.1 \text{ M}$ ) at various  $w_0$  values ( $w_0 = 7.6$  (■, experimental; —, calculated);  $w_0 = 5.5$  (\*, experimental; - · -, calculated);  $w_0 = 2.8$  (◆, experimental; —, calculated);  $w_0 = 0$  (▲, experimental; —, calculated)) and in benzene (●, experimental; ---, calculated).

TABLE 3

Effect of water on the Stern-Volmer constant  $K_{SV}$  and the equilibrium constant  $K$  in the system zinc tetraphenylporphyrin- duroquinone in reversed micelles of dodecylammonium propionate

$w_0$	$K_{SV}(k_q\tau_0)$ ( $\text{M}^{-1}$ )	$K$ ( $\text{M}^{-1}$ )
0	10.2	3.8
2.8	12.75	2.5
5.5	13.8	2.4
7.6	14.6	2.0
	14.2 <sup>a</sup>	—

$w_0 = [\text{H}_2\text{O}]/[S]$ ;  $[S] = 10^{-1} \text{ M}$ .

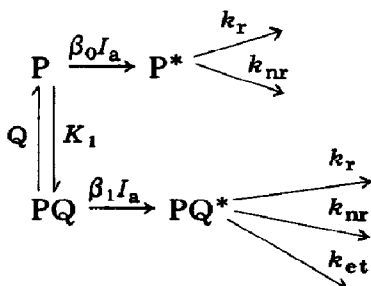
<sup>a</sup> In benzene.

Dynamic quenching experiments are in progress with these systems to obtain true quenching constants  $k_q$ .

### 3.2.2. Quenching by anthraquinone 2-sulphonate

The fluorescence emission of ZnTPP is also quenched by AQS as shown in Fig. 5 at several  $w_0$  values. No dynamic quenching is observed and therefore the results obtained are explained on the basis of ground state complexation which gives rise to static quenching according to the kinetics scheme





with

$$\frac{I_f^0}{I_f} = \frac{[\text{P}^*]^0}{[\text{P}^*] + [\text{PQ}^*]} = \frac{[\text{P}]^0}{[\text{P}]\{1 + K_1[\text{Q}]/(1 + k_{et}\tau_0)\}} \quad (9)$$

where  $K_1$  is the association constant and  $k_{et}$  is the electron transfer rate constant.

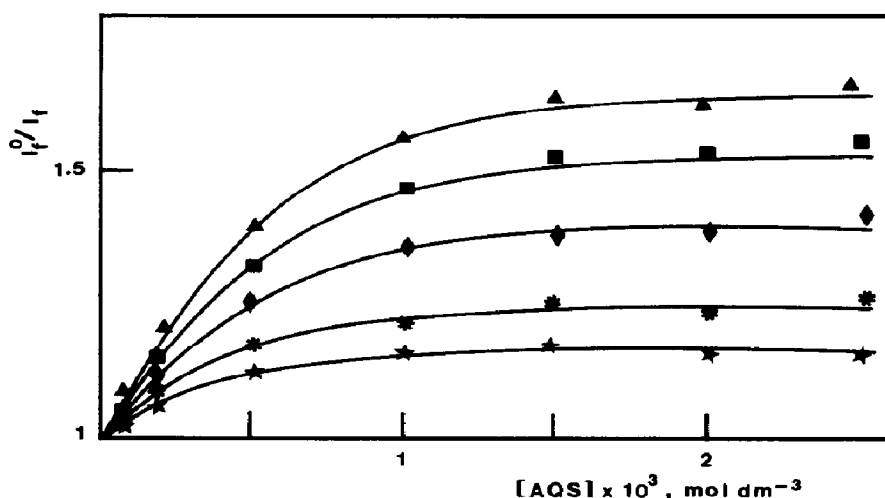


Fig. 5. Fluorescence quenching of ZnTPP by AQS in reversed micelles of BHDC ( $[\text{S}] = 5 \times 10^{-2} \text{ M}$ ) at various  $w_0$  values: —, calculated curves;  $\blacktriangle$ ,  $\blacksquare$ ,  $\blacklozenge$ ,  $\ast$ ,  $\star$ , experimental data ( $\blacktriangle$ ,  $w_0 = 0$ ;  $\blacksquare$ ,  $w_0 = 2$ ;  $\blacklozenge$ ,  $w_0 = 3$ ;  $\ast$ ,  $w_0 = 5$ ;  $\star$ ,  $w_0 = 10$ ).

Equation (9) can be adapted to a heterogeneous micellar medium to give

$$\frac{I_f^0}{I_f} = \frac{[\text{P}]_m^0}{\{(-a + B^{1/2})/2K_1\}[1 + 2K_1[\text{Q}]_m^0/\{2 - a + B^{1/2}(1 + k_{et}\tau_0)\}]} \quad (10)$$

with

$$[\text{P}]_m^0 = \frac{[\text{P}]^0 V^0}{V_m P}$$

$$[\text{Q}]_m^0 = \frac{[\text{Q}]^0 V^0}{V_m} = \frac{i([\text{S}] - C_{\text{CMC}}) V^0}{V_m N_A} \quad (11)$$

where  $N_A$  is the aggregation number and

$$B = a^2 + 4K_1[P]_m^0 \quad a = 1 + K_1([Q]_m^0 - [P]_m^0) \quad (12)$$

$$V_m = V^0([S] - C_{CMC})V_s M \quad (13)$$

where  $V_m$  is the micellar volume,  $V^0$  is the total volume,  $V_s$  is the partial specific volume of the surfactant and  $M$  is the molecular weight of the surfactant.

When a Poisson distribution for the quencher is also taken into account, the fluorescence intensity ratio is given by

$$\frac{I_f^0}{I_f} = \left\{ \sum_{i=0}^{\infty} P_i^q \left( \frac{I_f^0}{I_f} \right)_i^{-1} \right\}^{-1} \quad (14)$$

where  $P_i^q$  is the probability that the micelles contain  $i$  quenchers and  $(I_f/I_f^0)_i$  is the ratio of the fluorescence intensities if every micelle contains  $i$  quenchers.

A good fit of these curves to the experimental data was obtained by adjusting the parameters  $K_1$ ,  $N_A$  and  $k_{et}\tau_0$  which are given in Table 4. A very good fit was also obtained for intermediate values  $0 < w_0 < 10$  with eqn. (8), using  $I_f^0/I_f$  from eqn. (14).

TABLE 4

Effect of water on the association constant  $K_1$ , the aggregation number  $N_A$  and the electron transfer rate constant  $k_{et}$  in the system zinc tetraphenylporphyrin-anthraquinone 2-sulphonate in reversed micelles of benzyldimethyl-*n*-hexadecylammonium chloride

$w_0$	$K_1 \times 10^{-3}$ ( $M^{-1}$ )	$N_A$	$k_{et}\tau_0$
0	2.3	155	0.665
10	6.0	170	0.17

$$w_0 = [H_2O]/[S]; [S] = 5 \times 10^{-2} M.$$

The values of  $K_1$  and  $N_A$  have to be regarded just as orders of magnitude. However, it is clear that the aggregation number in these micelles is much higher than in DAP (30 - 60) [12] or AOT [13] owing to the facts that they have a lesser degree of ionic character and that the polar group is rather sterically hindered.

The experimental data can be compared with the titration curves with an identical "inflection" point in the two extreme situations which imply that the probe is located in nearby regions in the micelle although the emission and absorption spectra suggest an environment with different polarities. Therefore it seems possible to assume that, even at high  $w_0$  values where the porphyrin is located in the hydrophobic region of the micelle, it is still affected by the interface and consequently the quenching mechanism will be identical and only  $k_{et}$  will differ.

The data suggest the following interpretation. The quencher is located essentially at the interface in the region of greater polarity. However, there is an equilibrium between two forms of the porphyrin which is a function of  $p(w_0)$ . This equilibrium is dynamic with a rate of exchange between the two situations, so that at intermediate  $w_0$  values at a given wavelength two perturbed porphyrins (porphyrin-quinone complexes) may contribute to the charge transfer process.

Fluorescence decay measurements of these systems have already confirmed the existence of two components either at  $w_0 = 0$  or at  $w_0 = 10$  and the appearance of a much shorter component at  $[AQS] \geq 2 \times 10^{-2}$  M.

#### 4. Conclusion

The results obtained in this study emphasize the existence of several structures of surfactant assemblies in non-polar solvents [14].

The properties of reversed micelles depend critically on the water content, below the maximum hydration number. The binding of water with the polar surfactant head groups is affected by its ionic character.

The spectroscopic data obtained with BHDC suggest an equilibrium between open premicellar aggregates and reversed micelles with a polar interior which could not be made evident in DAP. The difference in the behaviour is attributed to the steric hindrance of the polar head group and the lack of hydrogen atoms in BHDC.

Two types of porphyrin-quinone interactions were detected in the systems studied.

(a) At the interface only static quenching, possibly due to a perturbed chromophore of the ground state quinone, is observed by means of steady state kinetics.

(b) In the non-polar phase the quenching is mainly dynamic, but it is affected by the distribution of quencher molecules in the micelle, particularly at very low water contents.

Time-resolved fluorescence decay studies in progress have provided evidence for a very fast intramicellar quenching at the interface. Further support for our conclusion, namely the occurrence of a dynamic equilibrium between two species of a solubilized probe to account for a common charge transfer mechanism in both organized assemblies formed in the absence and presence of water, will be reported in a forthcoming paper.

#### Acknowledgment

This work was supported by the Instituto Nacional de Investigação Científica, Portugal.

**References**

- 1 J. K. Thomas, *Acc. Chem. Res.*, **10** (1977) 133.
- 2 J. Fendler, *Acc. Chem. Res.*, **13** (1980) 7.
- 3 M. Wong, J. K. Thomas and M. Grätzel, *J. Am. Chem. Soc.*, **98** (1976) 2391.
- 4 I. Willner, W. E. Ford, J. W. Otewos and M. Calvin, *Nature (London)*, **30** (1979) 823.
- 5 C. A. Martin and L. J. Magid, *J. Phys. Chem.*, **85** (1981) 3938.
- 6 A. Kitahara, *Bull. Chem. Soc. Jpn.*, **28** (1955) 234.
- 7 M. Gouterman, in D. Dolphin (ed.), *The Porphyrins*, Vol. III, Academic Press, New York, 1978, p. 1.
- 8 G. C. Vogel and L. A. Searby, *Inorg. Chem.*, **12** (1973) 936.
- 9 G. C. Vogel and B. A. Beckmann, *Inorg. Chem.*, **15** (1976) 483.
- 10 M. Zulauf and H. F. Eicke, *J. Phys. Chem.*, **83** (1979) 480.
- 11 A. Yekta, M. Aikawa and N. J. Turro, *Chem. Phys. Lett.*, **63** (1979) 543.
- 12 E. Geladé and F. C. De Schryver, *J. Photochem.*, **18** (1982) 223.
- 13 M. Wong, J. K. Thomas and T. Nowak, *J. Am. Chem. Soc.*, **99** (1977) 4730.
- 14 J. C. Russell and D. G. Whitten, *J. Am. Chem. Soc.*, **104** (1982) 5937.