signals of ZnS were observed in either ZnS/Nafion or ZnS·CdS/Nafion. This indicates that the character of the CdS changes in the presence of Zn even though optical absorption measurements are dominated by features due to bulk CdS and ZnS.[3] We speculate that there may be a significant concentration of zinc ions in the CdS lattice. For the sequentially precipitated films, all the results are consistent with a physical mixture of the two sulfides with large interfacial areas of intimate contact. Based on the XRD of single-component films mentioned above, the crystal size of CdS was larger than that of ZnS. Thus, ZnS-(CdS/Nafion) films might have large CdS particles covered with small ZnS particles. For CdS(ZnS/Nafion) similar particle sizes might lead to clusters of small ZnS particles covered with a shell of CdS or to clusters of ZnS particles contacting larger CdS particles. In either case, the contact area would be lower than for the ZnS(CdS/Nafion). This might account for the poor hydrogen generation activity and the relatively small change in the Zn/Cd ratio that occurs with irradiation.

For unknown reasons, Cd^0 was observed in all three kinds of films after irradiation. Cd^0 did not form in single-component CdS/Nafion films. Thus, we conclude that the presence of ZnS is required for Cd^0 production. Gutierrez and Henglein[11] reported that Cd metal catalyzes hydrogen formation on CdS colloids. The presence of Cd^0 does not necessarily produce an active hydrogen generation catalyst since under our conditions irradiated CdS-(ZnS/Nafion) films contain Cd^0 and have very low activity. Consistent with other findings, including high quantum yields for H_2 using a photoelectrochemical cell[12] and strongly quenched luminescence,[13,14] we propose that Zn^{2+} in intimate contact with CdS is crucial. This conclusion is supported by photoelectrochemical measurements[15] showing an enhanced photocurrent in the presence of Zn^{2+} and a more negative value for the CdS flat band potential in the presence of Zn^{2+} and suggests that Zn^{2+} blocks CdS surface states. Since electron-hole recombination rates are sensitive to the presence of surface states, blocking them with Zn could enhance electron-hole pair separation and improve hydrogen generation activity as observed.

It is interesting that both of the high-activity films show similar Zn/Cd ratios (ca. 5) after irradiation (Table I). The Zn/F and Cd/F ratios increase in the relatively inactive CdS(ZnS/Nafion) film but decrease on the active films. At least two explanations are possible: (1) the photoassisted decomposition of the semiconductors or (2) movement of the particles to the interior in the presence of excess Na^+ ions (from the Na_2S solution). The important point is that for the active films the surface Zn/Cd composition changes during irradiation with visible light and reaches a kinetically stable composition which is active for hydrogen generation. This photochemical process occurs in the early stages of irradiation and is correlated with an induction period in the hydrogen generation activity.[1]

Acknowledgment. We acknowledge financial support of this work by the Gas Research Institute (Contract No. 5982-260-0756). National Science Foundation support of the X-ray photoelectron spectrometer by an equipment grant, CHE8201179, is also acknowledged.

Registry No. CdS, 1306-23-6; ZnS, 1314-98-3; H_2S, 7783-06-4; Na_2S, 1313-82-2; Nafion 117, 66796-30-3.

(11) M. Gutierrez and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **87**, 474 (1983).
(12) N. Neumann-Spallart and K. Kalyanasundaram, *Ber. Bunsenges. Phys. Chem.*, **85**, 1117 (1981).
(13) R. Rossetti and L. Brus, *J. Phys. Chem.*, **86**, 4470 (1982).
(14) A. Henglein, *Pure Appl. Chem.*, **86**, 1215 (1984).
(15) M. F. Finlayson, K.-H. Park, N. Kakuta, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber, and J. M. White, to be submitted for publication.

Dynamics of Excited-State Reactions in Reversed Micelles. 2. Proton Transfer Involving Various Fluorescent Probes according to Their Sites of Solubilization

Elisabeth Bardez, Eric Monnier, and Bernard Valeur*

Laboratoire de Chimie Générale,† Conservatoire National des Arts et Métiers, 75003 Paris, France
(Received: May 1, 1985)

Reversed micelles of bis(2-ethylhexyl)sulfosuccinate (AOT) in heptane were investigated with three acid fluorescent probes: 2-naphthol (NOH), sodium 2-naphthol-6-sulfonate (NSOH), and potassium 2-naphthol-6,8-disulfonate (NDSOH). These probes, which tend to undergo protolysis in the excited state, are well suited to the investigation of the acid-base reactivity of water molecules forming the aqueous core. The rate constants for deprotonation and back-recombination were determined by phase fluorometry as a function of the water content $w = [H_2O]/[AOT]$. These rate constants together with the spectroscopic properties of the probes provide information on their localization and the corresponding ability of the microenvironment to accept a proton. (i) NDSOH is localized around the center of the water pool and, at water contents, w, greater than about 10, its behavior regarding protolysis is identical with that in bulk water. (ii) NSOH resides in the vicinity of the interface and an amount of water of $w \sim 40$ is required for observing the same deprotonation rate as in bulk water whereas the rate of back-recombination is still much faster. (iii) NOH is localized at the interface and does not undergo deprotonation in the excited state whatever the water content. Efficiency and kinetics of proton transfer are thus strongly dependent on localization. The ability of water to accept a proton is related to is H-bonded structure and its protolytic reactivity is an image of its structure which changes as a function of the distance with respect to the interface.

Introduction

Owing to their ability to solubilize large amounts of water, reversed micelles offer a peculiar reaction medium, a kind of microreactor which exhibits, in some cases, catalytic effects.[1-3] Reversed micelles are thought to behave as membrane mimetic systems, their water core being similar to water pockets of bioaggregates.[4-6] Moreover, there is some analogy with the active

†Unité associée au CNRS No. 1103 "Physico-chimie Organique Appliquée".

(1) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press: New York, 1975.
(2) J. H. Fendler, *Acc. Chem. Res.*, **9**, 153 (1976).
(3) A. Kitahara, *Adv. Colloid Interface Sci.*, **12**, 109-140 (1980).

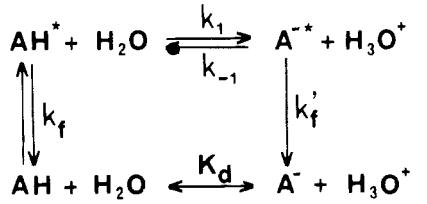
0022-3654/85/2089-5031$01.50/0

sites of enzymes. Furthermore, enzymes solubilized in reversed micelles can act as catalysts of biochemical reactions occurring in the surrounding organic phase.[7-9]

The catalytic properties of reversed micellar media and, in particular, the activity of entrapped enzymes strongly depend on the extent of hydration of the micelles and, consequently, on the solvation structure of reactants in relation to the "acidity" of the water pool as a microsolvent. The peculiar structure of water encased in reversed micelles, in conjunction with its solvation ability and its acid–base reactivity, is of major importance for the understanding of studies on reactivity.

In aqueous solutions, acidity is characterized by pH; the pK of solutes is determined in order to know whether they are in the basic or acidic form at a given pH. In micellar media, many authors suggest a similar approach and consider numerical values of pH and pK determined in an empirical way.[10-17] However, the water of the aqueous core is heterogeneous water whose properties are different from those of bulk water.[18-27] These properties gradually change as a function of the water content and depend on the distance from the polar head layer. It is obvious that this water does not show the same amphiprotonic character as bulk water. For these reasons, we believe that water acidity is best described by the concept of proton-transfer efficiency instead of the classical concept of pH. More precisely, in the protolysis of an acid ($AH + H_2O \rightleftharpoons A^- + H_3O^+$), water molecules act as proton acceptors and the efficiency of proton transfer is characterized by the rate constants for deprotonation and reprotonation. It is to be expected that these rate constants are dependent on the residence site of the acid in the micelle. In the present investigation, special attention is paid to localization effects.

Previous studies allowed analysis of the behavior of water molecules around the center of the water pool of AOT (sodium bis(2-ethylhexyl)sulfosuccinate) reversed micelles in heptane (or isooctane) by using pyranine, a very hydrophilic fluorescent probe.[28,29] In the present work, the same micellar system was investigated by other probes of different hydrophilic properties: 2-naphthol (NOH), sodium 2-naphthol-6-sulfonate (NSOH), and potassium 2-naphthol-6,8-disulfonate (NDSOH). The localization of these probes is expected to be different because the electrostatic repulsion from the anionic heads of the surfactant depends on the number of negative charges of the probe. It will be shown that NDSOH is localized around the center of the water pool whereas NOH resides at the interface and NSOH in the intermediate area. Evidence of these localizations will be provided by the spectroscopic properties of the probes in conjunction with the rates for proton transfer. The proton-transfer reaction that can be studied by fluorescence techniques occurs in the excited state according to the usual kinetic scheme: k_1 and k_{-1} are the rate constants for



deprotonation and back-recombination in the excited state, respectively; k_F and k'_F are the emission rate constants of AH* and A^{-*}: they are equal to the reciprocal of the lifetimes τ_0 and τ'_0 in the absence of an excited-state reaction.

Materials and Methods

Materials. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was obtained from Fluka A.G. and further purified by the procedure described in ref 30 using redistilled *n*-pentane as the extracting solvent.

2-Naphthol (NOH) was purchased from Prolabo and purified by recrystallization in toluene after treatment with activated charcoal.

Sodium 2-naphthol-6-sulfonate (NSOH) and potassium 2-naphthol-6,8-disulfonate (NDSOH) were prepared according to the methods described in ref 31. The structure of these compounds was checked by elemental analysis and ^1H NMR. NDSOH required further attention since the fluorescence lifetimes of the acidic and basic forms were different from those reported by Schulman and co-workers;[32] however, the ^{13}C NMR spectrum compared to data given in ref 33 confirmed the expected structure.[34]

Methods. The absorption spectra were recorded on a Kontron Uvikon 820 spectrophotometer. The corrected emission spectra were obtained on an Aminco SPF 500 spectrofluorometer interfaced to a Kontron PSI 80 microcomputer.

The fluorescence lifetimes and apparent lifetimes were measured on an SLM 4800 phase fluorometer operating at a modulation frequency of 18 MHz. Parasitic effects due to polarization were avoided thanks to a polarizer interposed in the excitation beam and oriented at 35° to the vertical. Appropriate filters or combinations of filters were used for the selection of the fluorescence of the basic form (3–67 Corning filter for NSOH; 2–73 Corning filter for NDSOH) and the acidic form (Balzers interferential filter at 366 nm + UG11 Schott filter for NSOH; Balzers interferential filter at 366 nm + 7–60 Corning filter for NDSOH).

All the experiments were performed at 25 °C using freshly prepared 0.1 M surfactant solutions. The probe concentration was kept below 5×10^{-5} M.

(4) P. P. Luisi, "Biological and Technical Relevance of Reversed Micelles", Plenum, New York, 1983.
(5) C. J. O'Connor, T. D. Lomax, and R. E. Ramage *Adv. Colloid Interface Sci.*, **20**, 21–97 (1984).
(6) J. H. Fendler, *Annu. Rev. Phys. Chem.* **35**, 137 (1984).
(7) F. M. Menger and K. Yamada, *J. Am. Chem. Soc.*, **101**, 6731 (1979).
(8) K. Martinek, A. V. Levashov, N. L. Klyachko, V. I. Pantin, and I. V. Berezin, *Biochim. Biophys. Acta* **657**, 277 (1981).
(9) A. V. Levashov, Y. L. Khmelnitsky, N. L. Klyachko, V. Ya. Chernyak, and K. Martinek, *J. Colloid Interface Sci.*, **88**, 444 (1982).
(10) R. E. Smith and P. L. Luisi, *Helv. Chim. Acta*, **63**, 2302 (1980).
(11) F. M. Menger and G. Saito, *J. Am. Chem. Soc.*, **100**, 4376 (1978).
(12) A. V. Levashov and V. I. Pantin, *Colloid J.*, **41**, 380 (1979).
(13) H. Fujii, T. Kawai, and N. Nishikawa, *Bull. Chem. Soc. Jpn.*, **52**, 2051 (1979).
(14) A. T. Terpko, R. J. Serafin, and M. L. Bucholtz, *J. Colloid Interface Sci.*, **84**, 202 (1981).
(15) O. A. El Seoud, A. M. Chinelatto, and M. R. Shimizu, *J. Colloid Interface Sci.*, **88**, 420 (1982).
(16) H. Fujii, T. Kawai, H. Nishikawa, and G. Ebert, *Colloid Polym. Sci.*, **260**, 697 (1982).
(17) O. A. El Seoud and M. R. Shimizu, *Colloid Polym. Sci.*, **260**, 794 (1982).
(18) M. Wong, J. K. Thomas, and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 2391 (1976).
(19) M. Wong, J. K. Thomas, and T. Nowak, *J. Am. Chem. Soc.*, **99**, 4730 (1977).
(20) F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *J. Am. Chem. Soc.*, **97**, 909 (1975).
(21) F. M. Menger, J. A. Donohue, and R. F. Williams, *J. Am. Chem. Soc.*, **95**, 286 (1973).
(22) G. D. Correll, R. N. Cheser, F. Nome, and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 1254 (1978).
(23) (a) B. Valeur and E. Keh, *J. Phys. Chem.*, **83**, 3305 (1979); (b) E. Keh and B. Valeur, *J. Colloid Interface Sci.*, **79**, 465 (1981).
(24) P. E. Zinsli, *J. Phys. Chem.*, **83**, 3223 (1979).
(25) M. Zulauf and H. F. Eicke, *J. Phys. Chem.*, **83**, 480 (1979).
(26) R. Kubik, H. F. Eicke, and B. Jönsson, *Helv. Chim. Acta*, **65**, 170 (1982).
(27) H. F. Eicke, *Chimia*, **36**, 241 (1982).
(28) E. Bardez, B. T. Goguillon, E. Keh, and B. Valeur, *J. Phys. Chem.*, **88**, 1909 (1984).
(29) M. J. Politi, O. Brandt, and J. H. Fendler, *J. Phys. Chem.*, **89**, 2345 (1985).
(30) J. Rogers and P. A. Winsor, *J. Colloid Interface Sci.*, **30**, 247 (1969).
(31) N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", E. Arnold, London, 1958, pp 261 and 269.
(32) G. Schulman, L. S. Rosenberg, and W. R. Vincent, *J. Am. Chem. Soc.*, **101**, 139 (1979).
(33) P. E. Hansen, *Org. Magn. Reson.*, **3**, 109 (1979).
(34) The assistance of the Institut de Topologie et de Dynamique des systèmes (Prof. J. E. Dubois), Université de Paris 7, is gratefully acknowledged.

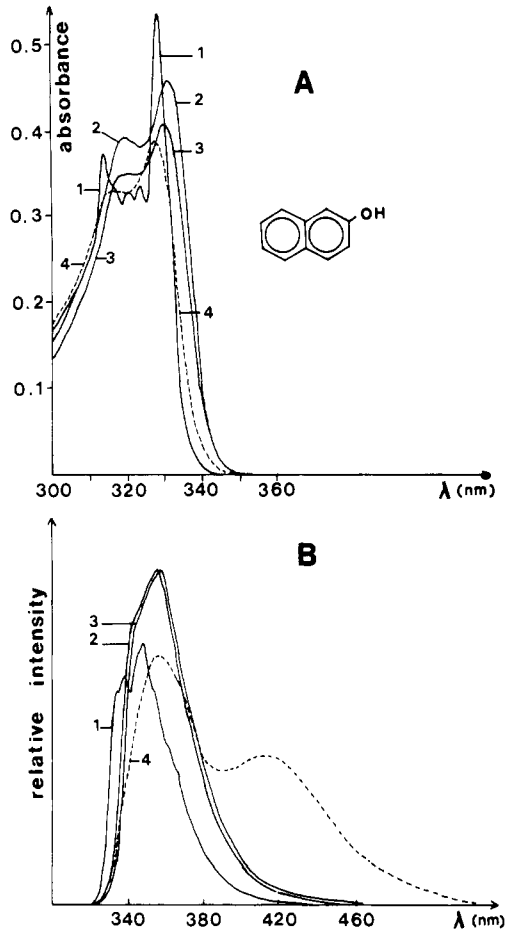


Figure 1. Spectra of 2-naphthol. (A) Absorption spectra: 1, in heptane; 2, in 0.1 M AOT at $w = 0$; 3, in 0.1 M AOT at $w = 42$; 4, in bulk water. (B) Corrected emission spectra ($\lambda_{exc} = 315$ nm): 1, in heptane; 2, in 0.1 M AOT at $w = 0$; 3, in 0.1 M AOT at $w \simeq 10$ to 40; 4, in bulk water.

The principle for the determination of the rate constants k_1 and k_{-1} is described in the first paper of the series.[28] k_1 and k_{-1} are given by

$$k_1 = \frac{\omega^2\tau' + 1/\tau_0 + (1 - \tau'/\tau_0)/\tau_{\Delta\phi}}{\tau'/\tau'_0 - 1} \quad (1)$$

$$k_{-1}[H_3O^+] = 1/\tau_{\Delta\phi} - 1/\tau'_0 \quad (2)$$

where τ and τ' are the apparent lifetimes of the acidic and basic forms, respectively, in the presence of an excited-state reaction. $\tau_{\Delta\phi}$ is an apparent differential lifetime relevant to the phase shift between the emission of the basic form and that of the acidic form (see ref 28 together with the supplementary material of that paper).

For irreversible deprotonation ($k_{-1} = 0$), $\tau_{\Delta\phi}$ should be replaced by τ'_0. Therefore, k_1 is given by

$$k_1 = \frac{\omega^2\tau' + 1/\tau_0 + (1 - \tau'/\tau_0)/\tau'_0}{\tau'/\tau'_0 - 1} \quad (3)$$

Results

The three probes have similar ground-state pK values (9.30,[35] 9.12,[36,37] 9.33[38] for NOH, NSOH, and NDSOH, respectively) and they are much more acidic in the excited state (pK^* = 2.8,[35] 1.66,[36,37] <1, respectively). In the present study, all the probes are thus in the acidic form before excitation, as confirmed by the absorption spectra, and then tend to undergo deprotonation as soon as they are excited. In AOT reversed micelles, the microenvironment of the probes is different from bulk water; the pK^* values given above are thus no longer valid and they depend on the site of solubilization. Therefore, the behaviors of the probes will not be compared in terms of pK^*.

TABLE I: Lifetimes of NSOH and NDSOH in Aqueous and Micellar Solutions

	NSOH	NDSOH
	Aqueous Solutions	
τ_0, ns	6.4[a]	8.4[b]
τ'_0, ns	11.4[c]	12.2[d]
	Micellar Solutions	
τ_0, ns	6.2[e]	6.4[f]
τ'_0, ns	10.7[g]	11.3[h]

[a] In 0.2 M $HClO_4$. The values 6.4 and 6.5 ns have been reported in ref 36a and 39, respectively. [b] In 5 M $HClO_4$. [c] In 0.1 M NaOH. The values 11.2 and 13.5 ns have been reported in ref 36a and 39, respectively. [d] In 0.1 M NaOH. [e] In 0.1 M AOT/heptane; $w = 1.7$ and $w = 2.8$ with 0.2 M $HClO_4$; $\lambda_{exc} = 287$ nm. [f] In 0.1 M AOT/heptane; $w = 2.8$ with 5 M $HClO_4$; $\lambda_{exc} = 310$ nm. [g] In 0.1 M AOT/heptane; $w = 20$ with 0.1 M NaOH; $\lambda_{exc} = 287$ nm. [h] In 0.1 M AOT/heptane; $w = 15$ with 0.1 M NaOH; $\lambda_{exc} = 310$ nm. In order to avoid hydrolysis effects of AOT, the measurements have been done immediately after the addition of acid or base.

2-Naphthol (NOH). As solid AOT is added to a naphthol solution in heptane without additional water, there is a gradual loss of vibrational fine structure of the lowest absorption band with appearance of isosbestic points. This means that the microenvironment of NOH becomes polar and that an equilibrium between free NOH and NOH bound to AOT is established. There is no further change at AOT concentrations greater than 8×10^{-2} M (Figure 1A). When water is added to an 0.1 M AOT solution, the shape of the spectrum is not significantly affected, but the extinction coefficient decreases and a slight blue shift is observed (1.1 nm at $w = 40$). It is noteworthy that, even at large amounts of water ($w \sim 45$), the absorption spectrum does not superimpose the spectrum observed in pure water (Figure 1A). Consequently, the interactions between NOH and AOT are slightly altered by hydration of the polar heads, but NOH is not solubilized in the aqueous core when water is added. Since NOH is not solubilized in heptane either (at AOT concentrations greater than 8×10^{-2} M), it is most likely held in proximity to surfactant polar heads of the reversed micelles.

As noticed for the absorption spectra, the fluorescence spectra in the presence of AOT are very different from those observed in pure heptane (Figure 1B). Moreover, the characteristic band of the basic form NO^{-*} does not appear whatever the water content (up to $w \sim 40$); therefore, no excited-state deprotonation occurs in such a micellar medium whereas the emission band of NO^{-*} appears when NOH is in an aqueous solution, as expected from the pK^* value.

2-Naphthol-6-sulfonate (NSOH). This compound is insoluble in heptane but soluble in water. It can be solubilized in AOT reversed micelles by adding a very small amount of a concentrated solution in water ($w = 0.53$). As water is further added, the adsorption spectrum of NSOH exhibits the same kind of changes as NOH: a decrease in extinction coefficient and a blue shift are observed. This shift is less pronounced beyond $w \sim 10$ (Figure 2A). However, even at a water content of $w \sim 40$, the absorption spectrum of NSOH does not superimpose exactly the spectrum obtained in bulk water.

The emission spectra reflect the competition between emission from the acidic form NSOH* and excited-state deprotonation followed by emission from the basic form NSO^{-*} (Figure 2B): addition of water causes the NSOH* emission band to decrease with a concomitant increase in the NSO^{-*} emission band. It should be noted that, for large amounts of water ($w \sim 50$), emission from the acidic form remains larger and that from the basic form smaller than in bulk water.

The fluorescence lifetimes in the absence of excited-state reaction, τ_0 for the acidic form and τ'_0 for the basic form, in aqueous and micellar solutions, are reported in Table I. The differential

(35) T. Förster, *Z. Elektrochem.*, **54**, 531 (1950).
(36) (a) A. Weller, *Z. Phys. Chem. (Wiesbaden)*, **17**, 224 (1958); (b) A. Weller, *Prog. React. Kinet.*, **1**, 187 (1961).
(37) O. Mäkitie, *Suom. Kemistil. B*, **35**, 1 (1962).
(38) O. Mäkitie, *Suom. Kemistil. B*, **37**, 17 (1964).

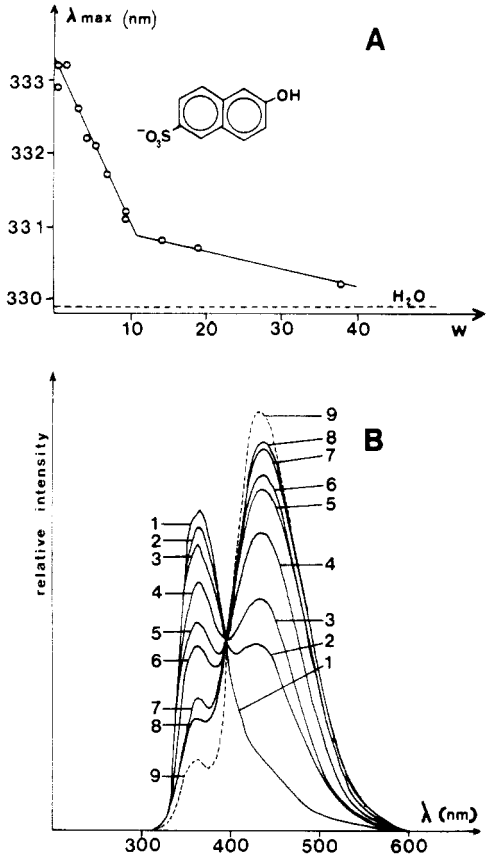


Figure 2. Spectroscopic data for NSOH in 0.1 M AOT/heptane. (A) Variations in absorption maximum wavelength of the lowest band as a function of added water. The dotted line represents the wavelength measured in bulk water. (B) Corrected emission spectra (λ_{exc} = 287 nm): 1, w = 2.7; 2, w = 5.6; 3, w = 6.9; 4, w = 9.5; 5, w = 14.4; 6, w = 19.9; 7, w = 38.3; 8, w = 57.5; 9, in bulk water.

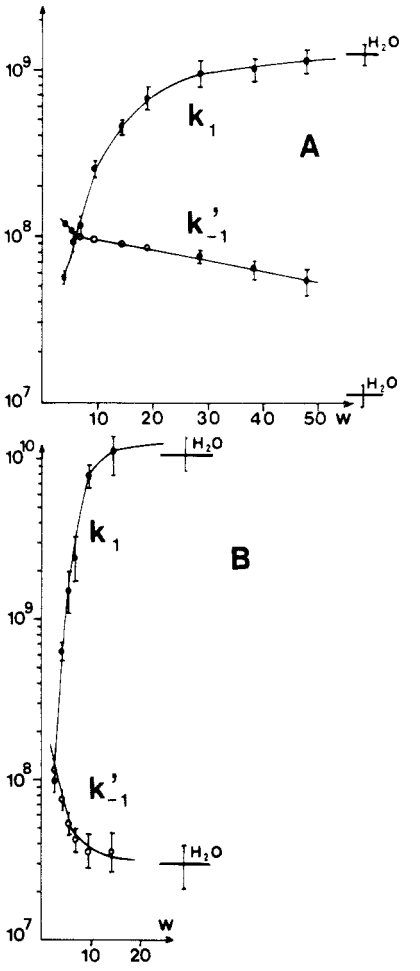


Figure 3. Variations in rate constants (in s^{-1}) of deprotonation (k_1) and back-recombination (k'_1) vs. water content for NSOH (A) and NDSOH (B). For comparison, the values obtained in bulk water are indicated.

lifetimes $\tau_{\Delta\phi}$ and the apparent lifetimes τ' of NSO^{-*} have been measured in AOT solutions as a function of w and in bulk water. These parameters allowed us to calculate the rate constants for deprotonation and back-recombination in the excited state by using the reversible model (see Materials and Methods). The rate constant for back-recombination is expressed as an overall rate constant k'_{-1} instead of $k_{-1}[H_3O^+]$ because this expression is relevant to diffusion-controlled recombination. It will be shown in the discussion that this condition is not fulfilled in the present study. The values of the rate constants are reported in Table II and their variations as a function of w are presented in Figure 3A together with the values measured in bulk water. It should be noted that an amount of water corresponding to $w \sim 40$ is required for observing the same deprotonation rate as in bulk water, whereas the rate of back-recombination is still five times larger than in bulk water.

2-Naphthol-6,8-disulfonate (NDSOH). This compound can be incorporated into AOT reversed micelles in the same way as NSOH. As water is added up to $w \sim 10$, the extinction coefficient increases without any shift of the absorption spectrum (Figure 4A). At water contents $w > 10$, there is no further change of this spectrum which superimposes that of NDSOH in bulk water. This behavior, which is reminiscent of what we have observed with pyranine,[40] is quite different from the behavior of NOH and NSOH.

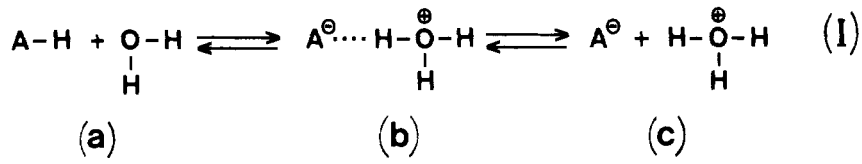
The fluorescence spectra exhibit the emission band of the basic form, but the intensity of this band increases more rapidly vs. w than in the case of NSOH (Figure 4B). The fluorescence spectrum remains unchanged beyond $w \sim 10$ and identical with the spectrum obtained in bulk water.

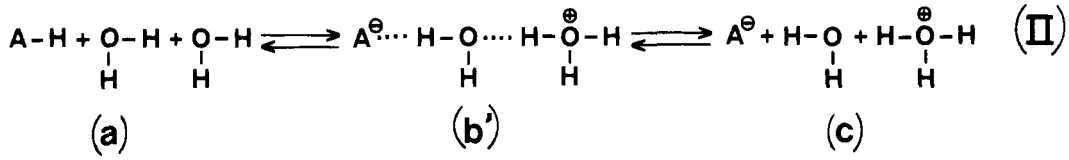
The values of τ_0 and τ'_0 are reported in Table I. From these values together with the values of $\tau_{\Delta\phi}$ and τ', the rate constants k_1 and k'_{-1} can be calculated, for $w < 6.5$, from eq 1 and 2 since proton transfer is reversible. On the other hand, for $w > 6.5$ and in bulk water, emission for NDSOH is so weak that proton transfer can be considered as irreversible and eq 3 has been used. The values of the rate constants (Table II and Figure 3B) show that the proton transfer rates become identical with those observed in bulk water beyond $w \sim 10$.

Discussion

Solubilization Sites of Naphthols in AOT Reversed Micelles. From the absorption and emission spectra, we have concluded that NOH resides at the interface. The presence of a hydroxyl group leads us to compare NOH with phenol, *p*-nitrophenol, and various substituted phenols which are also localized in the interfacial region;[11,41] NOH, like all these compounds, appears to be hydrogen-bonded to the polar head groups of AOT, the aromatic ring penetrating between the hydrocarbon tails of the surfactant. By a spectrophotometric method, we have determined the binding constant between ground-state NOH and 1 mol of AOT, in the absence of water (w = 0): we have found a value of 350 ± 30[42] which is identical with that reported by Magid and co-workers[41] for binding of phenol to AOT reversed micelles in isooctane. Since NOH is a much stronger acid in the excited state than in the ground state (see the pK values), NOH* is necessarily even more

(39) L. M. Rubeko and B. M. Uzhinov, *Zh. Prikl. Spektrosk.*, **31**(4), 734 (1979).
(40) E. Bardez and B. Valeur, unpublished results.
(41) L. J. Magid, K. Kon-No, and C. A. Martin, *J. Phys. Chem.*, **85**, 1434 (1981).
(42) The behavior of NOH and the determination of the AOT–NOH binding constant will be published in another paper devoted to the properties of the interface.





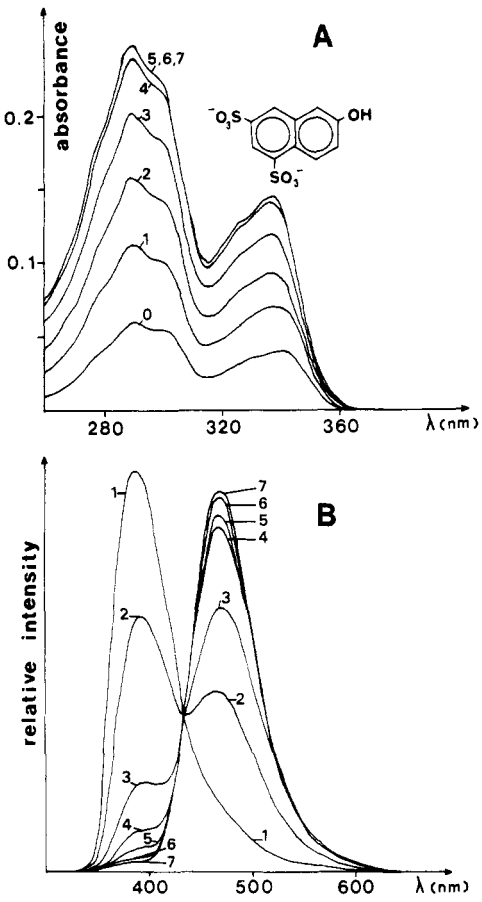


Figure 4. Spectra of NDSOH in 0.1 M AOT/heptane. (A) Absorption spectra. (B) Corrected emission spectra normalized to the same optical density at the excitation wavelength (310 nm): 0, $w = 0.53$; 1, $w = 1.6$; 2, $w = 2.7$; 3, $w = 4.2$; 4, $w = 5.6$; 5, $w = 6.9$; 6, $w = 9.6$; 7, $w = 14.4$.

tightly associated to polar heads. Addition of water does not induce solubilization of NOH in the aqueous core but modifies its environment; this compound is thus a probe for examining the ability of proton transfer in the interfacial region.

As regards NSOH, it is remarkable that an amount of water of $w \sim 40$ is required for observing the same deprotonation rate as in bulk water, but even at such a high water content, this molecule does not behave as in bulk water regarding absorption spectra and emission spectra; the changes in absorption spectra as a function of water content are similar to those of NOH anchored at the interface and no isosbestic point appears. Moreover, the rate constant for proton recombination does not recover at high water contents the value observed in bulk water (see below). For these reasons, NSOH is likely to be solubilized in the vicinity of the interface rather than in equilibrium between two solubilization sites, i.e., at the interface and in free water.

In contrast to NOH and NSOH, NDSOH can recover at $w \sim 10$ the same spectral properties and the same kinetic behavior as in bulk water. Beyond $w \sim 10$, as hydration of surfactant and Na^+ becomes complete, "apparently free water" can exist in the midst of the water core;[25,27] NDSOH is pushed away toward this region owing to the electrostatic repulsion between the anionic heads of the surfactant and the negative charge of the probe. A localization around the center of the water pool has been also observed for sodium perylene tetracarboxylate[23] and pyranine[28] which also bear more than one negative charge. Figure 5 illustrates the residence sites of the three probes.

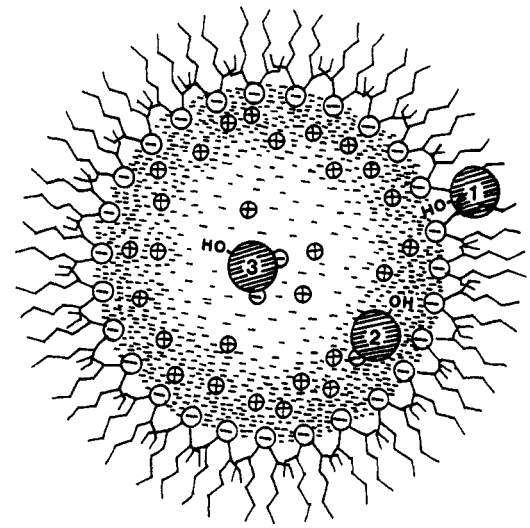


Figure 5. Schematic illustration of the residence sites of the probes in AOT reversed micelles: 1, NOH; 2, NSOH; 3, NDSOH. Length of the surfactant, 11 Å. Diameter of the water pool, 18 Å at $w = 3$; 36 Å at $w = 9$. Largest dimension of the naphthol derivatives, ~9 Å.

Absence of Deprotonation at the Interface. We have shown that NOH, localized at the interface and hydrogen bonded to polar heads, cannot undergo deprotonation in the excited state, whatever the water content. (A similar behavior has been observed for *p*-nitrophenol.[11]) This means that hydration does not cause the proton to be displaced from the hydrogen bond established with the AOT polar head groups, and that the proton is not transferred to a water molecule because the resulting ion pair (NO^-, H_3O^+) cannot be stabilized by a medium which is not polarizable enough.

Kinetics of Proton Transfer in the Aqueous Core. For protolysis of acids in aqueous solutions, the stepwise mechanisms I and II have been proposed. The existence of a hydrogen bridge between AH and a water molecule is a basic prerequisite. The nature of the intermediate is to be discussed as if proton transfer takes place directly (I) or via water molecules (II):[36b,43,44] indeed, oxygen acids, such as phenols, form strong hydrogen bonds to water which, because of its amphoteric nature, can act as a bifunctional link, and calculations have shown that simultaneous proton transfer

(43) E. Grunwald and D. Eustace in "Proton Transfer Reactions", E. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, Chapter 4.
(44) (a) M. Eigen and L. de Maeyer, *Proc. R. Soc. London, Ser. A*, **247**, 505 (1958); (b) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

TABLE II: Rate Constants of 2-Naphthol-6-sulfonate (NSOH) and 2-Naphthol-6,8-disulfonate (NDSOH) in AOT Reversed Micelles and in Bulk Water

	NSOH[a]		NDSOH[b]	
w	$10^{-9}k_1$,[c] s^{-1}	$10^{-7}k'_{-1}$,[c] s^{-1}	$10^{-9}k_1$,[c] s^{-1}	$10^{-7}k'_{-1}$,[c] s^{-1}
2.7			0.10	11.5
4.2	0.056	12	0.63	7.5
5.6	0.094	11	1.5	5.2
6.9	0.12	10	2.8	
9.6	0.26	9.8	9.1	
14.4	0.45	9.1	15	
19.2	0.68	8.6		
28.7	0.94	7.6		
38.3	1.0	6.4		
48.0	1.2	5.4		
H_2O	1.3	1.1	11	

[a] λ_{exc} = 287 nm. [b] λ_{exc} = 310 nm. [c] Accuracy: see error bars in Figure 3.

with one or two intervening water molecules will occur without supplementary energetic barrier.[45] Nevertheless, a water-separated ion-pair structure for the intermediate (b′) implies the three-dimensional hydrogen-bond network usually present in bulk water.

The backward diffusion-controlled rate constant for steps (c) → (b) or (c) → (b′) is usually of the order of 10^{10}–10^{11} M^{-1} s^{-1};[44b] consequently, an acidic medium ($[H_3O^+] \simeq 10^{-2}$–10^{-3} M) is required for the (diffusion-controlled) pseudo-first-order rate constant ($k_D[H_3O^+]$) to be competitive with the rate constant for emission of species whose lifetimes, in the present case, are about 1/ ns ($k_{em} = 1/\tau = 10^8$ s^{-1}). In a neutral or weakly acidic medium, the diffusion-controlled rate for recombination is slow with respect to the rate for emission and therefore it cannot be measured through fluorescence experiments. Consequently, the rate constant k'_{-1} that is measured is the rate constant for geminate recombination, (b) or (b′) → (a).

In AOT reversed micelles at water contents larger than $w \sim 10$, the kinetic behavior of NDSOH, residing around the center, indicates that the surrounding water is bulklike water regarding protolysis, as already observed in the case of pyranine.[28,29] A type II mechanism with water-separated ion pairs may thus be proposed. On the other hand, even at large amounts of water ($w \sim 40$), the recombination rate of NSOH is still five times higher than in aqueous solution; this observation provides additional evidence for the localization of NSOH: the fact that, at $w \sim 40$, the geminate recombination is still much faster than in bulk water means that the microenvironment of the probe is not able to solvate the ion-pair structure (b) or (b′). In the aqueous core, a region which is expected to behave in this way is the vicinity of the surfactant monolayer where water molecules are involved in the hydration of the polar heads and sodium ions.[25] This is consistent with the differences observed for absorption and emission spectra as compared with those obtained in bulk water. The behavior of NSOH regarding protolysis reflects the structure of water in the vicinity of the interface and the phenomena are even more striking in smaller aggregates.

As amounts of solubilized water are decreased ($w \lesssim 10$), a decrease in deprotonation rate is observed with a concomitant increase in the reprotonation rate with respect to bulk water, for both NSOH and NDSOH. Protolysis is thus hindered. It is well-known that, in such small micelles, the hydration of the polar heads and counterions is incomplete so that the whole water present is highly bound and oriented in solvation shells.[25] As in the interfacial region of larger micelles, the dielectric constant of such a medium is lower than in bulk water.[18] Consequently, it is to be expected that the reduction of protolysis results from structural features: (i) Available water molecules for proton transfer must be removed from the inner hydration shells, which requires substantial amounts of work and accounts for the enhancement of the activation energy of the reaction of deprotonation; (ii) Because of the lack of complete hydration, the initial formation of the hydrogen-bonded complex between AH and H_2O may be considered as an additional step in the overall mechanism and may significantly affect the kinetics of deprotonation; (iii) In a reduced water pool, proton transfer leads to the formation of contact ion pairs (b) which cannot be efficiently stabilized in a medium of low polarizability, as observed in the vicinity of the interface of larger micelles (see above). Consequently, enhancement of the rate for back-recombination is to be expected.

It should be noted that, in regard to the protolysis of an acid, there is a threshold corresponding to $w \sim 10$ beyond which water molecules able to accept a proton, as in bulk water, begin to appear in the center of the water pool. This limit separating regions with different solution behavior appears in various investigations using different techniques: light scattering[46] or proton correlation spectroscopy,[25] NMR,[19] fluorescence depolarization,[18,23] dielectric relaxation,[47] positron annihilation,[48] solvated electron absorption,[49] microwave conductivity,[50] etc. According to Eicke, this limit defines the transition region between swollen micelles and "microemulsions" in which water can be considered as a pseudophase.[25] In the microemulsion droplets ($w > 10$), the progressive evolution in protolytic reactivity of water when going from the interface to the center reflects the gradual change in the H-bonded water structure, i.e., from hydration water to a normal three-dimensional water network.

Conclusion

The present work clearly shows that the protolysis reaction of an acid in the water pool of AOT reversed micelles strongly depends on the localization of this acid. The three acid fluorescent probes that have been used are located at the interface or in the vicinity of the interface or around the center of the water pool depending on the number of negative charges they bear. They reflect large differences in the behavior of water molecules according to their localization. The ability of water to accept a proton is related to its H-bonded structure and its protolytic reactivity is an image of its structure which changes as a function of the distance with respect to the interface.

This investigation will be carried on by a study of protonation reactions involving basic probes with special attention to the kinetics of the phenomena. Recent works on the behavior of nitrogen heterocyclic[51,52] show the interest and the complexity of such reactions in reversed micellar media.

Acknowledgment. The authors are grateful to Dr. M. T. Le Bris and Mr. T. Sacaze, who synthesized NSOH and NDSOH.

Registry No. AOT, 577-11-7; NOH, 135-19-3; NSOH, 135-76-2; NDSOH, 13846-08-7; H_2O, 7732-18-5; heptane, 142-82-5.

(45) J. Busch and J. R. de La Vega, *Chem. Phys. Lett.*, **26**, 61 (1974).
(46) H. F. Eicke and J. Rehak, *Helv. Chim. Acta*, **59**, 2883 (1976).
(47) J. Peyrelasse and C. Boned, *J. Phys. Chem.*, **89**, 370 (1985).
(48) Y. C. Jean and H. J. Ache, *J. Am. Chem. Soc.*, **100**, 6320 (1978).
(49) M. P. Pileni, B. Hickel, C. Ferradini, and J. Pucheault, *Chem. Phys. Lett.*, **92**, 308 (1982).
(50) G. Bakale and J. M. Warman *J. Phys. Chem.*, **88**, 2927 (1984).
(51) J. Noroski and L. J. Cline Love, *J. Phys. Chem.*, **88**, 4176 (1984).
(52) J. Noroski and L. J. Cline Love, Proceedings of the 5th International Symposium on Surfactants in Solution, Bordeaux, France, 1984.