

**Surface analysis of polymer systems. 3.
Zinc sulfide.cntdot.cadmium sulfide/Nafion**

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thin Pt overlayer case,⁷ the oxide was also thin, probably highly defective and attached to bulk Ti. Heating to 760 K caused migration and segregation of the initially available reduced TiO_x species which were then easily detected at the Pt surface. Further incorporation of TiO_x in the Pt layer requires significantly higher temperatures and/or longer annealing times.²⁷ On the basis of the previous results of Ko and Gorte,^{12,13} a reduced Ti oxide diffuses deeper than the sampling volume of AES at high temperatures. Upon cooling it returns to the surface region forming a uniform layer on the Pt. This would leave a concentration of TiO_x beneath the surface as measured here.

Taken together, the available data indicates that, once formed, the reduced TiO_x ($x \approx 1$) species can easily diffuse into and out of the Pt. Since Ti-Pt alloys are well-known,²⁶ one possibility for the formation of the reduced titanium oxide is as follows. If we assume that the high temperature annealing process removes two oxygen atoms from the TiO₂ unit cell, Ti₂O₃ is formed at the interface. Ti₂O₃ is assumed because it is consistent with the observed stoichiometry and involves breaking the fewest bonds at the interface. In equilibrium with this process, the formation of dilute Pt-Ti and Pt-O compounds are proposed. The formation of these compounds provides enough energy for the overall process to be favorable thermodynamically. The diffusion of Ti and O would then occur through the Pt and away from the interface along the concentration gradient in a correlated but not simultaneous fashion. Bardi and Ross²⁶ have shown that a reduced TiO_x species can diffuse through Pt₃Ti. At high temperatures, entropy drives surface segregated TiO_x into the bulk. Upon cooling the surface back to 300 K, enthalpy factors dominate and cause the surface segregation of the reduced species. For thin films of TiO₂ on Pt, this process terminates with roughly 1 monolayer of TiO_x at the

surface with a concentration of TiO_x distributed throughout the Pt.

This model also predicts that the small Pt particles present in Pt/TiO₂ catalysts will incorporate TiO_x when the substrate is reduced. In this way, all of the Pt atoms within the particles are altered and can account for the small Pt BE shifts sometimes observed in earlier XPS studies.^{20,28} Extended thermal annealing of the thin film model catalysts supports this conclusion.

Summary

X-ray photoelectron spectroscopy has been used to characterize TiO₂ overlayers on polycrystalline Pt. The addition of TiO₂ increases (≤ 0.25 eV) the Pt(4f) BE. This is attributed to bonding between Pt and Ti³⁺ at the interface. Annealing to 1300 K under vacuum causes a significant increase in the Ti³⁺ surface concentration and a decrease in the total amount of Ti in the XPS sampling volume. For initial TiO₂ coverages greater than 1 monolayer an equilibrium amount of reduced Ti species is present on the surface after annealing (between 0.6 and 0.9 monolayer). Depth profiles indicate that diffusion of a reduced TiO_x ($x \approx 1$) species (with titanium in a 3+ oxidation state) occurs during annealing.

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(27) Y.-M. Sun, D. N. Belton, and J. M. White, to be submitted for publication.

(28) C. C. Kao, S. C. Tsai, M. K. Bahl, and Y. W. Chung, *Surf. Sci.*, **95**, 1 (1980).

Surface Analysis of Polymer Systems. 3. ZnS·CdS/Nafion

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X-ray photoelectron spectroscopy has been used to characterize the surfaces of Nafion films into which mixtures of CdS and ZnS have been precipitated by exposing ion-exchanged Nafion films to H₂S. For all the cases studied, precipitation led to segregation of the metals from interior ion-exchange sites to the surface where small sulfide particles were formed. Irradiation of the films with visible light in the presence of aqueous 0.1 M Na₂S solution produced H₂ and some Cd⁰. In the absence of ZnS, there was neither H₂ nor Cd⁰ production. When ZnS and CdS were coprecipitated or when ZnS was precipitated after CdS, very active films were formed and irradiation changed the surface Zn/Cd ratio to a value near 5. When CdS followed ZnS precipitation, irradiation did not change the Zn/Cd ratio from its initial value of unity and the films were inactive for photoassisted hydrogen generation. The results are discussed in light of other measurements on these materials which point to the importance of CdS surface state alteration by Zn.

Introduction

In previous papers, we have reported on mixed semiconductor catalysts supported on a variety of materials (particularly coprecipitated ZnS·CdS/Nafion and ZnS·CdS/SiO₂) that are active hydrogen evolution catalysts when irradiated with visible light.^{1,2}

(1) N. Kakuta, K.-H. Park, M. F. Finlayson, A. Ueno, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber, and J. M. White, *J. Phys. Chem.*, **89**, 732 (1985).

(2) A. Ueno, N. Kakuta, K.-H. Park, M. F. Finlayson, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber, and J. M. White, submitted for publication.

These catalysts have activities that are comparable with Pt·CdS/Nafion films and do not depend strongly on the support. These interesting materials have been studied in a variety of ways in an effort to understand the key features. In the absorption spectrum, two onsets were found corresponding to bulk CdS and ZnS interband transitions. Luminescence measurements indicated lattice vacancies and interstitials that participated in radiative relaxation. No evidence for solid solutions has been found.^{2,3}

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The hydrogen production activities of sequentially precipitated (CdS followed by ZnS) catalysts were the same as the coprecipitated catalysts, but the activity was much less when the precipitation order was reversed.^{1,2}

We have also reported the surface characterization of Pt-CdS/Nafion films using X-ray photoelectron spectroscopy (XPS).^{4,5} This work gave the following results: (1) Adsorbed S²⁻ on Nafion is easily oxidized to sulfate, and the hydrogen generation activity drops with increasing sulfate ion concentration. (2) Under conditions where cubic CdS is formed the surface concentration of CdS is ca. 140 times higher than under conditions where hexagonal CdS is formed. (3) Pt deposited by ion exchange and reduction of a Pt complex ion is concentrated in the surface region of the Nafion. (4) Sputter-deposited Pt (average thickness 100 Å) is distributed within the first several hundred angstroms of the Nafion surface. These results are consistent with a model in which Pt particles must be in close contact with CdS particles for highly active photogeneration of hydrogen.

In this paper, we report our surface characterization by XPS of CdS-ZnS/Nafion materials prepared by coprecipitation and sequential precipitation. This work extends previous reports on the CdS-Pt/Nafion.^{4,5} Here attention is given to changes in the XPS spectra that occur as the result of precipitation of the sulfides and as a result of irradiation with visible light.

Experimental Section

Nafion (117, 0.018 cm thick) membranes were used for all experiments. Films containing *coprecipitated* sulfides (denoted ZnS-CdS/Nafion) and *sequentially precipitated*, ZnS followed by CdS (denoted CdS(ZnS/Nafion)), or vice versa, films were prepared according to procedures detailed in previous papers.^{1,2} The methods involve incorporation of Cd²⁺ into Nafion by ion exchange and precipitation of the sulfides by addition of H₂S. For sequentially precipitated sulfides, the ion-exchange process was also done sequentially. Atomic absorption spectroscopy was used to measure Zn/Cd ratios.

For irradiation and hydrogen production, films (1 × 1 cm when dry) were immersed in Pyrex glass cells containing 3 mL of 0.1 M Na₂S. The vessels were degassed under vacuum with sonication to remove gases from the interior of the membrane and were purged with N₂. A water-filtered 450-W Xe lamp and a glass filter (Corning 3-72) were used. The latter removes wavelengths shorter than 440 nm. Irradiations lasted at least 2 days to make it easy to detect changes of the ZnS and CdS interfaces by post XPS analysis. After irradiation, the wet films were quickly placed under vacuum and dried overnight to avoid surface oxidation by contact with air.

XPS measurements were carried out using a Vacuum Generators ESCA Lab II system with Al K α radiation (1486.6 eV). The binding energies (BE) were all referenced to the surface hydrocarbon contamination C(1s) peak (284.5 eV). Auger transitions excited by Al K α X-rays were also measured. For the work reported here, no variations were detected by XPS across the surface of the sample.

Results and Discussion

Based on the XPS data for a number of Zn and Cd compounds,^{6,7} it is not possible to clearly identify the oxidation states by using only core level BE's. However, Auger parameters^{6,7} determined by the kinetic energy difference between Auger and XPS transitions show obvious differences. Therefore, Cd(MNN) and Zn(LMM) Auger peaks were measured and used in conjunction with core level BE's to calculate the Auger parameter.

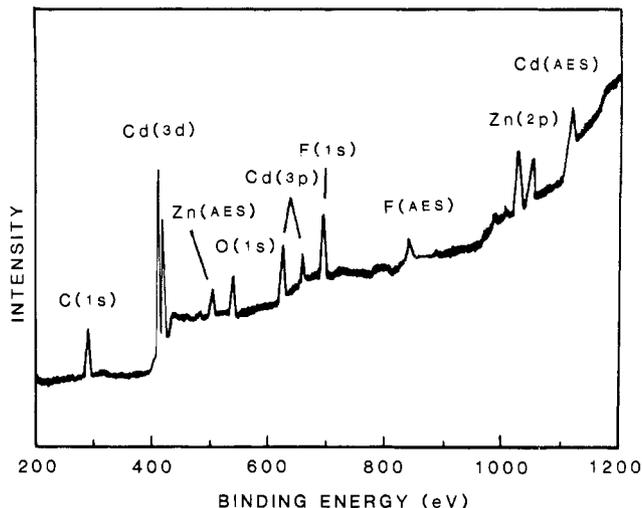


Figure 1. Broad-scan XPS spectrum of a ZnS-CdS/Nafion film.

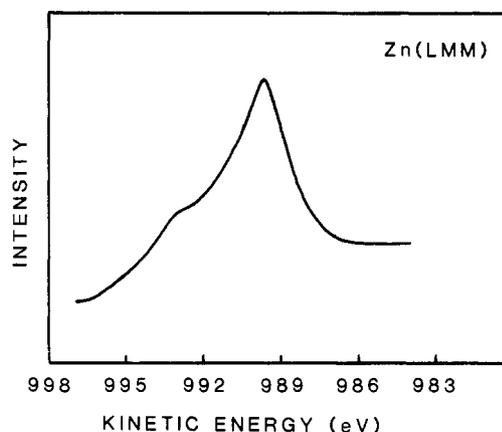


Figure 2. Zn(LMM) XAES spectrum of a ZnS-CdS/Nafion film.

XPS of semiconductor-incorporated Nafion films gives F(1s) and C(1s) BE's at 688.9 and 291.3 eV, respectively. These are consistent with our previous results.^{4,5} A summary of the present results is given in Tables I and II in the form of atomic ratios before and after irradiation and sulfiding.

ZnS-CdS/Nafion. As determined by atomic absorption, the mole ratio of Zn/Cd in the coprecipitated films was near unity and the concentration was consistent with a uniform saturation of ion-exchange sites throughout the Nafion prior to sulfiding. Broad-scan XPS of an ion-exchanged, but not sulfided, film shows Nafion, Cd(3d), and Zn(2p) peaks. A broad scan after sulfiding is shown in Figure 1. The BE's of Cd(3d) (405.4 eV) and Zn(2p) (1022.0 eV) are similar to those found in other work.^{4,8}

Figures 2 and 3a show the Zn(LMM) peak at 989.4 eV and the Cd(MNN) peak at 381.4-eV kinetic energy, respectively. The Auger parameters (kinetic energy difference plus the X-ray photon energy or the Auger kinetic energy plus the XPS binding energy) for zinc and cadmium are thus 2011.4 and 786.8 eV, respectively, in good agreement with the reported values for ZnS and CdS.⁹ A S(2p) XPS peak at 161.4 eV is assigned to the sulfide ion. Thus, the surface spectroscopy is consistent with a system dominated by ZnS and CdS particles formed by sulfiding ion-exchanged Nafion. We were unable to determine the exact surface stoichiometry of the sulfides because of the presence of residual surface sulfide bound to Nafion which was not removed by room-temperature washing. As noted previously,⁴ unreacted surface sulfide could be removed by washing with boiling water, a process which destroys the character of these ZnS-CdS systems.

(4) N. Kakuta, J. M. White, A. Campion, A. J. Bard, M. A. Fox, S. E. Webber, and J. M. White, *J. Phys. Chem.*, **89**, 48 (1985).

(5) N. Kakuta, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber, and J. M. White, submitted for publication.

(6) C. D. Wagner, W. N. Riggs, L. E. Davis, and G. E. Muilenberg, "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elmer, Eden Prairie, MN, 1979.

(7) D. Briggs and M. P. Seah, "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Wiley, New York, 1983.

(8) G. Schor, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 75 (1983).

(9) S. W. Goarenstroom and N. Winograd, *J. Chem. Phys.*, **67**, 3500 (1977).

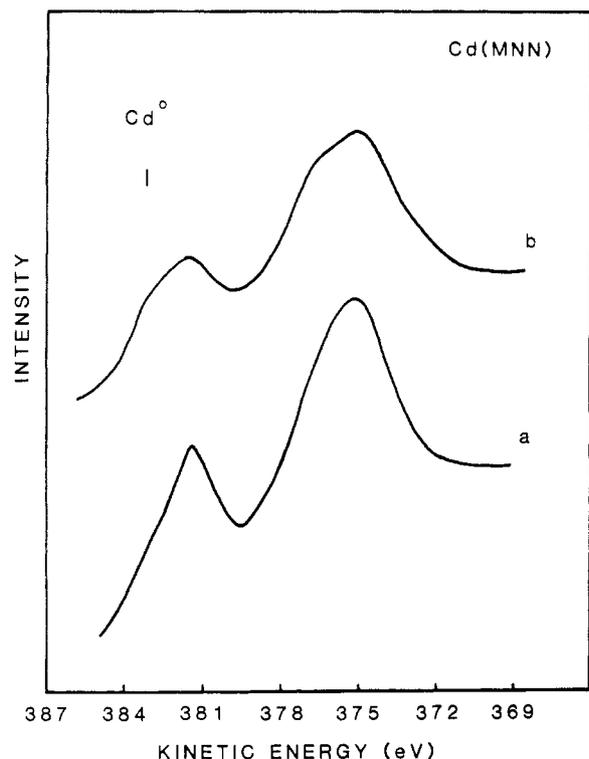


Figure 3. Cd(MNN) XAES spectra of ZnS-CdS/Nafion soaked in Na₂S (a) without and (b) with visible light irradiation.

TABLE I: Surface Zn and Cd Content^a by XPS Peak Area Analysis

system ^b	irradiated	Zn/Cd ^c	Zn/F	Cd/F
ZnS-CdS/Nafion	no	0.32	0.23	0.71
	yes	5.21	0.26	0.05
ZnS(CdS/Nafion)	no	19.2	20.7	1.08
	yes	5.25	1.93	0.37
CdS(ZnS/Nafion)	no	1.00	0.30	0.29
	yes	0.82	0.37	0.45

^a Account has been taken of atomic sensitivity factors.⁸ ^b See text for definition of systems. ^c Estimated uncertainty in all the ratios is $\pm 5\%$.

When the ZnS-CdS/Nafion film, in aqueous Na₂S solution, was irradiated with visible light ($\lambda > 440$ nm) for 2 days, it showed the same hydrogen generation activity as reported earlier.⁷ The BE's of Cd(3d_{5/2}) and Zn(2p) were equal to those of a fresh film. The irradiation caused no changes in the KE of the Zn(LMM) peak. However, there was a change in the Cd(MNN) region (Figure 3b) which had two peaks at 381.5 and 383.0 eV. On the basis of measured Auger parameters for cadmium compounds,^{6,7} we assign the low-KE peak (381.5 eV) to the Cd²⁺ ion and the high-KE peak (383.0 eV) to the Cd⁰ species.

With irradiation, the Cd/F ratio decreased to 7% of the fresh sample value (Table I). The Zn/Cd ratio changed from 0.32 to 5.21, suggesting that the surface becomes zinc-rich during irradiation but that it does so through the loss of Cd. The Cd/F ratio increased with Ar⁺ bombardment. No zinc or cadmium species were found in the sulfide solution after irradiation (by atomic absorption spectroscopy), ruling out, as expected, the possibility of permanent dissolution of these sulfides. These results show that irradiation caused a redistribution of the surface sulfides with CdS moving deeper into the Nafion.

Before and after irradiation, the S(2p) peak was located at 161.8 eV which is typical of sulfide.

ZnS(CdS/Nafion). For the ZnS(CdS/Nafion), XPS and XAES spectra peak positions for Zn and Cd were the same as for ZnS-CdS/Nafion. Before irradiation, the Zn/Cd ratio (Table I) was 19.2 which suggests, as expected, that the CdS layer is covered with ZnS.

As in previous work,^{1,2} the hydrogen generation activity with visible irradiation was almost the same as in the ZnS-CdS/Nafion

TABLE II: XPS Peak Area Analysis of Surface Atomic Ratios before and after Sulfiding^a

sample ^b	sulfiding	Zn/Cd ^c	Zn/F	Cd/F
ZnS-CdS/Nafion	before	1.07	0.01	0.01
	after	0.32	0.23	0.71
ZnS(CdS/Nafion)	before	0.1	0.10	0.97
	after	19.20	20.7	1.06
CdS(ZnS/Nafion)	before	3.80	0.79	0.21
	after	1.00	0.30	0.29

^a Account has been taken of atomic sensitivity factors.⁸ ^b See text for definition of systems. ^c Estimated uncertainty in the ratios is $\pm 5\%$.

case. Irradiation produced no changes in the XPS and XAES peak positions except for the Cd(MNN) Auger region which, as for ZnS-CdS/Nafion, contained peaks assigned to Cd²⁺ and to Cd⁰. During irradiation, the Zn/Cd ratio decreased from 19.2 to 5.25, the latter close to that of a ZnS-CdS/Nafion film after irradiation. During irradiation, the surface zinc concentration (Zn/F) decreased by 90% and the cadmium concentration (Cd/F) decreased by 65%. With a small amount of Ar⁺ bombardment, the surface cadmium content increased, but the zinc content did not change.

The films gave a S(2p) BE of 161.8 eV (sulfide) both before and after irradiation. No oxidized sulfur peaks were observed.

CdS(ZnS/Nafion). As reported, CdS(ZnS/Nafion) films had poor activity for hydrogen production and were about the same as for CdS(ZnS/SiO₂).² Before irradiation, XPS of the fresh film gives Cd(3d_{5/2}), Zn(2p), and S(2p) BE peaks at 405.2, 1022.3, and 161.8 eV, respectively. The Auger parameters for zinc and cadmium are consistent with results on fresh ZnS-CdS/Nafion and ZnS(CdS/Nafion) films. The Zn/Cd ratio is 1.00, a value unexpectedly low considering that the CdS was added after the ZnS. The Cd/F (0.29) and Zn/F (0.30) ratios in Table I are both significantly lower than for ZnS(CdS/Nafion). Thus, in CdS(ZnS/Nafion) the CdS and ZnS are not as concentrated at the Nafion surface.

Irradiation, as for the other films, changed the Cd(MNN) Auger region, indicating the formation of Cd⁰. Unlike the other films, both the Zn/F and Cd/F ratios increased and the Zn/Cd ratio changed only slightly during irradiation.

Effect of Sulfiding. In another set of measurements, the films were examined by XPS before and after sulfiding (Table II). For both ZnS(CdS/Nafion) and CdS(ZnS/Nafion) the results labeled "before" were measured with the first species sulfided and the second ion exchanged but not sulfided. These results indicate that the Cd²⁺ and Zn²⁺ ions which are bound to cation-exchange sites tend to move to the surface during sulfiding. It is not clear whether the formation of sulfide occurs before or after the cation leaves the exchange site. However, particularly in the ZnS(CdS/Nafion) case, the evidence suggests a layered material in which the Zn²⁺ migrates through and over the CdS that is present before it forms particles of ZnS. Table II also indicates that, before sulfiding, the Zn/F ratio for ZnS(CdS/Nafion) and the Cd/F ratio for CdS(ZnS/Nafion) are both higher than expected based on either the pure or the mixed semiconductor/Nafion systems.¹⁻³ Most likely, this is due to adsorption of Zn²⁺ or Cd²⁺ on the previously formed sulfide.

After ion exchange and before sulfiding, the ZnS-CdS/Nafion film has a Zn/Cd ratio near unity consistent with the solution mole ratio used. Thus, there is no strong preference for one of the ions at the exchange sites. After H₂S treatment, the surface was enriched in CdS. Qualitatively, in single-component films CdS was much more quickly formed (e.g. turned yellow) than ZnS (turned white). These results are consistent with our previous work on ZnS-CdS/SiO₂.²

X-ray diffraction (XRD)^{1,4,10} showed strong α -CdS peaks in CdS/Nafion, but ZnS-CdS/Nafion had small broad peaks with intensities too weak to make a positive identification. No XRD

(10) A. W.-H. Mau, C.-B. Huang, N. Kakuta, A. J. Bard, A. Campion, M. A. Fox, J. M. White, and S. E. Webber, *J. Am. Chem. Soc.*, **106**, 6537 (1984).

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, Cd⁰ was observed in all three kinds of films after irradiation. Cd⁰ did not form in single-component CdS/Nafion films. Thus, we conclude that the presence of ZnS is required for Cd⁰ production. Gutierrez and Henglein¹¹ reported that Cd metal catalyzes hydrogen formation on CdS colloids. The presence of Cd⁰ does not necessarily produce an active hydrogen generation catalyst since under our conditions irradiated CdS-(ZnS/Nafion) films contain Cd⁰ and have very low activity. Consistent with other findings, including high quantum yields for H₂ using a photoelectrochemical cell¹² and strongly quenched luminescence,^{13,14} we propose that Zn²⁺ in intimate contact with

CdS is crucial. This conclusion is supported by photoelectrochemical measurements¹⁵ showing an enhanced photocurrent in the presence of Zn²⁺ and a more negative value for the CdS flat band potential in the presence of Zn²⁺ and suggests that Zn²⁺ 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 Na₂S 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

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Registry No. CdS, 1306-23-6; ZnS, 1314-98-3; H₂S, 7783-06-4; Na₂S, 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

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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 $w = [\text{H}_2\text{O}]/[\text{AOT}]$. 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 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.

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).