# **Disliane-Modified Mordenite Zeolites**

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The effective pore size of H-mordenite zeolite can be decreased by implantation of disilyl compounds. Chemisorption of disilane at high temperature results in denser packing of the implanted entities on the external surface. This in turn enhances the pore narrowing effect. After hydrolysis-dehydration, the external surface of the disilanated zeolite can be reactivated by partial rehydration; thus a successive modification of the zeolite surface is possible. A narrowing of the pore size occurs without altering the internal pore structure or the active sites of these modified zeolites. The inert nature of the dehydrated disilanated zeolites eliminates the nonselective catalysis imposed by the active external surface of H-mordenites. This results in the formation of an efficient gas separator and a highly shape selective catalyst.

#### Introduction

Crystal voids and channels in zeolite structure provide an extensive surface to accentuate catalytic transformation and sorption accumulation. Generally speaking, the activity of acid-catalyzed hydrocarbon conversion is based on the number and strength of Brønsted acid sites and high rates of hydrogen-transfer reaction. The selectivity of the zeolite is determined by geometrical influence of the environment on the formation of the transition state, and the diffusion of products through zeolitic orifice. Therefore, preservation of sufficient acidic sites and modification of the pore architectures of zeolite are considered important factors in the field of catalysis and separation.<sup>1-7</sup>

Isomorphous substitution of framework elements<sup>8-12</sup> and incorporation of metal clusters and obstacle entities into the zeolite<sup>1-7,13-15</sup> are two promising perspectives for chemical modification of zeolites. These processes involve reactions via aqueous solution equilibrium,<sup>8-10,14,16</sup> solid-solid reaction and gas- or liq-uid-phase chemisorption.<sup>1-7,11,12,15,17</sup> We have previously reported the structural modification of H-mordenite zeolites by chemisorption of disilane and their resulting sorption properties.<sup>5,18</sup> Depending on the temperature at which chemisorption occurs, the disilane reacts with the zeolite in two distinct ways. At low temperature (253-303 K) implantation of the disilane occurs throughout the zeolite (i.e., both of the external and internal surface), while at high temperature (373-473 K) a preferential reaction of disilane with the hydroxyl groups at the pore entrances

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occurs. The latter process results in only a modification of the external zeolite surface.

Implantation of disilane on both the internal and external surfaces of the zeolite causes changes in both the pore dimensions and the electrostatic field inside the zeolite channels. Specific adsorption of oxygen over nitrogen has been observed on the highly disilanated zeolite. In the case where the disilane is only found on the external surface of the zeolite, there is a more pronounced pore narrowing effect and only a small decrease in sorption capacity of the zeolite. However, due to the inactive character of the modified external surface, the resulting pore size cannot be changed in a precise and continuous way by successive chemisorption of disilane. It is therefore necessary to develop a method for fine-tuning the pore size of the substrate without affecting its internal acid sites and volume. It is also the intention of the present paper to extend these investigations to study the shape-selective catalysis properties of the modified zeolites, in addition to the separation and encapsulation properties of the modified zeolite as reported by Vansant and co-workers.<sup>2,4,7,18,19</sup>

#### **Experimental Section**

A synthetic Na-mordenite LP with a Si to Al ratio of 5.5 from the Norton Co. (England) was used as a starting material. This was then converted to the NH<sub>4</sub> form (2.4 mmol NH<sub>4</sub><sup>+</sup>  $g^{-1}$  zeolite). These NH<sub>4</sub>-mordenites were deammoniated at 733 K under vacuum resulting in the formation of H-form zeolites. Approximately 20% of the total Al content was removed from the mordenite framework.<sup>20</sup> The external surface area and void volume of H-mordenite were determined by nitrogen adsorptions at 77 K on hydrated and dehydrated zeolites. The external surface area was found to be 4.0  $m^2 g^{-1}$  and the void volume was 0.22 cm<sup>3</sup> g<sup>-1</sup>.

Surface modification of the zeolite by chemisorption of disilane was carried out according to the method described by Vansant and co-workers.<sup>5,7</sup> A dynamic gas adsorption apparatus allowing continuous circulation of disilane through the zeolite bed (ca. 2 g) was used. During rehydration of a zeolite, a further 50 mg of zeolite was used gravimetrically to monitor the amount of water adsorbed. The pressure of water vapor during partial hydration of the zeolite was kept lower than 10<sup>-3</sup> mbar at the chemisorption temperature.

Sorption measurements of Xe, Kr, Ar, O<sub>2</sub>, and N<sub>2</sub> were carried out volumetrically in situ after each step in the modification process. The adsorptions of n-butane and water were obtained in a quartz microbalance. Infrared spectra were recorded on a Nicolet 5 DXB spectrometer using a MTEC 100 photoacoustic detector (PAS) with 4 cm<sup>-1</sup> resolution. Samples were transferred in a dry nitrogen purged glovebox. The photoacoustic cell itself was purged with ultradry helium. A mirror velocity of 0.16 cm/s

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**Figure 1**. *n*-Butane adsorption kinetics (293 K) on modified H-mordenites chemisorbed with 0.22 mmol  $g^{-1}$  disilane at 423 K: (O) on H-mordenite; ( $\Theta$ ) after chemisorption of disilane with R = 2; ( $\Theta$ ) after hydrolysis-dehydration treatment.

and 500 scans were used for all the FTIR measurements.

Cracking of *n*-hexane and 2,2-dimethylbutane was performed in a flow reactor. The reaction was carried out at 573 K over a disilanated H-mordenite catalyst (0.2 g of zeolite crushed to 60-100 mesh), which was pretreated at 723 K in air for 4 h. Helium was used as a carrier gas and passed through a hexane saturator at 273 K. For each run 2 mL of the hydrocarbon mixture was injected. Products were collected in a liquid nitrogen trap prior to analysis by a FID gas chromatograph.

## **Results and Discussion**

n-Butane Sorption on Disilanated Mordenites. Two grams of H-mordenite that had been dehydrated at 733 K overnight in vacuo were reacted with 2 mmol of disilane at 423 K for a period of 1 h; 0.22 mmol  $g^{-1}$  Si<sub>2</sub>H<sub>6</sub> was chemisorbed. The R value (i.e., the ratio of evolved  $H_2$  to chemisorbed  $Si_2H_6$ ) reached 2.0. For comparison, another sample was prepared in which the same amount of disilane was chemisorbed at 293 K. These chemisorption conditions are known to result in two types of surface modification of the zeolite<sup>5,18</sup> (i.e., an external surface chemisorption on the zeolitic crystals vs uniform chemisorption throughout the entire zeolite surface). The disilane modification of the zeolite is neither a low reactivity or a slow diffusion controlled and limited process. Chemisorption at higher temperature (373-473 K) results in an increase in reactivity, so that the incoming disilane immobilizes earlier on its diffusion path compared with chemisorption at low temperature. The implanted groups efficiently decrease the accessibility of the internal channels to other disilane molecules, which then results in the limitation of this modification by the low-diffusion of disilane through the constricted channels. The differences in the effective pore narrowing size of the two modified samples can be readily proven when *n*-butane is selected as probe molecule. The relative uptakes of butane vs the square root of time are plotted in Figures 1 and 2. The results show that the adsorption of butane by the zeolite modified at high temperature (HT sample) was significantly suppressed. On the other hand, a faster uptake of *n*-butane can be observed on the zeolite modified with the same amount of disilane at low temperature 293 K (LT sample), even though this sorption is a diffusion-controlled process. As the number of the new bonds formed between disilyl groups and the zeolite framework (indicated by the R value) increases this imposes an enhanced narrowing effect on the pore opening size.<sup>18</sup> Such an obscurity on the sorption rates of *n*-butane in the two samples can be eliminated when the LT sample is heated to give the same R value as the HT sample. This thermal treatment causes a decrease in the rate of uptake by the LT sample. However, the rate is still greater than that for the adsorption on the HT sample. A quantitative analysis can be made when the sorption profiles of these samples are expressed according to the equation



**Figure 2.** *n*-Butane adsorption kinetics (293 K) on modified H-mordenites chemisorbed with 0.22 mmol  $g^{-1}$  disilane at 293 K: (O) on H-mordenite; ( $\square$ ) after chemisorption of disilane with R = 1.1; ( $\square$ ) after thermal treatment giving R = 2; ( $\square$ ) after hydrolysis-dehydration treatment.

TABLE I: Diffusion Coefficients for *n*-Butane on Different Modified Zeolites (in  $10^{-16}$  cm<sup>2</sup>/s)

sorbent	parent sample	chemisorpn of 0.22 mmol g <sup>-1</sup> disilane	thermal treatment giving $R = 2$	hydrolysis- dehydrn
HT sample	4233.6	0.36	0.36	exclusion
LT sample	4233.6	27.2	15.5	0.46

where  $M_t$  and  $M_{\infty}$  are the amounts of sorbate taken up at time t and  $\infty$ . A and V are the external crystal surface area and volume, respectively. K is the ratio of the amount of sorbate in the gas phase to that in the solid phase at  $t = \infty$ . The diffusion coefficients for *n*-butane are given in Table I. When calculating the diffusion coefficients, it was assumed that the sorption amount at equilibrium is constant throughout the samples.

When comparing the adsorption on the HT and the thermally treated LT samples, it is seen that *n*-butane can penetrate the mordenite channels blocked by disilyl groups which have formed two bonds and the zeolite framework. Therefore, the enhanced pore narrowing effect on the HT sample can be explained as a result of denser packing of the disilyl groups on the external surface of the zeolite. This also accounts for the lower sorption rates that were obtained with an increasing the amount of disilane chemisorbed in the modified zeolite.<sup>18</sup> Moreover, a similar observation has been made that the initial sorption or desorption rate also decreases for the nonparallel 8-ring zeolites.<sup>21</sup> These phenomena can also be correlated to the additional mass-transport resistance results from the sorbate passing through the interval space constituted by the constricted channels of the zeolites.

Successive Modification. When water vapor was introduced at 473 K to hydrolyze the disilyl groups chemisorbed in the zeolite, hydrogen was further evolved. The R value reached 6.6 for both of the samples. R values between 6 and 7 normally indicate partially broken  $\equiv$ Si $\equiv$ Si $\equiv$  bonds in the disilyl groups, since each reacted or cleaved bond during the chemisorption or hydrolysis processes produces one molecule of H<sub>2</sub>.

chemisorption:  $\equiv$ Si-H + HO-Si $\equiv \rightarrow \equiv$ Si-O-Si $\equiv +$ H<sub>2</sub> (2)

hydrolysis: 
$$\equiv$$
Si-H + H<sub>2</sub>O  $\rightarrow \equiv$ Si-OH + H<sub>2</sub> (3)

$$\equiv Si - Si \equiv + 2H_2O \rightarrow 2(\equiv Si - OH) + H_2$$
(4)

After dehydration of a hydrolyzed HT sample at 733 K overnight, an additional narrowing of the pore size as evidenced by a complete exclusion of n-butane, and a significant decrease of Xe sorption rate and capacity was observed. However, for other smaller

$$M_t/M_{\infty} = 2A(1+K)(Dt/\pi)^{1/2}/(VK)$$
(1)



**Figure 3.** Xe adsorption kinetics (273 K) on the successively modified H-mordenites. (O) on H-mordenite; ( $\odot$ ) after chemisorption of 0.22 mmol g<sup>-1</sup> disilane at 473 K; ( $\odot$ ) after hydrolysis-dehydration treatment, ( $\blacktriangle$ ) the second cycle chemisorption and consequently treatment; ( $\blacksquare$ ) the third cycle modification.

sorbates (Kr, Ar,  $O_2$ , and  $N_2$ ) their sorption behavior is almost unchanged. As previously indicated, the newly formed compounds show no reactivity toward disilane after the hydrolysis-dehydration treatment. There are two factors that are attributed to the inert character of the modified zeolite surface. There are as follows.

1. The inactive behavior of the new disilanol groups, as a result of dehydroxylation during the thermal treatments

$$= Si - OH + HO - Si = \rightarrow = Si - O - Si = + H_2O \qquad (5)$$

After hydrolysis of the substrate chemisorbed with disilane, a very high concentration of silanol (Si-OH) groups was formed (see eq 2-4). However, it has been observed that chemisorption of 0.27 mmol of disilane results in a 30.6-mg increase in the mass of the zeolite. The increment of mass is correlated to the incorporated hydrolyzed disilyl groups and can be expressed as  $SiO_{1.7\pm0.1}H_x$ . Therefore, such dehydroxylation reactions must be assumed during there treatments. It also can be concluded that considerable  $\equiv Si-O-Si\equiv$  bonds have been formed in the zeolite framework. Moreover, no additional peak or increase in intensity due to the new disilanol groups has been observed in the hydroxyl region of the infrared spectrum, even on the partially hydrolyzed disilanated sample at 473 K.

2. Complete blocking or exlusion effects by the disilyl obstructions in the zeolite toward a second dose of disilane. It is remarkable that hydrolysis of the disilyl groups also results in further reduction of the pore opening size.<sup>18</sup>

In order to obtain a further narrowing of the pore size of the zeolite without affecting its internal system, a second chemisorption cycle was performed on the modified substrate which had adsorbed ca. 0.76 mmol  $g^{-1}$  of water. The reaction temperature of the sample was increased stepwise from ambient temperature to 473 K during 3 h. A chemisorption of 0.04 mmol  $g^{-1}$  Si<sub>2</sub>H<sub>6</sub> and a production of 0.164 mmol  $g^{-1}$  H<sub>2</sub> were obtained. After a hydrolysis-dehydration treatment, the effective pore size as evaluated by sorption kinetics was dramatically decreased as shown by the lower sorption rate of Xe (Figure 3). When the zeolite was rehydrated (ca. 0.70 mmol  $g^{-1}$  water) and reacted with disilane again, ca. 0.03 mmol  $g^{-1}$  of Si<sub>2</sub>H<sub>6</sub> was further chemisorbed. A complete exclusion of Xe and decrease in the Kr sorption rate were observed. For sorption of smaller molecules such as Ar and  $H_2O$ (Figures 4 and 5) the zeolites almost retain their original capacities. This suggests that the successive modification process results in effective pore narrowing and does not influence the internal sorption volume, so that the successive chemisorption of Si<sub>2</sub>H<sub>6</sub> on the external zeolite surface could be assumed.

It should be noted that, after the second rehydration process, although the substrate still contained ca. 1.6 mmol  $g^{-1}$  hydroxyl groups and 0.7 mmol of water per gram of zeolite, a modification degree of only 0.03–0.04 mmol  $g^{-1}$  disilane was obtained. This degree can be associated with 1–2 layers of external surface chemisorption when a close packing of the chemisorbed Si<sub>2</sub>H<sub>6</sub> on



Figure 4. Ar adsorption kinetics (273 K) on the successively modified H-mordenites. (O) on H-mordenite; ( $\odot$ ) after chemisorption of 0.22 mmol g<sup>-1</sup> disilane at 473 K; ( $\odot$ ) after hydrolysis-dehydration treatment; ( $\blacktriangle$ ) the second cycle chemisorption and consequently treatment; ( $\blacksquare$ ) the third cycle modification.



Figure 5.  $H_2O$  adsorption kinetics on (O) H-mordenite and on ( $\Delta$ ) successively modified H-mordenite.

the crystal is assumed. The s-shape uptake of Xe (Figure 3) is unambiguous evidence of a so-called skin effect on the mass transport,  $^{22,23}$  which has been correlated to external surface controlled sorption.

The successive modification was followed by using infrared measurements. The deammoniated H-mordenite clearly shows two types of hydroxyl groups at 3740 and 3610 cm<sup>-1</sup>. The lowfrequency OH groups associated with a Brønsted site are known as bridging hydroxyl, whereas the higher frequency hydroxyls are assigned to terminal silanol SiOH groups at the outer surface or at defect site.<sup>24-26</sup> On chemisorption of disilane the characteristic stretching vibrations of Si-H groups appear in the 2313-2213-cm<sup>-1</sup> region. Chemisorption of disilane also gives rise to a new absorbance band at 935 cm<sup>-1</sup> and a shoulder at 870 cm<sup>-1</sup>. Hydroylsis-dehydration results in a complete disappearance of the Si-H vibrations and the band at 935 cm<sup>-1</sup>, as well as the band associated with the terminal silanol groups. A slight decrease in the band representative of the bridging hydroxyl was also observed. A broadening of the band at 870 cm<sup>-1</sup> was also obtained due to this treatment. After partial rehydration, the reappearance of the silanol group at 3740 cm<sup>-1</sup> probably provides the anchoring points for further chemisorption (Figure 6, spectrum d). It is noteworthy that the maintenance of the acidic bridging OH groups

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TABLE II:	Product	<b>Distribution</b> i	in the	Cracking	of	Hexanes
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conversion		product distribution, % <sup>a</sup>										
catalyst	rate, %	C <sub>2</sub>	C2=	C3	C3=	i-C4	C <sub>4</sub>	C <sub>4</sub> =	i-C <sub>5</sub>	C <sub>5</sub>	coke, %	
				I. n-H	lexane Cra	acking						
HM	99.2	0.4	1.7	50.7	1.3	26.9	16.0		1.9	1.1	24.7	
$HM + 0.04^{b}$	99.5	0.4	1.5	56.9	0.8	22.3	15.7		1.5	0.8	28.1	
HM + 0.11	87.2	0.6	2.5	71.7	2.3	8.6	10.8	0.7	1.8	1.0	27.4	
HM + 0.14	64.2	0.9	5.0	77.4	3.4	4.0	7.5		1.1	0.7	27.9	
HM + 0.17	60.5	1.2	5.9	76.9	3.0	3.9	7.5		0.9	0.7	25.8	
			I	I. 2,2-Dim	ethylbutar	ne Crackin	g					
HM	96.7	0.4	1.2	51.0	1.1	26.5	16.2		2.5	1.2	24.7	
HM + 0.04	96.1	0.4	1.5	56.3	1.1	22.7	14.8		2.0	1.1	27.4	
HM + 0.11	16.5	0.7	4.8	72.7	2.9	6.4	9.8		1.6	1.2	27.0	
HM + 0.17	0.0											

a = indicates olefin: i-C<sub>4</sub> and i-C<sub>5</sub>, isobutane and isopentane. Others are aliphatics. <sup>b</sup> Indicates the amount of disilane chemisorbed in mmol g<sup>-1</sup>.



Figure 6. FTIR-PA spectra of the successively modified zeolite: (a) H-mordenite; (b) after chemisorption at 423 K; (c) hydrolysis-dehydration of the disilanated mordenite; (d) partial rehydration; (e) after the third cycle modification.

at  $3610 \text{ cm}^{-1}$  and the framework vibrations between 400 and 1250 cm<sup>-1</sup> of the modified zeolite is indicative of the disilanation process taken place on the external surface. The overall reduction of pore opening size of the successively modified zeolite is also a reflection of the high stability of these structural obstructions in alumino-silicate zeolites, which were introduced via the chemisorption of their hydrides.<sup>2,7,19</sup>

The apparent reduction of the pore size by the successive modification process, therefore, possibly envisages the following situations. (i) A reaction between disilane and hydroxyl groups on the external surface, which results in new disilyl groups attached to the zeolite framework. The hydroxyl groups are probably restored on the surface during the partial rehydration process. These hydroxyl groups could be the terminal silanol Si-OH, as indicated by FTIR-spectra in Figure 6, or the hydroxyl groups attached to detrital aluminum in the zeolite. Indeed, a migration of expelled aluminum into the surface has been observed for hydrolyzed zeolite according to an XPS study.<sup>27</sup> (ii) Shrinkage



Figure 7. Reactant shape selectivity of disilanated mordenite: ( $\blacksquare$ ) *n*-hexane cracking and ( $\odot$ ) 2,2-dimethylbutane cracking.



Figure 8. Product shape selectivity of *n*-hexane cracking on disilanated mordenite:  $(\blacksquare)$  propane and  $(\bullet)$  isobutane.

of the unit cell as the result of a partly substitution of the smaller Si atom for Al in the framework, or the Si occupation of the defect sites created during the deammoniation. However, the second factor is more insignificant, as no additional pore reduction has been observed if by only prolonging hydrolysis (473 K). Moreover, it is unlikely the isomorphous substitution can account for the overall reduction of the effective zeolite pore size.

Cracking of Hexanes. In order to confirm the fine controlling of the pore opening size without affecting the catalytic active site in the zeolite, cracking of hexanes was carried out on the Hmordenite modified with disilane at 423 K, which had undergone a hydrolysis-dehydration treatment. It was found that the disilanated H-mordenites possess both extremely high reactant and product shape selectivity, as shown in Figures 7 and 8. The modified zeolite (chemisorption with 0.11 mmol of disilane per gram of zeolite) exhibits an important shape selectivity. Indeed, the conversion rate for 2,2-dimethylbutane was significantly depressed while a conversion of 90% n-hexane was obtained. Although it is uncertain whether the low conversion of 2,2-dimethylbutane occurs on the external surface or inside the intracrystalline channels, the low production of isobutane suggests a considerable product selectivity. With an increase of the disilanation degree, a complete inhibition of the cracking of large molecule has been observed. It is not undoubtedly attributed to

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the inert external surface and overall pore size reduction of the disilanated zeolite. More detailed information on the selectivity of the cracking reaction is presented in Table II. The remarkable increase in propane production compared to isobutane indicates the product shape selectivity. Obviously such effects are caused by the narrowing pore size, so that the smaller molecules can easily diffuse out of the zeolite channels. The smaller diffusion ability of large components inside the zeolite channels causes a further conversion. It is believed that the influence of the geometry-restricted transition state is smaller compared to the product shape selectivity in the disilanated zeolite.

**Registry No.** Xe, 7440-63-3; Kr, 7439-90-9; Ar, 7440-37-1; O<sub>2</sub>, 7782-44-7; N<sub>2</sub>, 7727-37-9; H<sub>2</sub>O, 7732-18-5; disilane, 1590-87-0; butane, 106-97-8; hexane, 110-54-3; 2,2-dimethylbutane, 75-83-2.

# Electron Spin Resonance and Electron Spin Echo Modulation Spectroscopic Studies of the Photolonization of Phenothiazine Derivatives in Alkyl Sulfate and Alkyltrimethylammonium Bromide Micellar Solutions

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Electron spin echo modulation and electron spin resonance of photoionized  $\omega$ -phenothiazin-9-ylalkanesulfonate with alkyl =  $C_3H_7$ ,  $C_6H_{13}$ , and  $C_{12}H_{25}$  ( $PC_{\pi}S$ ), 9-alkylphenothiazinesulfonate with alkyl =  $CH_3$  and  $C_{12}H_{25}$  ( $C_nPS$ ), and methylphenothiazine have been studied as a function of the surfactant alkyl chain length of sodium alkyl sulfate and alkyltrimethylammonium bromide micellar solutions in  $D_2O$ , with alkyl = decyl, dodecyl and tetradecyl. Deuterium modulation effects from x-doxylstearic acid interactions with water deuteriums indicate that only the decyl surfactants form micelles with significant water penetration at the micellar interface. The efficiency of charge separation upon phenothiazine photoionization mainly depends on the strength of the phenothiazine cation-water interactions which is partially controlled by the phenothiazine and surfactant alkyl chain lengths, suggesting that a particular location of the phenothiazine group near the micellar interface is required to optimize the photoefficiency for charge separation.

# Introduction

Surfactant systems are commonly used as models in the study of photoinduced electron-transfer processes.<sup>1-4</sup> Photoionization and charge separation processes in these organized molecular assemblies are significantly affected by several structural factors. It has been shown that the monophotonic photoionization process of N, N, N', N'-tetramethylbenzidine (TMB) in aqueous micellar solutions is dependent on micellar counterions, micellar size and shape, micellar charge, the presence of surface active additives such as alcohols or crown ethers that affect the micellar surface charge density, and the structure of the micelle interface.<sup>5-14</sup> In particular, it has been shown that the photoefficiency of TMB in the charge separation process depends (1) upon the  $TMB^+$ water interaction at the micellar interface, (2) upon the micellar surface charge, and (3) upon the water organization or structure at the micellar interface. These results have also been confirmed with other lipophilic systems, such as TMB adsorbed at the interface of polymeric latexes.14

Recent kinetic results<sup>15,16</sup> based on the oxidative quenching of excited triplets of (5,10,15,20-tetrakis(4-sulfonatophenyl)porphinato)zinc(II) ion by alkylmethylviologen derivatives solubilized in dihexadecyl phosphate vesicles suggest that the changes in electron acceptor kinetics are dependent on the viologen alkyl chain length, i.e., on the viologen location at the vesicle interface. Furthermore, an optimal photoionization yield has been found for alkylruthenium complexes (C<sub>5</sub> and C<sub>17</sub>) with hexylmethyl- and octylmethylviologen in sodium dodecyl sulfate micellar solutions.<sup>17</sup> All these results suggest that a particular location of the photoionizable molecule with respect to the micelle or vesicle interface is necessary to optimize the photoionization yield. In this study results are reported for phenothiazine derivatives solubilized in micellar solutions of alkyl sulfate (anionic) and alkyltrimethyl-

#### **TABLE I: Structures of Alkylphenothiazines**



ammonium bromide (cationic) surfactants. Two different approaches to change the phenothiazine group location with respect

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