Registry No. 4 (copolymer), 118476-48-5; $(MeCN)_2PdCl_2$, 14592-56-4; $(Ph_3P)_2PdCl_2$, 13965-03-2.

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An NMR Study of the Solubilization of Aromatic Compounds in Aggregates of Poly(maleic acid-*co*-butyl vinyl ether) and Dodecyltrimethylammonium Bromide

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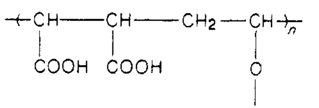
Introduction

Poly(maleic acid-*co*-butyl vinyl ether) (PMA-BVE, I) is a water-soluble hydrophobic polymer,[1] which undergoes a transition from a compact conformation to an expanded form with increasing ionization of the carboxylic acid groups.[2] The interactions between fully ionized PMA-BVE and cationic surfactants have recently been investigated by Binana-Limbele and Zana,[3] using solubilized pyrene as a fluorescence probe. The results of this study lead the authors to suggest that mixed micelles are formed with units of PMA-BVE and the cationic surfactants, which provide a nonpolar environment for the solubilized pyrene. Fluorescence probe studies of other polymer–surfactant aggregates in aqueous solution have also recently appeared.[4-8] These studies clearly indicate that polymer–surfactant complexes can solubilize some hydrophobic aromatic probe molecules into a nonpolar environment, similar to micellar solutions. It is of interest to further characterize the primary sites of solubilization in polymer–surfactant systems using other techniques. Ring current induced ^1H NMR shifts have been used to determine the location of aromatic solubilizates in micelles;[9-14] yet the technique has not been widely applied to polymer–surfactant systems.[15] If aromatic ring current induced shifts are observed for protons of the surfactant alkyl chain or for those of the polymer hydrophobic side chain, this is a clear indication of an average close proximity to the aromatic solubilizate, even though the absence of a ring current effect may only mean independent isotropic motion, rather than a large separation.[16] In this paper we report ring current shifts for surfactant and polymer side-chain proton resonances due to the solubilization of benzene, naphthalene, acridine, and pyrene in fully ionized PMA-BVE/dodecyltrimethylammonium bromide (DTAB) aggregates.



I

Experimental Section

PMA-BVE was prepared in our laboratory by the copolymerization of maleic anhydride and butyl vinyl ether in benzene using benzoyl peroxide as initiator.[17] Maleic anhydride and butyl vinyl ether (Aldrich) were purified by recrystallization from distilled benzene and by distillization at 93–94 °C, respectively. The butyl copolymer was dissolved in tetrahydrofuran (THF) and then successively precipitated into diethyl ether and vacuum dried. The resulting copolymer was added to a solution containing an equivalent amount of NaOH and kept at 80 °C for about 7 h; then excess HCl was added and the solution was dialyzed exhaustively against distilled water. The purified acid form of PMA-BVE was freeze dried and stored under vacuum. The copolymer was analyzed by means of IR, ^1H NMR, viscosity, and potentiometric titrations. The viscosity molecular weight of the copolymer anhydride in THF was determined to be 3.8×10^6.

The degree of neutralization, α', of PMA-BVE is defined as 1 for the acid form of the polymer neutralized with 2 equiv of base per monomer unit. The $\alpha' = 1$ sample used in the ^1H NMR measurements was obtained by titrating solid PMA-BVE (acid form) with 0.1120 m NaOD in D_2O. The pH of the final solution was about 8.5. At this pH, α' is very close to α, the degree of ionization of the polymer.

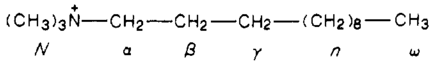
DTAB (Sigma) was purified by repeated recrystallization from acetone; the sample was the same as that used in an earlier surfactant-binding study.[18]

Polymer–surfactant solutions were prepared by slowly adding concentrated DTAB stock solution in D_2O to the PMA-BVE stock solution ($\alpha' = 1$) of known concentration. Although precipitation of a polymer–surfactant complex may occur due to local excesses of DTAB during addition, all solutions studied were completely clear after about 1 h of stirring. Aromatic solubilizates were added to the polymer–surfactant solution. All solutions were prepared by mass, and all concentrations are given as molalities (mol/kg of D_2O). Polymer concentrations are given on a monomer basis. D_2O was 99.8% pure (ICN).

^1H NMR spectra were recorded at 361.053 MHz (8.48 T), using a Nicolet 360NB spectrometer. The residue HOD ($\delta = 4.63$ ppm) was used as an internal reference for the proton spectra. All NMR measurements were carried out at 24 ± 1 °C.

Results and Discussion

The ^1H NMR spectrum of 0.020 m DTAB is shown in Figure 1a; the spectrum was assigned by using standard double resonance techniques.[15] The notation used to describe the various protons of surfactant segments is as follows:



$$\underset{N}{(CH_3)_3\overset{+}{N}}-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-\underset{\gamma}{CH_2}-\underset{n}{(CH_2)_8}-\underset{\omega}{CH_3}$$

The ^1H NMR spectrum of PMA-BVE(0.045 m)/DTAB(0.020 m) is shown in Figure 1b. Spectral assign-

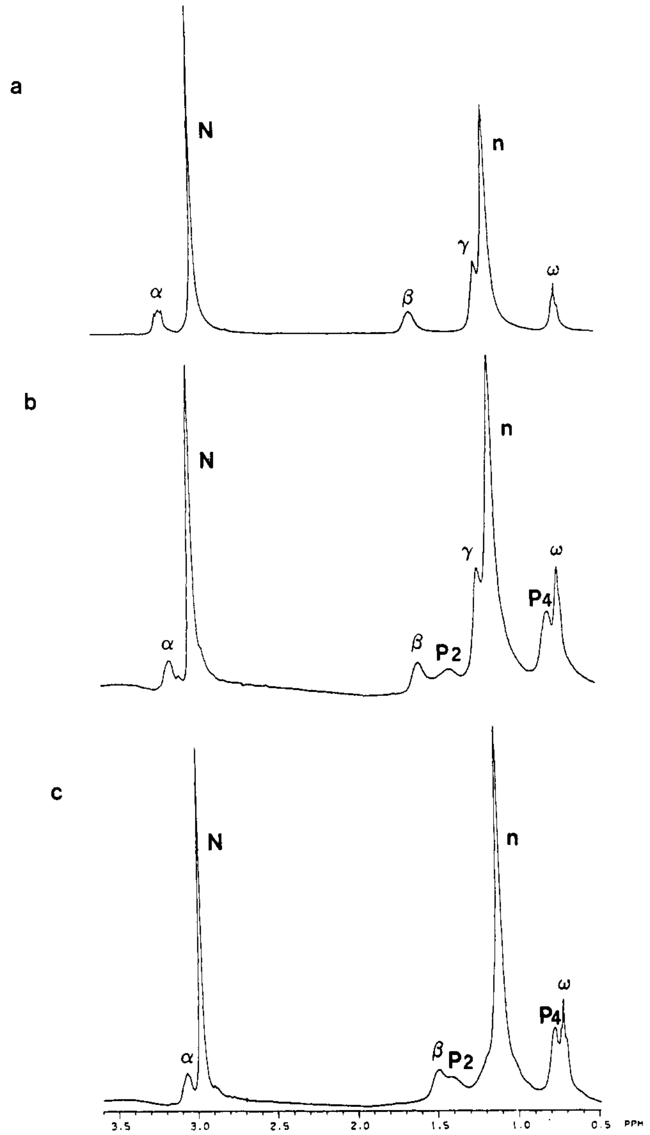


Figure 1. ^1H NMR spectra of DTAB (a), PMA-BVE/DTAB (b), and PMA-BVE/DTAB/benzene (c). Concentrations: DTAB, 0.020 *m*; PMA-BVE ($\alpha' = 1$), 0.045 *m*; benzene, 0.030 *m*.

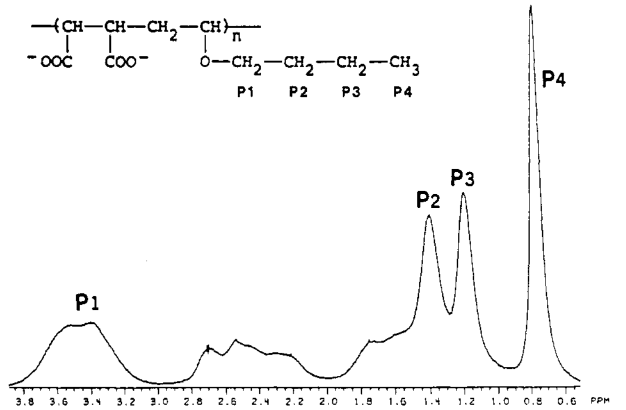


Figure 2. ^1H NMR spectrum of 0.045 *m* PMA-BVE ($\alpha' = 1$) solution.

ments were made by comparing the spectrum of the polymer–surfactant system with those of the polymer ($\alpha' = 1$) solution and of the surfactant solution at the same concentrations. The PMA-BVE ($\alpha' = 1$) spectrum (Figure 2) was assigned by standard double-resonance techniques. Proton spin–lattice relaxation time (T_1) measurements also indicate that T_1 increases continuously from the first CH_2 group to the terminal CH_3 group in the PMA-BVE ($\alpha' = 1$) side chain.[19] In Figures 1 and 2, the ^1H resonance of the *n*th CH_2 group in the polymer side chain is denoted P*n* with $n = 1$ being the CH_2 group adjacent to the ether oxygen. Figure 1c shows the low-frequency portion of a typical PMA-BVE/DTAB/aromatic solubilizate spectrum (PMA-BVE, 0.045 *m*; DTAB, 0.020 *m*; benzene, 0.030 *m*).

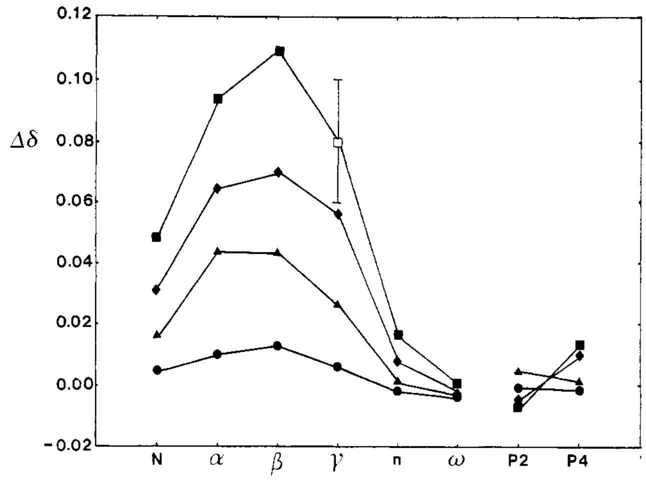


Figure 3. Changes in proton chemical shifts (in ppm) of DTAB and PMA-BVE upon addition of benzene to the PMA-BVE/DTAB solution. $\Delta\delta = \delta$ (in PMA-BVE/DTAB) − δ (in PMA-BVE/DTAB/benzene). Concentrations: PMA-BVE, 0.045 *m*; DTAB, 0.020 *m*; benzene, (●) 0.005 *m*, (▲) 0.010 *m*, (◆) 0.020 *m*, and (■) 0.030 *m*.

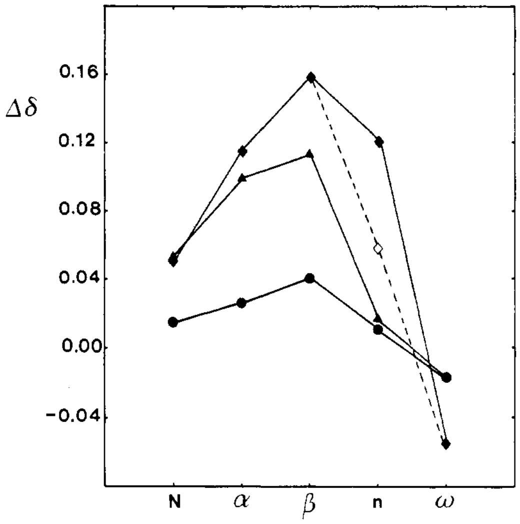


Figure 4. Changes in proton chemical shifts (in ppm) of DTAB upon addition of 0.001 *m* pyrene to the PMA-BVE(0.080 *m*)/DTAB(0.040 *m*) solution (●), 0.005 *m* naphthalene (▲), and 0.005 *m* acridine (◆) to PMA-BVE(0.045 *m*)/DTAB(0.020 *m*) solutions. ◇ denotes the peak separated from the $(CH_2)_n$ proton resonance upon the solubilization of acridine. $\Delta\delta = \delta$ (in PMA-BVE/DTAB) − δ (in PMA-BVE/DTAB/aromatic solubilizate).

Ring current induced shifts observed when 0.005, 0.010, 0.020, and 0.030 *m* benzene were solubilized in PMA-BVE/DTAB (PMA-BVE, 0.045 *m*; DTAB, 0.020 *m*) solutions are shown in Figure 3. The aromatic ring current shifts of the proton resonances of the surfactant are in the order β-CH_2 > α-CH_2 > γ-CH_2 > N-CH_3; almost no effect on the $(CH_2)_n$ and ω-CH_3 resonances is observed, indicating that the benzene is primarily solubilized near the surfactant headgroup. Estimated errors in the $\Delta\delta$ values given in Figures 3 and 4 are ±0.002 ppm, except for the case of the γ-CH_2 at the highest benzene concentration, where the proton resonance overlaps with the $(CH_2)_n$ proton resonance.

Information about the structure of the polymer–surfactant aggregate can also be obtained from the aromatic ring current induced shifts of the polymer proton resonances. Although Binana-Limbele and Zana have suggested mixed micelle formation in the PMA-BVE/DTAB system,[3] the interior structure is still unknown. If in PMA-BVE/DTAB aggregates polymer side chains are in close proximity to surfactant α-CH_2, β-CH_2, and γ-CH_2 groups, ring current induced shifts should be also observed in the proton resonances of polymer side chains. In fact, when benzene is solubilized in PMA-BVE/DTAB solutions, very small ring current shifts are observed for polymer P2 and P4 proton resonances, while large shifts are observed for α-CH_2, β-CH_2, and γ-CH_2 proton resonances of DTAB. These observations suggest that the polymer side chain is not in close proximity to the α-, β-, and γ-methylene protons of the surfactant. We also used ω-phenylbutylammonium chloride as a solubilizate in the PMA-BVE/DTAB system.[20] Aromatic ring current induced shifts were observed not only for the α-CH_2, β-CH_2, and γ-CH_2 proton resonances of the surfactant but also for the surfactant $(CH_2)_n$ and polymer side-chain proton resonances upon the solubilization of ω-phenylbutylammonium chloride in the PMA-BVE/DTAB aggregates, indicating that some of the phenyl groups of the solubilized ω-phenylbutylammonium chloride and the polymer side chains are located near the center of the polymer–surfactant aggregates. Our ^{1}H NMR chemical shift study of the poly(maleic acid-*co*-styrene)/DTAB system[15] also indicates that the phenyl group of poly(maleic acid-*co*-styrene) interacts strongly with the surfactant central methylene groups, $(CH_2)_n$, and with the ω-CH_3 group, but less with the *N*-CH_3 and the α-CH_2 groups. On the basis of these observations, the structure of the aggregate of PMA-BVE/DTAB appears to be one where the butyl ether side chain of the polymer and the main methylene chain of the surfactant are on average located in the interior, with the ion-pairing carboxylate groups of the polymer and the headgroup of the surfactant on the surface. Solubilized benzene is close to the surface of the polymer–surfactant aggregate and to the surfactant α-, β-, and γ-methylene groups.

Sites of solubilization of naphthalene, acridine, and pyrene were also investigated by observing their induced ring current shifts along the surfactant alkyl chain in PMA-BVE/DTAB solutions. Ring current shifts of 0.005 *m* naphthalene in 0.045 *m*/0.020 *m* PMA-BVE/DTAB, 0.005 *m* acridine in 0.045 *m*/0.020 *m* PMA-BVE/DTAB, and 0.001 *m* pyrene in 0.080 *m*/0.040 *m* PMA-BVE/DTAB systems are shown in Figure 4. These results indicate that naphthalene, acridine, and pyrene are also primarily solubilized near the surfactant headgroup in the polymer–surfactant aggregates. Recent photophysical studies also demonstrated that in micellar solution pyrene is solubilized in the micelle–water interfacial region.[21] It is of interest to note that, from an earlier ^{1}H NMR study of ring current shifts, it was concluded that pyrene was solubilized in the interior of cetyltrimethylammonium bromide (CTAB) micelles.[22] In this earlier study, the pyrene concentration was 0.01 M, much higher than what is used in the fluorescence studies or in the present work. In the case of acridine solubilized in PMA-BVE/DTAB solution, the surfactant $(CH_2)_n$ proton resonance is separated into two peaks, denoted ♦ and ◊ in Figure 4, similar to the case of 1-methylnaphthalene solubilized in CTAB micelles.[23]

When there is excess anionic polyelectrolyte in solution, the complexes with cationic surfactants are negatively charged.[4,5] The PMA-BVE/DTAB aggregate was shown to have negative charge from fluorescence lifetime measurements of solubilized pyrene.[3] In anionic sodium dodecylsulfate (SDS) micelles, ring current induced ^{1}H shifts seem to indicate that aromatic molecules are distributed evenly throughout the micelle.[14] In this PMA-BVE/DTAB system, the solubilization of aromatic molecules is similar to the case of cationic alkyltrimethylammonium micelles, with the aromatic molecules solubilized near the surfactant headgroup. These results indicate that the sign of surface charge is not an important factor for the time-average position of aromatic molecules in micelles.

Conclusion

Solubilization of the aromatic molecules benzene, naphthalene, acridine, and pyrene in polymer–surfactant PMA-BVE/DTAB solution has been investigated by ^{1}H NMR spectroscopy. On the basis of the observed aromatic ring current induced ^{1}H shifts, it can be concluded that these aromatic compounds are primarily solubilized near the headgroups of DTAB in PMA-BVE/DTAB aggregates. Very small ring current induced ^{1}H shifts on the polymer PMA-BVE alkyl side chain were observed upon solubilization of the aromatic molecules, indicating that the polymer side chain is probably not close to the headgroups of the surfactant.

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Registry No. (PMA)(BVE) (copolymer), 38193-45-2; DTAB, 1119-94-4; benzene, 71-43-2; naphthalene, 91-20-3; acridine, 260-94-6; pyrene, 129-00-0.

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