Interactions of a Hydrophobically Modified Polymer with Oppositely Charged Surfactants

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The interaction of a hydrophobically modified anionic polymer (PMAOVE) with a cationic surfactant (DTAB) was studied using a multi-technique approach: turbidity, surface tension, and viscosity measurements, as well as EPR (5-doxyl stearic acid) and fluorescence (pyrene) probe techniques were used. In the investigated pH range (4−10), the cationic surfactant headgroups interact with the anionic carboxylic groups of the polymer backbone. In addition, nonpolar interactions of the surfactant chains with the *n*-octyl chains of PMAOVE stabilize the PMAOVE−DTAB complexes. Charge neutralization of the anionic polymer by the cationic surfactant leads to precipitation of the PMAOVE−DTAB complex at a certain DTAB concentration range. Further addition of DTAB causes a charge reversal of the complex and, subsequently, resolubilization of the precipitate. At an acidic pH (pH = 4), a second precipitation was observed, which is probably caused by conformational changes in the PMAOVE−DTAB complex. This second precipitate can be resolubilized by further addition of surfactant. At a neutral and basic pH, this second precipitation is absent. EPR analysis indicates that the surfactants form an ordered structure at the extended polymer chain at a neutral and basic pH, whereas at an acidic pH, a less ordered surfactant layer is formed on the coiled polymer with more hydrophobic microdomains.

Introduction

Hydrophobically modified polyelectrolytes (HMPs) have gained increasing interest in the last decades because of their unusual rheological properties and unique associative behavior.[1−5] The formation of complexes between surfactants and HMPs in aqueous solutions is of special interest due to the important practical applications in detergency, cosmetics, food, and paints.[6,7] These complexes result from electrostatic and hydrophobic forces and raise some fundamental questions about the polymer−surfactant interactions controlling their behavior.[6−9] Attractive interactions, either weak (between nonionic polymers and anionic surfactants) or strong (between oppositely charged polyelectrolytes and surfactants), provide the driving force for the complex formation.[6,7,10]

The role of these attractive interactions has become of considerable interest only in the past decade, and a number of questions are still debated.[11−20] In the present study, we investigate the interactions between a hydrophobically modified anionically charged copolymer poly(maleic acid/octyl vinyl ether) (PMAOVE; Scheme 1) and a surfactant of opposite charge, dodecyl trimethyl ammonium bromide (DTAB; Scheme 1). The interactions were studied by means of a multi-technique approach, involving the computer aided analysis of electron paramagnetic spectra (EPR) obtained by adding the paramagnetic probe 5-doxylstearic acid (5-DSA; Scheme 1), which inserts itself in surfactant aggregates. EPR analysis, together with measurements of turbidity, surface tension, viscosity, and fluorescence spectroscopy, provide an

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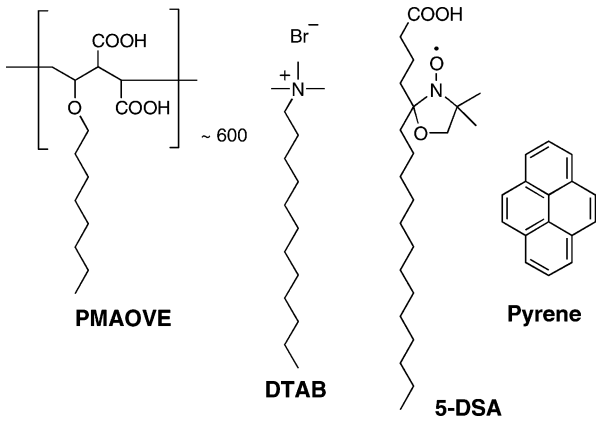
Scheme 1. Structures of the Polymer, Surfactant, and Probes



overall view of the PMAOVE + DTAB system as a function of the surfactant concentration. Different pH conditions were tested to understand the extent and strength of the interactions.

Experimental Procedures

Materials. Polymers. The hydrophobically modified polymer, PMAOVE, provided by International Specialty Products, Inc., was synthesized using free radical polymerization of a 1:1 mol ratio of maleic anhydride and octyl vinyl ether in toluene with Vazo-69 (azobisvaleryl nitrile) as the initiator. The polymer was purified twice by first dissolving in acetone (5% w/w) followed by precipitation with an excess of *tert*-butyl alcohol (40 times in volume). The residual solvent was removed in a vacuum at 50 °C to a constant mass. The anhydride moiety of the polymer was then hydrolyzed in triple-distilled water to make an approximately 5% (w/w) solution. The solution was stirred at 500 rpm at 70 °C for about 12 h and then freeze-dried. As determined by gel permeation chromatography, the weight average molecular weight (MW) was 160 000 Da with a polydispersity index of 1.23.

Probes and Additives. The spin probe 5-DSA (Aldrich, 99+% pure; Scheme 1), pyrene (Aldrich), DTAB (Aldrich, 99+% pure), and NaCl (Fluka, 99.5% pure) solutions of 0.1 N hydrochloric acid (Fisher Scientific) and 0.1 N NaOH (Fisher Scientific) were used as received. Triple-distilled water was used in all experiments.

Methods. Turbidity Measurements. Turbidity measurements were performed on a DRT-100B turbidity meter (HF Scientific, Inc.) using 20 mL glass vials as sample containers. Prior to each measurement, the instrument was calibrated with a 0.02 ntu (normalized turbidity units; a.u.) standard solution, which was provided by the manufacturer.

EPR Measurements. EPR spectra were recorded using a Bruker EMX spectrometer operating at the X band (9.5 GHz). All EPR spectra were recorded at 22 ±1 °C. The concentration of the probe molecule (5-DSA) used in all the studies was 10^{-4} M. The desired portions of 5-DSA in chloroform were added to a glass vial, and the solvent was evaporated. Then, the aqueous polymer and polymer−surfactant solutions of desired concentrations and volumes were added to the vials under stirring. EPR spectra of these solutions were recorded 24 h after sample preparation using Pyrex capillary tubes (1 mm inner diameter) as the sample container.

Surface Tension Measurements. The surface tension of the surfactants and the polymer−surfactant solutions was measured by the Wilhelmy plate technique using a sandblasted platinum plate as the sensor. The pull exerted on the sensor was determined using a Beckman microbalance (model LM600). The entire assembly was kept in a draft-free plastic cage at a temperature of 25 ±0.05 °C. For each measurement, the sensor was in contact with the solutions for 30 min to allow equilibration.

Viscosity Measurements. A calibrated capillary viscometer (Canon Instruments) was used for measuring the relative viscosity on the basis of that of the triple-distilled water at 25 ± 0.05 °C. The viscometer was cleaned with chromic acid and triple-distilled water and thoroughly dried with acetone before the measurements. The efflux time for triple-distilled water was checked before every measurement for reproducibility of the results.

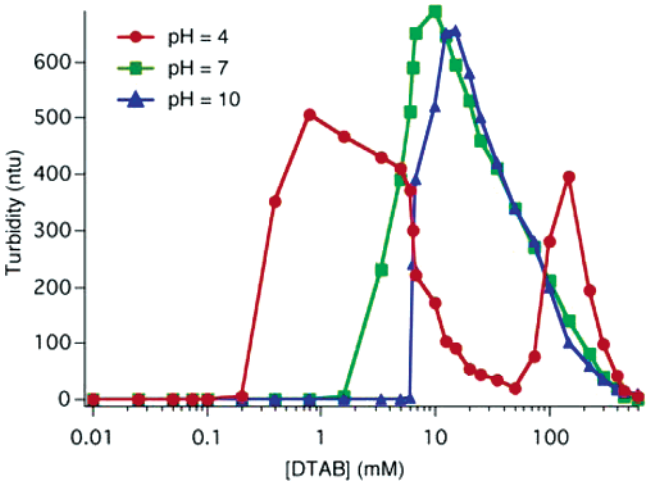


Figure 1. Turbidity of solutions containing PMAOVE (0.1% w/w) and different concentrations of DTAB at pH = 4, 7, and 10.

Fluorescence Measurements. Fluorescence spectra were recorded on a SPEX FluoroMax 2 spectrofluorometer (Jobin Yvon, Inc.) using pyrene (0.05 mM) as the fluorescence probe at an excitation wavelength of 335 nm. For micropolarity measurements, fluorescence intensities at the peak maxima of 373 nm (I_1) and 383 nm (I_3) were recorded using sample cells of a 10 mm path length. The solutions were used without further treatment (no centrifugation).

Results and Discussion

Turbidity Measurements. Turbidity measurements were performed to investigate the solubility of PMAOVE in the presence of the surfactant DTAB. Figure 1 shows the variation of the turbidity as a function of DTAB concentration at pH = 10, 7, and 4. At pH = 10, transparent solutions of PMAOVE (0.1% w/w) and DTAB (0−6 mM) were observed as indicated by the low turbidity parameter (∼0). However, a further increase of the DTAB concentration (>6 mM) caused a sharp increase in the turbidity parameter, and a white precipitate was observed. This precipitate was redissolved after further increase of the DTAB concentration (>20 mM) as indicated by the decreasing turbidity parameter. At a neutral pH (pH = 7), a similar function of the turbidity with increasing DTAB concentrations was observed. The precipitation and resolubilization occurred at slightly smaller DTAB concentrations (2 and 15 mM, respectively). At an acidic pH (pH = 4), a very different solubility behavior of PMAOVE in the presence of increasing concentrations of DTAB was observed (Figure 1). The turbidity curve shows two maxima (two precipitation regions) at [DTAB] = 0.6 and 200 mM followed by resolubilization after each precipitation step.

Surface Tension Measurements. Surface tension measurements are commonly used to probe micellization and aggregation in surfactant containing solutions. Figure 2 shows the variation of the surface tension as a function of DTAB concentration for the DTAB solution in the absence and in the presence of PMAOVE at pH = 4 and 10. The surface tension values at pH = 7 are very similar to the values at pH = 10 with a minor shift of the maximum to lower DTAB concentrations. In case of precipitation, the surface tension was measured for the supernatant solution after centrifugation. For pure DTAB solutions without PMAOVE, a sharp decrease in surface tension was observed in a narrow DTAB concentration range, which corresponds to the

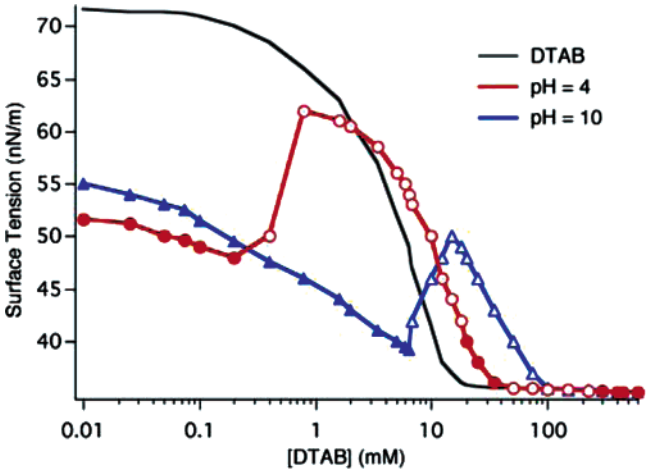


Figure 2. Surface tension as a function of DTAB concentration in the absence and presence of PMAOVE (0.1% w/w) at pH = 4 and 10. In case of precipitation, the solutions were centrifuged. The data points for the centrifuged solutions are marked as open circles (pH = 4) and open triangles (pH = 10).

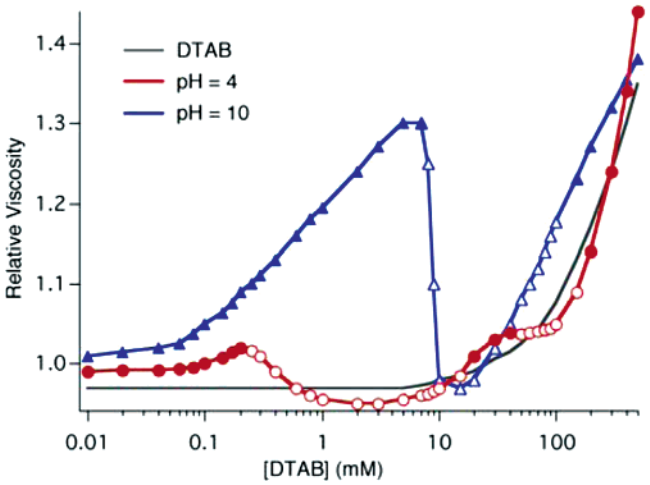


Figure 3. Relative viscosity as a function of DTAB concentration in the absence and presence of PMAOVE (0.1% w/w) at pH = 4 and 10. In case of precipitation, the solutions were centrifuged. The data points for the centrifuged solutions are marked as open circles (pH = 4) and open triangles (pH = 10).

cmc of the surfactant (cmc = 15 mM).[26] Solutions of PMAOVE (0.1% w/w) show a significantly lower surface tension (55 mN/m) than pure water (70 mN/m) due to the adsorption of the C8 chains of the maleic acid backbone on the air−solid interface.[21] The addition of small amounts of DTAB decreased the surface tension slightly due to PMAOVE−DTAB interactions. At pH = 4 and DTAB concentrations between 0.6 and 12 mM, precipitation was observed. After centrifugation, the supernatant showed an increased surface tension (Figure 2), due to the loss of PMAOVE and DTAB in the precipitate. Similarly, at pH = 10 in the precipitation region (7 mM < [DTAB] < 100 mM), the surface tension of the supernatant increases. At very high DTAB concentrations ([DTAB] > 100 mM), all the curves in Figure 2 converge to a low surface tension value (35 mN/M), which is the value for pure DTAB micelles. At these high DTAB concentrations, also in the presence of PMAOVE, the surface tension is dominated by the DTAB micelles due to its large excess as compared to the polymer. A similar dominance of the surfactant property at very high surfactant concentrations was observed for the PMAOVE−SDS system.[21]

Viscosity Measurements. Figure 3 shows the variation of the relative viscosity as a function of DTAB concentration for DTAB solutions in the absence and in the presence of 0.1% PMAOVE at pH = 4 and 10. The viscosity values at pH = 7 are very similar to the values at pH = 10 with a minor shift of the maximum to lower DTAB concentrations. In the case of precipitation, the solutions were centrifuged, and the viscosity was measured for the supernatant solutions. As expected, in the absence of PMAOVE, the viscosity increases above the cmc (15 mM) due to the formation of micelles. In the presence of 0.1% PMAOVE at pH = 4, the viscosity increased slightly with increasing concentrations of DTAB up to a concentration of 0.4 mM, indicating complexation. At DTAB concentrations between 0.5 and 15 mM, precipitation was observed, and the viscosity of the supernatant decreased due to the loss of polymer (Figure 3). Upon further increase of the DTAB concentration, the precipitate redissolved, and the viscosity increased.

A stronger effect of PMAOVE−DTAB complexes on the viscosity was observed under basic conditions (pH = 10). With increasing concentrations of DTAB up to 6 mM, the viscosity increased strongly, which indicates that bulky structures are formed in the complexation of PMAOVE with DTAB (Figure 3). In a DTAB concentration range from 6 to 25 mM, precipitation of the PMAOVE−DTAB complexes occurred, and the viscosity of the supernatant dropped to a viscosity value similar to pure water due to the loss of the polymer. At DTAB concentrations above 25 mM, the precipitate redissolved, and the viscosity increased.

EPR Analysis. The experimental methods discussed previously provided information about the bulk properties of solutions containing PMAOVE−DTAB complexes. To investigate the PMAOVE−DTAB supramolecular complexes on a molecular level, EPR was employed using the free radical 5-DSA (Scheme 1) as a spin probe.

The physical behavior of the PMAOVE + DTAB system changed significantly as a function of the DTAB concentration and of the pH. Figure 4a shows selected EPR spectra of this system at pH 7. The spectra between 0 and 20 mM of DTAB show the superposition of two signals: a narrow three line signal due to free 5-DSA radicals in fast motion (termed fast component) and a broader signal where the anisotropic magnetic components are largely resolved, arising from slow moving radicals (termed slow component). The analysis of these components was performed by computing the line shape by means of the well-established procedure of Freed et al.[22−23] The main parameters that were varied were (1) the magnetic components of the hyperfine **A** tensor (for the coupling between the unpaired electron spin and the nitrogen nuclear spin). The increase in the A_{zz} component corresponds to the increase of the environmental polarity of the nitroxide.[24] (2) The perpendicular component of the correlation time for the rotational diffusional motion, τ_{perp}, was varied in the simulation of the EPR spectra. A Brownian model was assumed. The increase in τ_{perp} reports on the increased microviscosity of the nitroxide environment. (3) If necessary, an order parameter, *S*, had to be included in the calculation, due to the insertion of the probe in an ordered surfactant layer. *S* varies between 0 and 1, where 1 corresponds to the maximum order. Figure 4b,c shows the computations (red dashed lines) obtained

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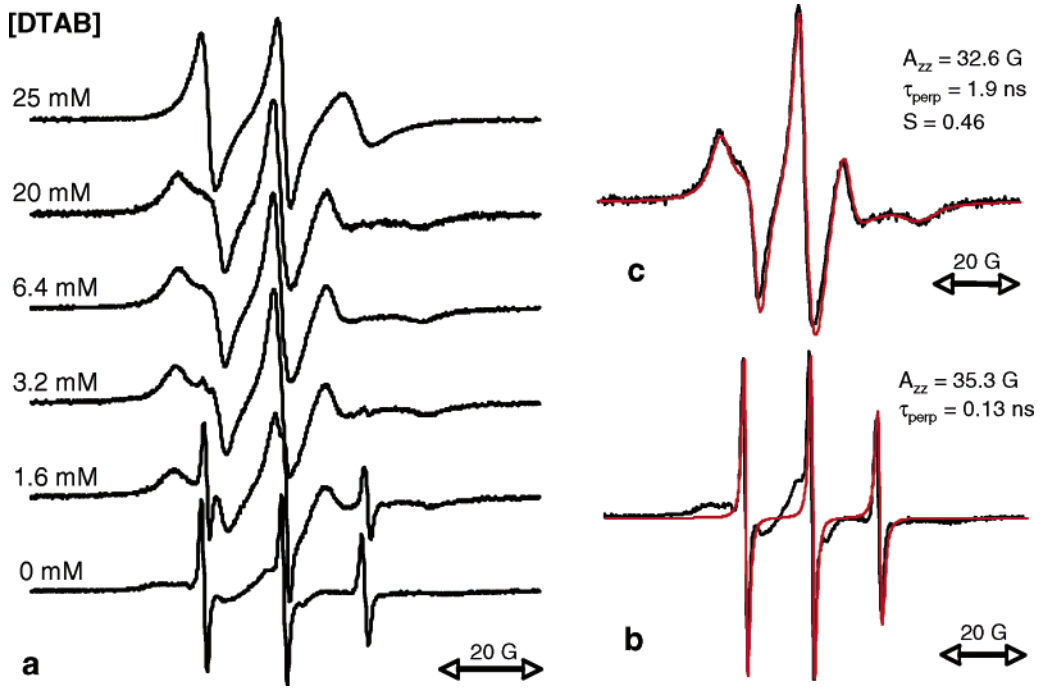

Figure 4. (a) Selected experimental EPR spectra of 5-DSA in PMAOVE (0.1% w/w) + DTAB mixtures at different DTAB concentrations and pH = 7. (b and c) Experimental (black line) and computed (red dashed line) spectra of PMAOVE water solution (0.1% w/w) at pH = 7 in the absence (b) and presence of [DTAB] = 6.5 mM (c). The main parameters used for computations are also shown.

for the fast component and the slow component, respectively, at [DTAB] = 0 mM and [DTAB] = 6.5 mM (experimental spectra as black lines). For the computation of the slow component, the order parameter (S) needed to be included in the simulation. Probably, the positively charged surfactant headgroups electrostatically interact with the negatively charged PMAOVE groups, while the surfactant chains form an ordered structure at the polymer surface. This supports the view of an open extended conformation of the polymer, where the negatively charged groups are exposed to electrostatic interactions with the surfactant heads.

We could expect that at pH = 7, the maleic acid groups are only partly deprotonated. However, the EPR spectra at pH = 10 are similar to those at pH = 7, except that the order parameter is higher (e.g., $S = 0.48$ at [DTAB] = 6.5 mM) and the mobility parameter is lower (e.g., $\tau_{perp} = 2$ ns at [DTAB] = 6.5 mM) for the slow moving probes.

Another interesting feature for the PMAOVE + DTAB system at pH = 7−10 is the progressive increase of the relative intensity of the slow component with respect to the fast component from [DTAB] = 0 mM to [DTAB] = 6−7 mM: the relatively few free probes are progressively extracted from the solution and are absorbed into the surfactant layer at the polymer surface. This is shown in Figure 5a, which reports the variation of the relative intensity of the slow motion signal with respect to the fast motion one as a function of the DTAB concentration. The disappearance of the fast motion signal results from the progressive neutralization of the polymer charge that decreases repulsion and allows the free hydrophobic radicals to be hosted at the polymer surface.

Corresponding to the variation of the relative intensity shown in Figure 5a, the slow motion spectrum is also slightly modified, indicating a small variation in the chain packing: both the order parameter and the rotational mobility slightly increased by increasing the DTAB concentration up to about 10 mM of DTAB. But, the computation parameter that better reports on the structural variations of the system is the A_{zz} value, indicating the variation of the polarity in the nitroxide environment.[24] The plot of A_{zz} as a function of DTAB concentration is shown in Figure 5b. The environmental polarity of the probes decreases (decrease of A_{zz}) when the surfactants neutralize the polymer charged sites and the doxyl group absorbs into the hydrophobic microdomains of PMAOVE.[25] Therefore, the decrease in polarity is slowed down at pH = 10 with respect to pH = 7.

The neutralization of the polymer charge finally leads to the precipitation of the polymer, which, as indicated by an arrow in Figure 5a, occurs at a slightly higher DTAB concentration at pH = 10 with respect to pH = 7, due to the higher amount of deprotonated acidic groups at pH = 10. However, both for pH = 7 and for pH = 10, at [DTAB] ≥ 25 mM, the slow motion signal disappears, and a different three line signal is found, which is characteristic of 5-DSA probes inserted in fluid DTAB micelles. This can be compared with the formation of DTAB micelles at the cmc reported in the literature (15 mM);[26] micelle formation is delayed to a higher DTAB concentration by the presence of the polymer. At these DTAB concentrations, as discussed next, the charge reversal due to DTAB aggregates at the PMAOVE surface leads to resolubilization of the PMAOVE−DTAB complexes.

The insertion of surfactants in the hydrophobic PMAOVE microdomains, the formation of PMAOVE−surfactant complexes, and the shift of the cmc of the surfactant caused by PMAOVE have also been shown for the PMAOVE−SDS system.[21] However, the PMAOVE−SDS complexes do not show surfactant−layer ordering and precipitation of the complex followed by resolubilization. In the PMAOVE−SDS complexes, mostly the nonpolar chains of SDS interact with the nonpolar side chains of PMAOVE. However, in the PMAOVE−DTAB complexes, the charge interactions of the positively charged surfactant headgroup with the negative polymer groups (maleic acid) dominate.

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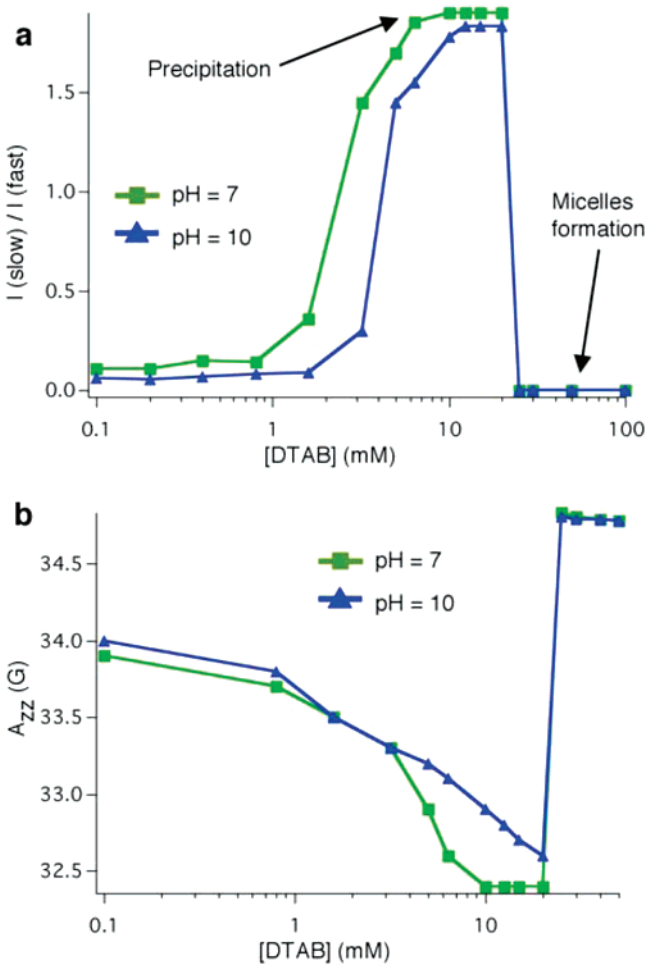

Figure 5. (a) Variation of the relative intensity of the slow component of the EPR spectra as a function of DTAB concentration for the PMAOVE−DTAB mixtures at pH = 7 and 10. (b) Variation of A_{zz} parameter (polarity parameter) extracted from computation of the EPR spectra as a function of DTAB concentration for the PMAOVE−DTAB mixtures at pH = 7 and 10.

The protonation of the polymer at pH = 4 provides a significantly different situation. Figure 6 shows selected experimental (full lines) and computed (dashed lines) spectra of the PMAOVE + DTAB system at pH = 4 at different DTAB concentrations. Comparing A_{zz}, which reports on polarity, with the values at pH = 7 and 10 (Figure 5b), a lower environmental polarity of the probes at pH = 4 was observed than at pH = 7 and 10. The lower polarity of the probe environment suggests that the probes are inserted in more hydrophobic microdomains at the PMAOVE interface.

For simulating the EPR spectra at pH = 4, no order parameter was needed to compute the slow motion signal, which indicates that the surfactant does not form an ordered layer at the polymer surface. Therefore, the rotational correlation time (τ_{perp}) allows tracking of the structural variations of the system with increasing DTAB concentrations, as is shown in Figure 7. The analysis of the graph in Figure 7 shows two different maxima of τ_{perp}. At first, precipitation occurred at a much lower DTAB concentration (the mobility began decreasing at [DTAB] = 0.4 mM, and the correlation time for motion reached its maximum at [DTAB] = 0.8 mM) with respect to pH = 7 since there are only a few charged acidic groups at pH = 4 and the polymer is in a coil

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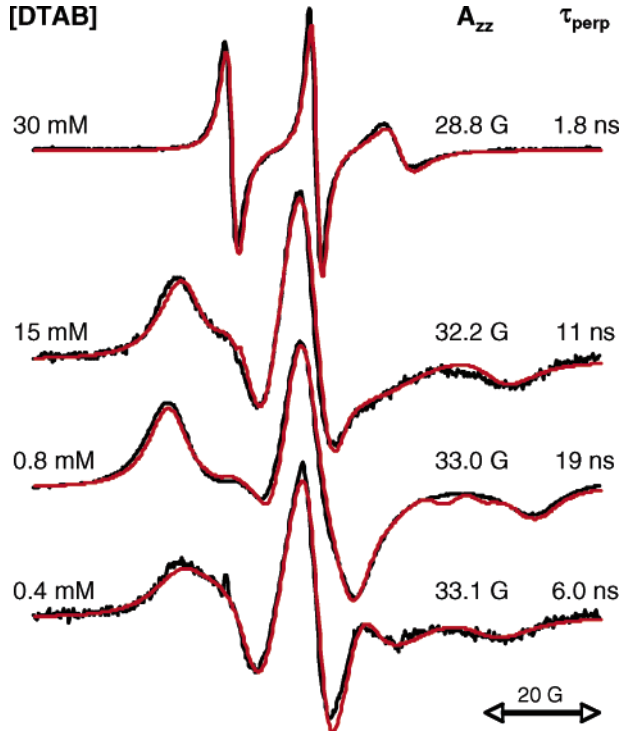

Figure 6. Selected experimental EPR spectra (black line) and computed spectra (red dashed line) of 5-DSA in PMAOVE (0.1% w/w) + DTAB mixtures at different DTAB concentrations and pH = 4. The main parameters used for computations are also shown.

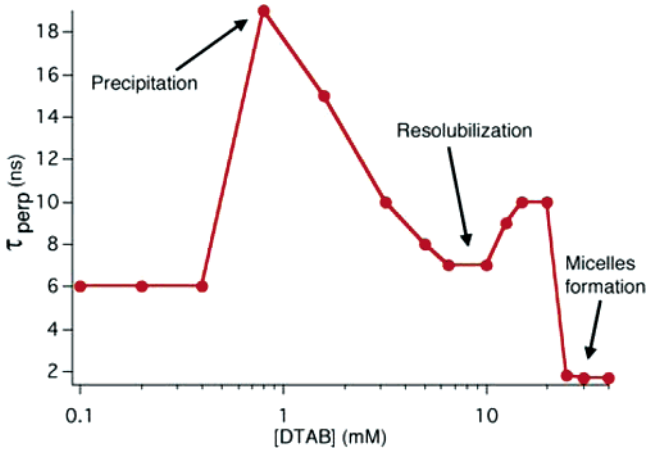

Figure 7. Variation of τ_{perp} as a function of DTAB concentration for PMAOVE water solutions (0.1% w/w) at pH = 4.

conformation. Therefore, neutralization of the ionized carboxylic groups of PMAOVE occurred at lower DTAB concentrations. Then, by increasing the DTAB concentration, the polymer resolubilized due to charge reversal and consequent repulsion between chains. At DTAB concentrations in between 10−15 mM, τ_{perp} began to increase again, which could be caused by the onset of the second precipitation. However, as turbidity measurements show, the second precipitation region was between 60−300 mM DTAB (Figure 1). It is feasible that at DTAB concentrations larger than 20 mM, significant amounts of free DTAB micelles are present in solution. Because 5-DSA and PMAOVE are negatively charged, the probe molecule (5-DSA) probably relocates into the positively charged free DTAB micelles. Therefore, 5-DSA cannot sense structural changes of PMAOVE−DTAB complexes at higher DTAB concentrations ([DTAB] > 20 mM). This preferential localization of the probe inside the

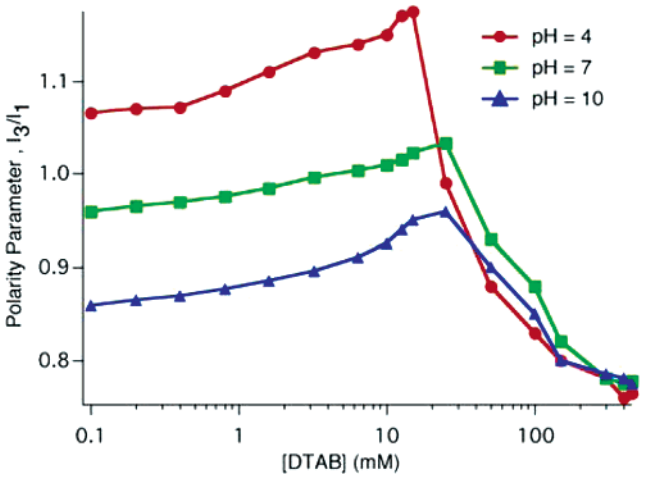

Figure 8. Vibrational fine structure (I_3/I_1) of pyrene fluorescence as a function of the DTAB concentration of aqueous solutions in the presence of PMAOVE (0.1% w/w) at pH = 4, 7, and 10.

free DTAB micelles is supported by the similarity of the EPR spectra at [DTAB] > 20 mM in the presence and absence of PMAOVE.

In summary, the EPR analysis allowed for an understanding of the supramolecular interactions between polymer and surfactant at a molecular level, which is difficult to attain by other techniques. For instance, at pH = 7, the presence of the order parameter suggests a strong ordering of the surfactant molecules on the surface of the charged polymer backbone, where the interaction is mainly driven by the hydrophilic groups. At pH = 4, instead, the EPR analysis shows a substantially different kind of spectra (e.g., a substantially different kind of interaction), where the absence of an order parameter and a significantly lower hyperfine constant (A_{zz}) suggest a hydrophobic driven aggregation.

Fluorescence Measurements. Fluorescence spectroscopy has been shown to be a useful technique to study surfactant systems using pyrene as a probe.[29−33] The vibrational fine structure of the pyrene fluorescence depends strongly on the polarity of the environment. The ratio between the intensities of the third (I_3) and the first (I_1) fluorescence peaks of pyrene is commonly used as a polarity parameter.[29,30] Because pyrene is a nonpolar molecule and practically insoluble in water (solubility $\sim 10^{-7}$ M), it readily absorbs into less polar microdomains of polymer−surfactant complexes. In the absence of DTAB, polarity parameters (I_3/I_1) of 1.07, 0.96, and 0.86 were observed for PMAOVE at pH = 4, 7, and 10, respectively. The decrease in the polarity parameter (I_3/I_1) corresponds to an increased polarity with increasing pH, which is caused by an increased ionization of the carboxylic groups. This increased ionization causes an electrostatic repulsion between the adjacent polymer segments, resulting in a more stretched conformation of the polymer and reduced hydrophobic clustering.[34] Addition of DTAB to PMAOVE up to a concentration of 20 mM causes a gradual increase of the polarity parameter (Figure 8). This increase corresponds to a decreased polarity of the PMAOVE/DTAB complex, indicating that the DTAB molecules come in contact with the hydrophobic nanodomains of PMAOVE. More hydrophobic PMAOVE nanodomains hosting

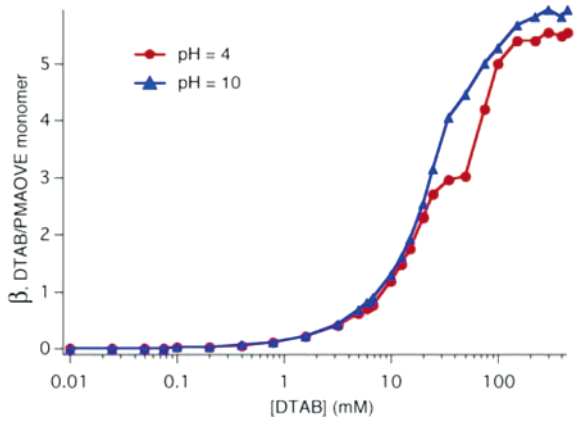

Figure 9. Binding isotherms of DTAB to PMAOVE at pH 4 and 10.

pyrene were formed at pH = 4 with respect to pH = 10, which is in agreement with the EPR results. The enhanced hydrophobicity at pH = 4 arises from the hydrogen bonding of the acidic groups and the consequent coiled conformation of the polymer. At DTAB concentrations larger than 20 mM, the polarity parameter decreases for all measured pH values (Figure 8), suggesting the formation of more polar aggregates as compared to the nonpolar polymer nanodomains. With a further increase of the DTAB concentration (>400 mM), the polarity parameter of pure DTAB micelles ($I_3/I_1 = 0.75$) was reached, indicating that pyrene is predominantly located in free DTAB micelles. The dominance of free DTAB micelles at these high concentrations was also observed by other techniques, such as EPR and surface tension.

Degree of Binding of DTAB to PMAOVE. To estimate the number of DTAB molecules interacting with PMAOVE at different pH values, binding isotherms were determined. The degree of binding of surfactant ions, β, is defined as the fraction of available sites occupied by the surfactant as a function of free surfactant concentration and is calculated using the expression given by

$$\beta = (m_D - m_D^f)/m_p$$

where m_D is the total surfactant concentration, m_D^f is the free surfactant ion concentration, and m_p is the polyion concentration. The polyion concentration is defined as the concentration of total monomer units (i.e., $COO^- + COOH$) of PMAOVE. The binding of surfactant molecules to the polymer and the relationship between pH and degree of protonation were obtained using procedures described elsewhere.[35−37]

The parameters characterizing the cooperative binding were estimated from a formalism for ligand binding by a linear site lattice, which was originally developed for the description of the helix−coil transition in polypeptides, based on the nearest-neighbor interaction model.[27,28]

By assuming the nearest-neighbor interactions to be between the hydrophobic parts of the bound surfactant ions, the degree of binding, β, is represented by two parameters, y and u

$$2\beta - 1 = (y - 1)/[(1 - y)^2 + 4y/u]^{1/2}$$

$$\text{with } y = Kum_D^f$$

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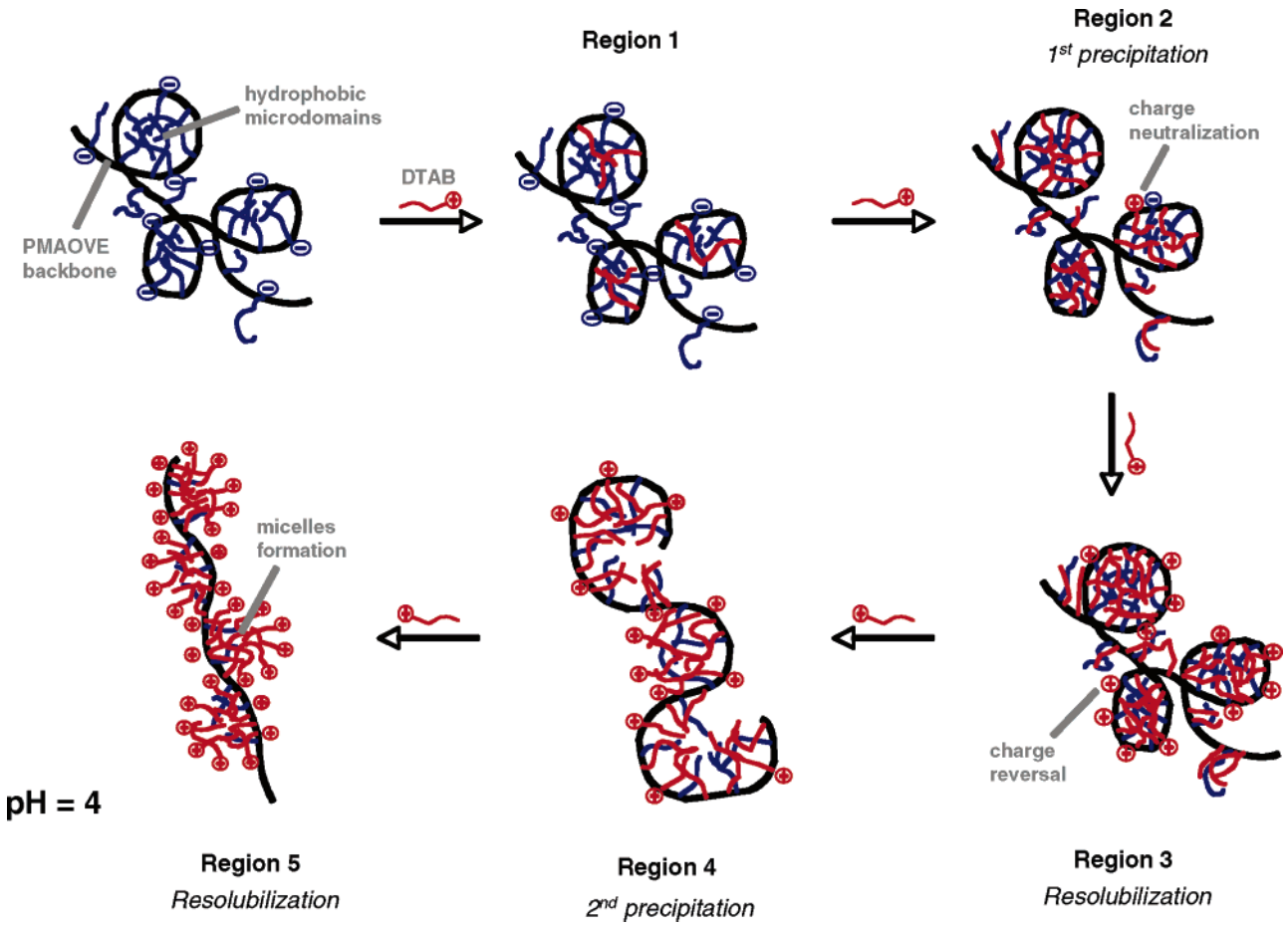
Scheme 2. Model for PMAOVE−DTAB Interactions as Function of DTAB Concentration at pH = 4



where K is the intrinsic binding constant between the surfactant ion and an isolated polyion binding site, and u is a cooperativity parameter, which is determined by the hydrophobic interaction between two adjoining bound surfactant ions. These parameters can be calculated from the following relationship at the half-bound point ($\beta = 0.5$):

$$-\log(m_D^f)_{0.5} = \log Ku$$

$$(d\beta/d \ln m_D^f) = u^{0.5}/4$$

Application of the previous formalisms allows one to obtain the binding isotherms, which are shown in Figure 9. At pH = 4, the binding isotherm shows a two-step process. At the onset of the first precipitation (~0.6 mM), only 30% of the ionized carboxylic groups is occupied by DTAB molecules. When the turbidity at pH 4 reaches its first maximum ([DTAB] = 0.6 mM; Figure 1), DTAB surfactants occupy only 50% of the ionized carboxylic groups. With a further increase in DTAB concentration (1.6 mM < [DTAB] < 50 mM), the turbidity decreases because the complex becomes more polar and, therefore, is more soluble in water. This suggests that the new interaction between added DTAB molecules with the PMAOVE/DTAB complex is mostly hydrophobic and that mixed micelles are formed on the nonpolar polymer backbone. As approximately 50% of the ionized carboxylic groups is still unoccupied, further addition of DTAB increases the possibility of these DTAB molecules to diffuse in and interact with those unoccupied carboxylic sites, resulting in the second precipitation.

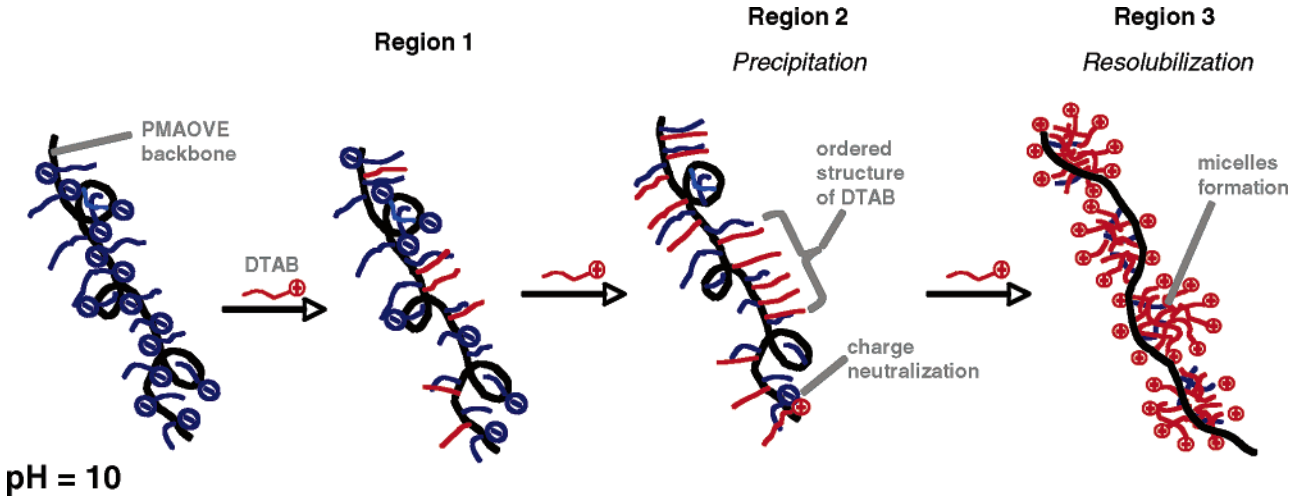
At pH = 10, a one-step binding isotherm was observed (Figure 9), which is consistent with the observation of only one precipitation region (Figure 1). The high dissociation of the carboxylic groups at the polymer at pH = 10 induces a stretched conformation. Therefore, the carboxylic groups are more accessible to DTAB molecules at pH = 10 in comparison to that at pH = 4. The precipitation point was observed when 90% of the ionized carboxylic groups was occupied by DTAB molecules. The higher degree of dissociation of the carboxylic acid groups and their higher accessibility at pH = 10 as compared to pH = 4 cause a shift of the precipitation region to higher DTAB concentrations (6 mM < [DTAB] < 500 mM) (Figure 1).

The binding isotherms reach a plateau at DTAB concentrations above ~500 mM with a maximum number of approximately six DTAB molecules per ionized carboxylic group in the PMAOVE−DTAB complex (Figure 9). The excess DTAB molecules are not involved in the PMAOVE−DTAB complex and form regular DTAB micelles. This micelle formation at high DTAB concentrations is supported by EPR and fluorescence experiments, where the probe molecules (5-DSA and pyrene, respectively) showed properties identical to pure DTAB micelles without PMAOVE because the probe molecules were predominantly located inside the excess DTAB micelles rather than inside the PMAOVE−DTAB aggregates.

Conclusion: A Model for the PMAOVE−DTAB Interactions at pH = 4 and 10

On the basis of the results from EPR spectroscopy, fluorescence spectroscopy, and turbidity, viscosity, and surface tension measurements, a model is proposed for the interactions between PMAOVE and DTAB at pH 4 (Scheme 2) and pH 10 (Scheme 3; to be considered equivalent to pH = 7).

Scheme 3. Model for PMAOVE−DTAB Interactions as Function of DTAB Concentration at pH = 10



pH = 4, Region 1 (0 mM < [DTAB] < 0.6 mM). PMAOVE formed a highly coiled structure, with the nonpolar chains forming hydrophobic nanodomains (Scheme 2). When small amounts of DTAB were added to PMAOVE solutions, only negligible changes in the parameters analyzed from the various techniques were observed. At approximately 0.4 mM DTAB, a significant change in properties was observed by EPR, turbidity, surface tension, and fluorescence analysis. Because of the decrease in the mobility and polarity tested by the EPR and the fluorescent probes, and because the turbidity and the surface tension increased, it was concluded that the positively charged DTAB headgroups interacted with the negatively charged carboxylic groups on the polymer backbone, whereas the DTAB chains inserted in the C_8 chain domains of PMAOVE.

pH = 4, Region 2 (0.6 mM < [DTAB] < 0.8 mM); First Precipitation. The turbidity, surface tension, and correlation time for the motion of the EPR probe reached the maximum. Precipitation was observed, which was caused by charge neutralization.

pH = 4, Region 3 (0.8 mM < [DTAB] < 50 mM). As the DTAB concentration was increased (0.8 mM < [DTAB] < 50 mM), more DTAB surfactants interacted with carboxylic groups to form mixed aggregates of PMAOVE−DTAB on the PMAOVE backbone. This addition of DTAB to the PMAOVE−DTAB complex caused a charge reversal, which allowed for resolubilization of the precipitate.

pH = 4, Region 4 (50 mM < [DTAB] < 300 mM); Second Precipitation. A second precipitation was observed, which was probably caused by reconformation of the coiled PMAOVE structure to an open extended conformation.

pH = 4, Region 5 ([DTAB] > 300 mM). At [DTAB] >300 mM, the precipitated PMAOVE−DTAB complex dissolved again, retaining the open extended conformation of the polymer and the micellar structure of DTAB interacting with PMAOVE (Scheme 2). The properties of the solutions were dominated by the DTAB micelles due to the large excess of DTAB to PMAOVE units (excess >100-fold).

pH = 10, Region 1 (0 mM < [DTAB]< 7 mM). At a basic (and neutral) pH, most maleic acid groups of PMAOVE were ionized (Scheme 3). This high charge density resulted in a more open conformation as compared to pH = 4. Addition of DTAB caused an increase in viscosity and polarity and a decrease in surface tension. The positively charged surfactant headgroups probably interacted with the negatively charged carboxylic groups of the polymer backbone. In addition, the nonpolar interactions with the surfactant chains and octyl side chains of the polymer contributed to the complex stability. EPR studies showed that this PMAOVE−DTAB interaction was highly ordered (increased order parameter *S*).

pH = 10, Region 2 (7 mM < [DTAB] < 20 mM); Precipitation. Further addition of DTAB caused a charge neutralization of the ionized polymer carboxylate groups by the oppositely charged surfactant headgroups, which made PMAOVE−DTAB insoluble in water and caused precipitation.

pH = 10, Region 3 ([DTAB] > 20 mM). Addition of more DTAB molecules caused a charge reversal and, subsequently, resolubilization of the PMAOVE−DTAB complex. Because of the maintenance of an open conformation of PMAOVE in all the ranges of the DTAB concentration, only one precipitation region was found at pH = 10.

From the previous results, it is concluded that the pH of the solution plays a critical role in the formation of polymer−surfactant complexes and their solubility.

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