

# Investigation of the mobility of amphiphilic polymer—AOT reverse microemulsion systems using electron spin resonance

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## Abstract

Amphiphilic polymers can be used as tools to manipulate the behavior of reverse microemulsions. EPR spectroscopy employing the spin probe 5-doxyl stearic acid was used to study the adsorption of a comb type polymer (polymaleic anhydride octyl vinyl ether) and a diblock polymer (polybutadiene–ethylene oxide) onto reverse microemulsion droplets formed from Aerosol-OT/heptane/water. The findings indicate that the comb type polymer was adsorbed by the reverse microemulsion drops at low polymer concentrations causing a structural change of the micelle.

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## 1. Introduction

Reverse microemulsions are important for both theoretical studies as model systems consisting of nearly monodisperse spheres, and for investigation of many practical applications. The Aerosol-OT/hydrocarbon/water reverse microemulsion system allows for the creation of nanoscale water domains with very high interfacial surface area. These properties have enabled reverse microemulsions to be used in a variety of special applications including microreactors for polymerization [1–18], adjustable templates to create inorganic nanoparticles [2–4,19–27], and also as a means to increase enzyme activity when placed in reverse microemulsions [3,4,23,28–34].

The effects of amphiphilic polymers in solution on the behavior of reverse microemulsions were investigated in this study using electron spin resonance (ESR) for the system containing the block copolymer of polybutadiene–

polyethylene oxide and a comb type polymer of polymaleic anhydride octyl vinyl ether. A difunctional carboxylic acid (six carbon chain adipic acid) was used as a novel additive for the AOT reverse microemulsion system, and other simple additives were examined for reference purposes.

## 2. Experimental

### 2.1. Materials

Surfactant: sodium diethylhexylsulfosuccinate (Aerosol-OT or AOT) from Sigma (SigmaUltra grade, 99% purity by thin layer chromatography, <0.1% insolubles) was further purified following the methods of previous researchers [28, 35–38] by dissolving in methanol and treating with activated carbon. The activated carbon–methanol–AOT slurry was then filtered through a Pall Ultipor® 0.45 µm nylon membrane and the methanol was removed using a rotovap.

Heptane and methanol: HPLC grade heptane and methanol (99.9%) from Sigma–Aldrich was used as received.

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Water: the water used in this study was semiconductor grade with a resistance of  $18 \text{ M}\Omega \text{ cm}^{-1}$ , and total oxidizable carbon (TOC) content of less than 1 part per billion. The water was purified by reverse osmosis, ozone, UV light, ion exchange resin and  $0.04 \mu\text{m}$  filtration. Upon contact with air, some carbon dioxide was absorbed, and this gave the water a pH of 6.5.

Block copolymer: poly(butadiene)–poly(ethylene oxide) [PBd-b-PEO] used was from Polymer Source. This polymer was specified to have the following molecular weights and polydispersities: PBd:  $M_w = 5200$ ,  $M_n = 5000$ ,  $M_w/M_n = 1.05$ ; PEO:  $M_w = 6240$ ,  $M_n = 6000$ ,  $M_w/M_n = 1.04$ . The PBd was >92% of the 1–4 addition product.

Hydrophobically modified Comb Polymers: polymaleic anhydride octyl vinyl ether (PMAOVE) was a gift from International Specialties Products (ISP) and is also known by the trade name Octyl Gantrez<sup>®</sup>. The molecular weights and polydispersity index were determined from size exclusion chromatography as the following:

(1) low molecular weight:  $M_w = 30,800$ ,  $M_n = 7300$ ,  $M_w/M_n = 4.22$ ;

(2) high molecular weight:  $M_w = 180,000$ ,  $M_n = 69,200$ ,  $M_w/M_n = 2.60$ .

Spin probe: 5-doxyl stearic acid [2-(3-carboxypropyl)-4,4-dimethyl-2-tridecyl-3-oxazolidinyloxy], free radical, purchased from Aldrich, was used as the spin probe for the ESR studies. The spin probe is a carboxylic acid and therefore expected to have the polar head group positioned in the water core of the reverse microemulsion with the hydrocarbon tail extending out into the heptane. The location of the nitroxide free radical group at the 5 carbon position allows it to be sensitive to the local environment of the AOT hydrocarbon tails (6 carbon long). The probe was first dissolved in heptane at a concentration of  $1 \times 10^{-3} \text{ M}$  and then added to the reverse microemulsions. A concentration of  $5 \times 10^{-5} \text{ M}$  probe in the reverse microemulsion samples was used for all ESR studies. Such a low concentration is not expected to have any effect on the AOT reverse microemulsion drops.

## 2.2. Methods

### 2.2.1. Electron spin resonance (ESR)

Nitroxides, such as 5-doxyl stearic acid, are known to exhibit EPR spectra that depend on the mobility of the spin probe and the polarity of the probe environment. They have been used to evaluate the microstructure of adsorbed layers of surfactants and polymers at the solid/liquid interface and also in lipid bilayers and microemulsions [39].

For this investigation, a Bruker EMX-EPR spectrometer that operated at a microwave field of 9.5 GHz (X-band) was used. The computer aided analysis of the EPR spectra was performed by means of the program by Budil and Freed [40]. The  $g_{ii}$  components for the coupling between the electron spin and the magnetic field were taken constant (2.0085, 2.0065, 2.0033). The  $A_{ii}$  components of the hyperfine tensor, for the coupling between the electron and the nuclear

spins, were also constant for all computations (7 G, 7 G, 31 G). These values were indicative of a low polar environment of the radical group as expected for the doxyl group embedded in a lipid bilayer or a micelle. The main parameters which change from one system to another were the order parameter,  $S$  ( $S$  can vary from 0 to 1 indicating transitions from an isotropic fluid motion to varying degrees of restrained motion up to a perfectly ordered state), and the correlation time for the rotational motion,  $\tau$ . A Brownian model was assumed for the rotational diffusional motion with a constant anisotropy ( $\tau_{\text{par}}/\tau_{\text{perp}} = 10$ ). Therefore we report and discuss the variation of the  $\tau_{\text{perp}}$  and  $S$  parameters in the system we analyzed.

In addition, a simplified method [41] was used to extract the order parameter,  $S$ , from the EPR spectra in cases where a good agreement with the  $S$  values derived from simulations (using the program by Budil and Freed) was observed.

$$S = a_0/a_N \left[ (A_{\parallel} - A_{\perp})/A_{zz} - \frac{1}{2}(A_{xx} + A_{yy}) \right],$$

where  $a_0/a_N$  is the polarity correction factor (hyperfine splitting constants,  $a_N = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$  and  $a_0 = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$ ). The values for the hyperfine tensor principal components are those obtained from computation.  $A_{\parallel}$  and  $A_{\perp}$  were measured from the experimental EPR peak distances.

Reverse microemulsions were prepared in glass vials. Water or a water–polymer mixture was added to AOT–heptane solutions and vigorously shaken for one minute and sonicated for an additional minute to form the reverse microemulsions.

The amphiphilic polymers were dissolved in water by heating to  $50^\circ\text{C}$  and stirring for 4 h using a magnetic stirrer. The polymer–water solution was cooled and then added to the AOT–heptane solutions. The polymer–reverse microemulsion samples were placed on an automated shaker for 24 h prior to the tests.

## 3. Results

Electron spin resonance spectroscopy (ESR) was used to obtain information about the surfactant film rigidity. The probe chosen was 5-doxyl stearic acid which has been studied previously with similar AOT reverse microemulsions [41–44] and is known to position itself at the water–surfactant interface with the nitroxide free radical located in the AOT hydrocarbon tail region.

### 3.1. Varying water/AOT ratio [ $R$ ], constant additive concentration

The AOT/heptane/water reverse microemulsion was evaluated at different  $R$  ratios ( $[\text{H}_2\text{O}]/[\text{AOT}]$ ) from 0 to 50 in the presence of various polymeric and simple additives and the spectra are presented in Fig. 1.

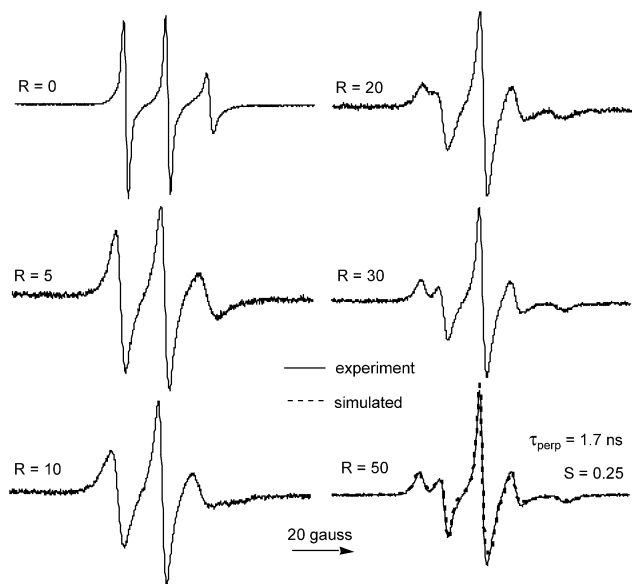


Fig. 1. ESR spectra for the heptane/AOT/water reverse microemulsion system at 0.1 M AOT/heptane concentration with varying  $R$  [ $\text{H}_2\text{O}/\text{AOT}$ ] ratios.

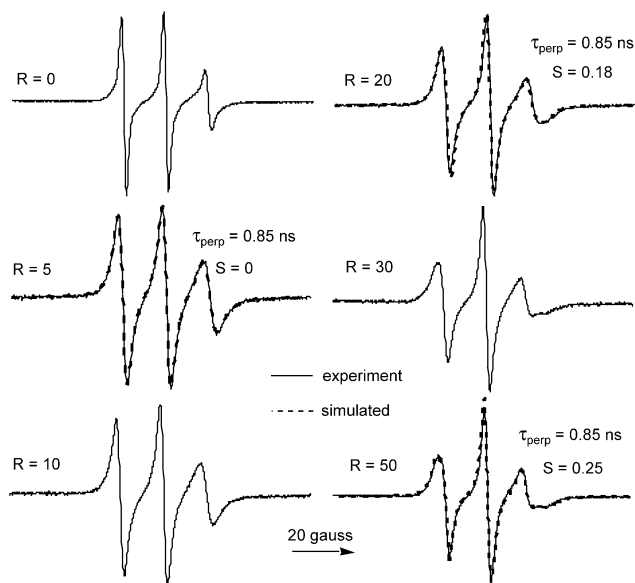


Fig. 2. ESR spectra for the heptane/AOT/1.5% 180 K MW PMAOVE reverse microemulsion system at 0.1 M AOT/heptane concentration with varying  $R$  [ $\text{H}_2\text{O}/\text{AOT}$ ] ratios (pH of 1.5% PMAOVE = 3.2).

As the  $R$  ratio is increased the EPR spectrum changes due to reorganization of the surfactant layer into a more ordered structure of the surfactant. The main change occurs between  $R = 0$  and  $R = 20$ , then the line shape changes only little between  $R = 30$  and  $R = 50$ . The dashed line spectra in Fig. 1 show a representative simulation.

Sets of experiments were conducted using a 1.5% weight solution of 180 K MW PMAOVE instead of water for  $R$  varying from 0 to 50. The ESR spectra associated with these samples are presented in Fig. 2.

The spectra with the 1.5% PMAOVE also show significant changes in the line shape as the  $R$  ratio is increased.

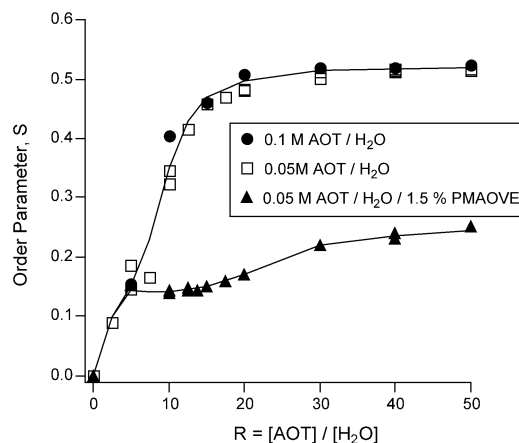


Fig. 3. Effect of varying  $R$  [ $\text{H}_2\text{O}/\text{AOT}$ ] on order parameter,  $S$ , for water and 1.5% PMAOVE (probe = 5-doxyl stearic acid at concentration =  $5 \times 10^{-5}$  M,  $T = 22^\circ\text{C}$ ).

The dashed lines represent simulated spectra. The rotational mobility remains constant, at the limit of slow motion/fast motion conditions ( $\tau_{\text{perp}} = 8.5 \times 10^{-10}$  s), whereas the order parameter increases with the increase of the  $R$  ratio. However, the increase in  $S$  for the samples in the presence of PMAOVE is smaller than obtained in the absence of the polymer. The variation of the order parameter as a function of  $R$  is plotted for both systems (with and without PMAOVE) in Fig. 3.

The order parameter,  $S$ , is a measure of the spin probe arrangement in a supramolecular assembly and varies from 0 to 1 with  $S = 1$  being in a completely ordered (crystalline) state and  $S = 0$  in a completely random state. The heptane/AOT/water system was found to have  $S$  values ranging from 0 at  $R = 0$  to 0.55 at  $R = 50$ . The order parameter increased rapidly to about  $R = 20$  and then remained fairly constant. The effect of the added 1.5% PMAOVE was to lower the order parameter ranging from 0 at  $R = 0$  to 0.25 at  $R = 50$ . This implies that the addition of the comb type polymer is influencing the surfactant layer to become less ordered and the spin probe becomes more mobile.

### 3.2. Constant water/AOT ratio $R = 40$ , varying additive concentration

A number of experiments were performed with varying concentrations of additives at a fixed  $R$  ratio of 40 where the reverse microemulsion is comprised of clear swollen micelles characteristic of a free water zone in the interior of the drop. The goal of these tests is to determine from the influence of the additives on probe mobility as to how the additives are adsorbed onto the reverse emulsion drops. Trials were run for the  $R = 40$ , 0.05 M AOT/heptane reverse microemulsion system with varying amounts PMAOVE with a molecular weight of 30.8 kg/mol. The ESR spectra are shown Fig. 4.

The addition of PMAOVE caused a change of the EPR spectra, which resulted in an increase in mobility of the spin

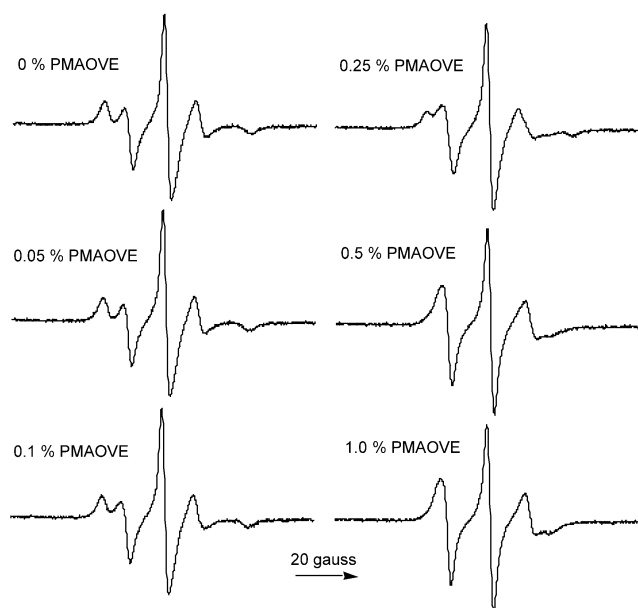


Fig. 4. ESR spectra for the  $R = 40$ , 0.05 M heptane/AOT reverse microemulsion system with varying PMAOVE concentrations.

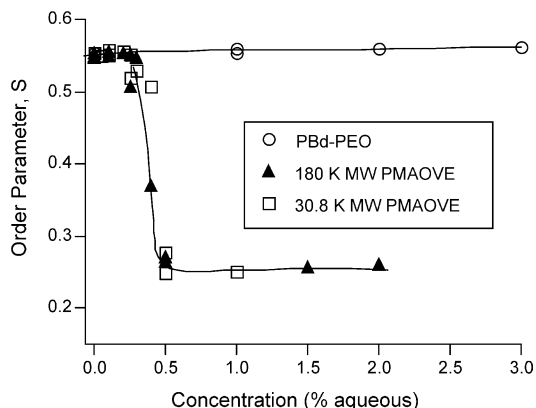


Fig. 5. Effect of PMAOVE and Pbd-PEO concentration on order parameter,  $S$ , for  $R = 40$  (probe = 5 doxyl stearic acid at concentration =  $5 \times 10^{-5}$  M,  $T = 22^\circ\text{C}$ ).

probe (0% PMAOVE  $\tau_{\text{perp}} = 1.7 \times 10^{-9}$  s; 1% PMAOVE  $\tau_{\text{perp}} = 8.5 \times 10^{-10}$  s) and a decrease of the ordering parameter (0% PMAOVE  $S = 0.55$ ; 1% PMAOVE  $S = 0.25$ ). This indicates a structural change of the spin probe environment. Similar experiments were carried out with PMAOVE of 180 kg/mol MW polymer and nearly identical results were obtained.

Conversely, when PBd-PEO was added to the AOT reverse microemulsion, no effect was observed on the EPR spectra.

To summarize and compare these results, the order parameter  $S$  was plotted as a function of the percentage of added polymer, 30.8 K MW PMAOVE, 180 K PMAOVE, and PBd-PEO, to the AOT reverse microemulsions at  $R = 40$  (Fig. 5).

Both molecular weight PMAOVE polymers showed similar effects on the EPR spectra. The order parameter for low

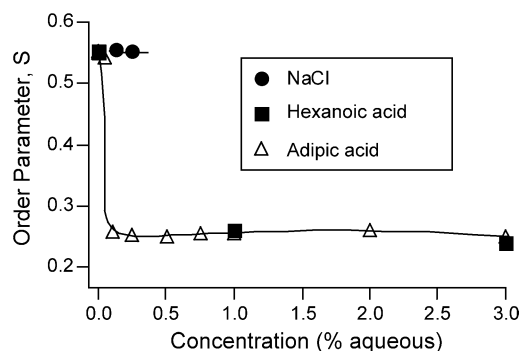


Fig. 6. Effect of NaCl, adipic acid and hexanoic acid concentration on order parameter,  $S$ , for  $R = 40$  (probe = 5-doxyl stearic acid at concentration =  $5 \times 10^{-5}$  M,  $T = 22^\circ\text{C}$ ).

PMAOVE concentrations was 0.55 and at a concentration range of 0.4–0.5% PMAOVE, the order parameter decreased suddenly to 0.25 and remained at 0.25 up to a concentration of 1% PMAOVE. The addition of PBd-PEO was found to have no effect on the order parameter which remained at 0.55 for PBd-PEO concentrations up to 3%.

The effect of nonpolymeric additives was also investigated using EPR for the  $R = 40$  reverse microemulsion systems as a reference to establish how less complicated systems will behave. Additives were selected to establish how ionic strength, pH, monocarboxylic acid, and dicarboxylic acid structures influence the structure of reverse microemulsions. Sodium chloride, adipic acid and hexanoic acid were added to the AOT reverse micelles and the EPR spectra of the spin probe were analyzed to extract the order parameter (Fig. 6).

The presence of salt, NaCl, did not show any effect on the order parameter. Adipic acid (a dicarboxylic acid) caused the order parameter to decrease in magnitude from 0.55 to 0.25 in a very narrow concentration range of 0.05–0.1% adipic acid. The order parameter then remained at a value of 0.25 up to the tested maximum adipic acid concentration of 3%.

The same value of the order parameter,  $S = 0.25$ , was observed after addition of hexanoic acid at concentrations of 1 and 3% indicating a similar influence of the dicarboxylic acid, adipic acid, and the monocarboxylic acid, hexanoic acid on the reverse micelle structure (probed by 5-doxyl stearic acid).

Conductivity was previously reported [44,45] at varying temperatures for the reverse microemulsion systems with and without additives. The electrical percolation temperature is defined as the temperature at which the conductivity suddenly rises several orders of magnitude. Electrical percolation results are plotted in Fig. 7 where  $\Delta\text{EPT}$  is the difference between the temperature at which the electrical percolation occurred for the system with additive and the simple 0.2 M AOT/heptane,  $R = 40$  case.

The NaCl additive was found to have the most pronounced effect by shifting the EPT to higher temperatures even with only small quantities (0.06–0.12%). The adipic acid and then hexanoic acid had the next measurable in-

fluence with opposite effects, adipic acid having a negative slope and hexanoic acid a positive slope. The PMAOVE comb type polymer showed a negative slope, with the 180 K molecular weight polymer having a small but distinguishable difference with a more negative slope than the 30.8 K polymer. The PBd-PEO exhibited the least effect per % additive with a slightly positive slope.

#### 4. Discussion

As discussed earlier, the decrease in probe mobility and the increase in the order parameter depicted in Figs. 1 and 3 for the simple reverse microemulsion can be attributed to the growth of the reverse microemulsion drops with increasing  $R$  values [43]. The probe mobility is based on a combination of the tumbling motion of the droplets and the lateral diffu-

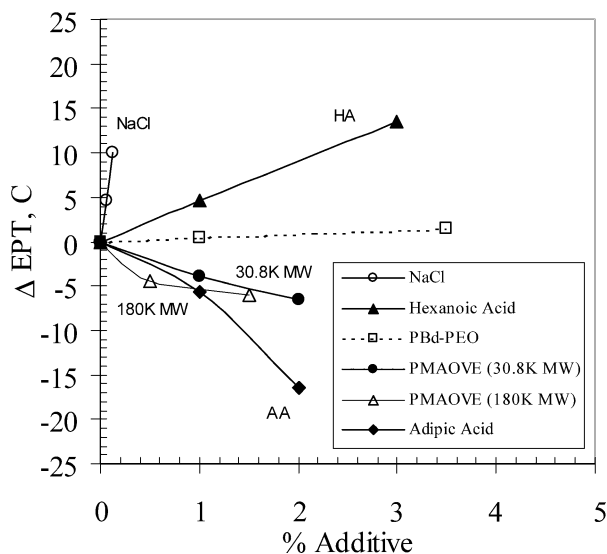


Fig. 7. Electrical percolation results as  $\Delta$  electrical percolation temperature (EPT) versus the % additive concentration in aqueous solution.

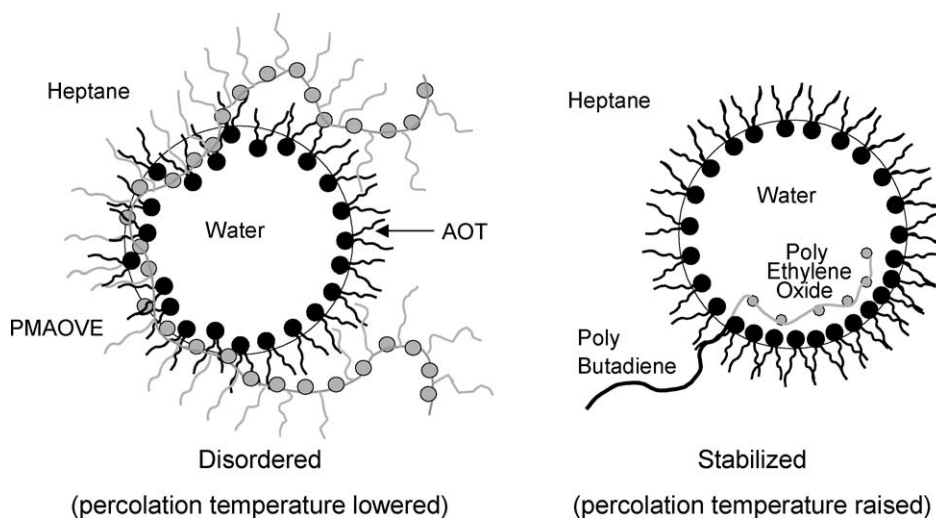


Fig. 8. Adsorption of PMAOVE disrupts AOT packing order.

sion of the probe on the surface of the drops. As the drops become larger, the rate of drop tumbling is decreased and the effective measure of the probe mobility is limited to the lateral molecular diffusion on the drop surface. This explains why the continuous increase in the drop size does not affect the order parameter as now the lateral diffusion is expected to be constant with respect to drop size.

Addition of 1.5% PMAOVE causes a decrease in the order parameter (Figs. 2 and 3). The lowered order parameter of the spin probe suggests that the surfactant monolayer is less organized and less structured. Previous studies using dynamic light scattering [44,45] indicate that the addition of the PMAOVE has minimal effects to the drop size for values varying from  $R = 20$  to  $R = 50$  and that the rearrangement of the system to form water pools around the carboxylic acid groups of the PMAOVE polymer is unlikely in this region. Three possible effects could cause the decreased order parameter:

- (1) Film rigidity: a schematic representation of the reverse micelles are shown in Fig. 8. PMAOVE may affect the surfactant layer around the water drops by lowering the film rigidity by decreasing the AOT packing density or order.
- (2) Bridging: PMAOVE adsorption could either accelerate the collision rate between the drops or increases the number of effective collisions by a “bridging effect” so that the AOT film is being parted and reformed at a higher rate. This possible mechanism is depicted in Fig. 9.
- (3) pH effect: the adsorption of the anionic PMAOVE causes the water pH to be lowered. This leads to protonation of the 5-doxyl stearic acid spin probe and makes it less polar. The protonated spin probe then moves away from the water core more into the AOT tail region where the nitroxide free radical group is able to rotate more

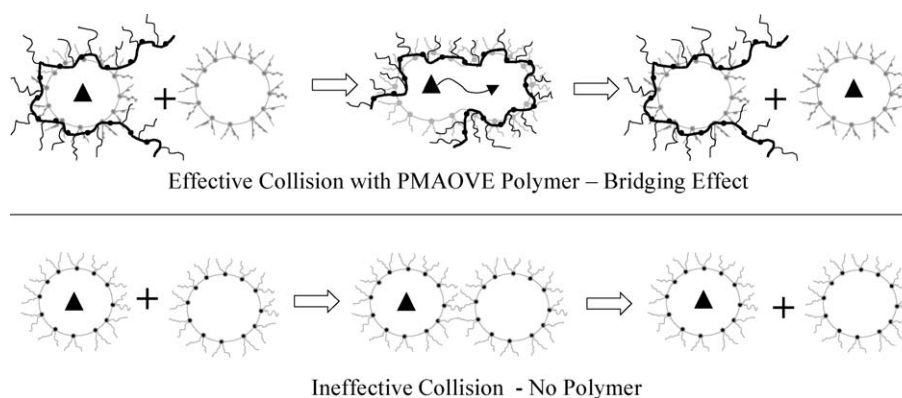


Fig. 9. Bridging of two reverse emulsion droplets by PMAOVE increases effective collision rate (triangles represent ionic species dissolved in water pool interior).

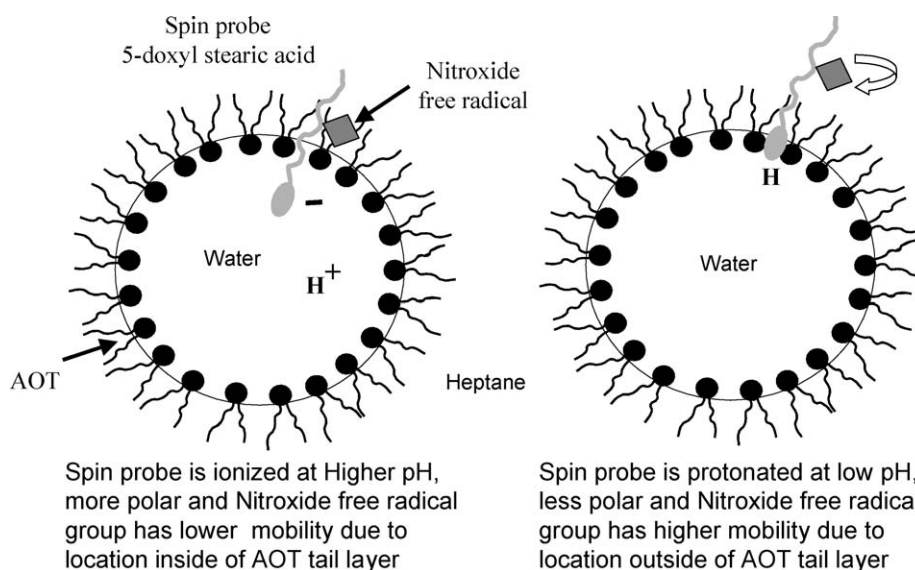


Fig. 10. Effect of pH on spin probe location and mobility.

freely. The two cases of low and high pH are shown in Fig. 10.

Previous studies [43] on the effect of buffered pH solutions on the ESR spectra of nitroxide probes in reverse microemulsions of isooctane/AOT/water revealed a dramatic shift in the spectra in the pH range of 4.6–8.5.

The effect of varying polymer concentrations on the  $R = 40$  reverse microemulsion system is provided in Fig. 4 for 180 K MW PMAOVE. Similar data was obtained for the 30.8 K MW PMAOVE (not shown). The order parameters for both MW PMAOVE polymers are presented in Fig. 5 along with the diblock polymer PBd–PEO. Both molecular weight PMAOVE polymers had similar effects on lowering the order parameter above 0.4% concentration. This indicates that the polymer chain length did not affect the spin mobility. Based on the weight percent, the amount of adsorbed carboxylic groups for both molecular weight polymers would be the same and this information would support the pH controlled mechanism. Below 0.4%

concentration, it is likely that the PMAOVE polymer is soluble in the heptane phase and not associated with the drops.

The presence of the diblock polybutadiene–polyethyleneoxide, PBd–PEO, would be expected to have some influence on the film rigidity as found by electrical percolation; however, the ESR may not be in the right time domain to measure these effects. ESR reflects the rotational molecular diffusion of the spin probe in the surfactant layer, which is of the order of  $1 \times 10^{-9}$  s while the time scale for the drops collision is about  $1 \times 10^{-7}$  s.

The effects of nonpolymeric additives were investigated by ESR and electrical conductivity studies for comparison in the interest of elucidating the mechanisms of the polymeric additives behavior. The electrical percolation temperature threshold can be used as a measure of how the heptane/water/AOT reverse microemulsion has been altered for either more attractive (higher rate of effective collisions) or less attractive (lower rate of effective collisions) interactions between drops. The additives influence the electrical perco-

lation temperature by changing the surfactant film rigidity or by altering the interaction forces between drops.

Salt (increase of ionic strength) can be expected to have a significant influence on increasing the film rigidity as suggested by electrical percolation tests (Fig. 7). The lack of any effect on the ESR spectra (Fig. 6) suggests that the time frame of the spin probe motion is much faster than that of the AOT film in terms of how it interacts with other drops in collisions.

Hexanoic and adipic acids were studied because they are carboxylic acids and similar in this way to PMAOVE. They had opposite effects based on the electrical percolation results with hexanoic acid stabilizing the reverse microemulsion film and with adipic acid destabilizing the film (Fig. 6). The ESR results did not correlate with the conductivity experiments and in both cases the addition of these acids caused a decrease of the ordering of the monolayer, probably because both experimental methods, EPR and electrical percolation, probe processes in different time domains. These results, along with the lack of change observed in the ESR spectrum by PBD-PEO and sodium chloride, suggest that the model described in Fig. 10 (“pH effect”) might explain best the increase in spin probe mobility and decrease of the order parameter by addition of the acid PMAOVE. It is reported that the apparent pH at the AOT/water interface is basic (pH 7.7) [43] and can approach pH 9 at low  $R$  values [46]. Therefore, 5-doxyl stearic acid could be deprotonated ( $pK_a = 7.45$ ; stearic acid) [47]. As a consequence, the carboxylic group of the spin probe is located at the polar water/sulfonate interface and the nitroxide free radical is located in the tightly packed AOT tail region (Fig. 10, left). After addition of acids (PMAOVE, hexanoic acid, and adipic acid) the carboxylic group gets protonated and the spin probe moves inside the less polar region of the micelle leaving the nitroxide exposed to the less ordered hexane/AOT region (Fig. 10, right).

## 5. Conclusions

ESR was found to be a useful technique to monitor the adsorption of the comb type polymer PMAOVE onto reverse microemulsion drops, but not for the diblock polymer PBD-PEO. Based on electrical percolation and ESR experiments with sodium chloride, adipic acid and hexanoic acid, it was concluded that deprotonation/protonation effects of the spin probe could explain the changes in the ESR spectra after addition of PMAOVE polymer. Here the carboxylic groups from PMAOVE lower the pH of the reverse microemulsion drop and this leads to protonation of the 5-doxyl stearic acid probe. The protonated spin probe is less polar and relocates further away from the water core leading to increased mobility of the nitroxide.

The influence of the polymeric and nonpolymeric additives on the film rigidity or AOT structural packing and the possible bridging mechanism could not be evaluated by the

ESR method due to the probe motion having a different time domain than rates of the drop collision or AOT film restructuring.

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