Poly(oxyethylene) Adsorption in Water/Oil Microemulsions: A Conductivity Study

Wolfgang Meier

Institut für Physikalische Chemie, Dept. Chemie, Universität Basel, Klingelbergstr. 80, CH-4056 Basel, Switzerland

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The effect of poly(oxyethylene) on the L2 phase of an anionic and a nonionic microemulsion system is studied. Attractive interactions between anionic surfactant and the polymer lead to polymer adsorption at the interface. The resulting increase of the surfactant monolayers’ elastic bending modulus of up to about 10% results in a shift of temperature-induced droplet cluster formation. For nonionic systems only sterical considerations are important due to repulsive interactions between the polymer and the surfactant.

Introduction

A large number of biologically and industrially important emulsions and dispersions are made from polymers and surfactant. While the surfactant usually determines the structure, the polymer influences mainly the rheological properties. Water soluble polymers, like poly(oxyethylene) or proteins, however, interact with interfaces built up by surfactants, thus influencing also the structure of the whole system. To understand complex biologically or technologically relevant dispersions, it is necessary to investigate more simple model systems.

Microemulsions, i.e. thermodynamically stable mixtures of oil, water, and surfactant, can be formed with a well-defined structure. For high oil content we have water-in-oil (w/o) microemulsions with nanometer-sized water droplets in a continuous oil phase. Due to a selective solubility, water soluble polymers like poly(oxyethylene) (POE) are confined to the water core of these nanodroplets (1) (see Figure 1). This restricted spatial environment of the polymer chain together with the presence of the surfactant at the surface of the droplets can be expected to lead to an interesting interplay between sterical repulsion and surfactant–polymer interactions. In this context one can imagine mainly two situations: (i) repulsive interactions between polymer and surfactant (e.g. nonionic surfactants and POE) and (ii) attractive interactions (e.g. anionic surfactants and POE).

In case i, the features of the system will be mainly determined by sterical considerations (1e). Hence, the degree of polymerization of the POE can be expected to be of significance. For attractive interactions between the polymer and surfactant (ii), one expects an adsorption of the polymer to the oil/water interface. This adsorption modifies the properties of the interface, especially the flexibility of the interface, which is a sensitive quantity determining the phase behavior of the microemulsion. In this case sterical repulsion will become of minor importance.

Figure 1. Poly(oxyethylene) within the water droplets of a w/o microemulsion.

Polymers of higher molecular weight, which are larger than the droplet system, may create their own water/surfactant cavities. That means they can be dissolved within nanodroplet clusters or even may cause phase separation. (2d)

In this paper we describe the influence of POE of different molecular weight on the phase behavior of microemulsions based on an anionic surfactant (AOT) and on a nonionic surfactant (C12E5). To study the influence of the polymers of different molecular weight we use the temperature Tc, where the formation of an infinite droplet cluster occurs in the w/o microemulsion/polymer system which is traced by electric conductivity. It will be shown that the character of the interactions between polymer and surfactant is of major influence.

Experimental Section

Materials. Microemulsions were prepared by mixing appropriate weight fractions of the surfactants, water, and oil. In combination with the anionic surfactant AOT (sodium bis(2-ethylhexyl)lsulfo succinate), isooctane was used as the oil phase, in combination with the nonionic surfactant C12E5 (pentaethylene glycol monododecylether) n-octane. The surfactants (s) and oils

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(o) were obtained from Fluka (highest grade available); the water (w) bidistilled.

For phase diagrams the weight fraction \( w/w = (w + s)/(w + s + o) \) was kept constant at \( w/w = 0.35 \) and \( r_w = w/s \) which determines the size of the droplets at \( r_w = 2.5 \). Assuming for both surfactants (AOT and \( \mathrm{C}_{12}\mathrm{E}_5 \)) a head group area at the interface of 0.57 nm\(^2\), the diameter of the water cores of the nanodroplets can be calculated to be about 20 nm.

POE with molecular weights of 600–11000 g mol\(^{-1}\) were obtained from Fluka, higher molecular weights (20000–1000000 g mol\(^{-1}\)) from Polysciences, Inc. They were further purified by repeated precipitation from methanol and diethyl ether and finally freeze-dried. The molecular weights of the individual polymers were determined by light-scattering and gel permeation chromatography. The polydispersity \( M_w/M_n \) of the polymers was in the range \( M_w/M_n = 1.1–1.3 \). Assuming Gaussian statistics for the polymer coil and excluded volume interactions, the end-to-end distance of the POE with molecular weight \( \leq 11000 \) g mol\(^{-1}\) is calculated to be \( \leq 16 \) nm. When this value is compared with the geometric data of the microemulsions, it is evident that this series easily fits into the water core of the droplets. The POE series with molecular weight higher than 200000 g mol\(^{-1}\) exceed by far the droplet dimensions.

**Results and Discussion**

Water soluble polymers in w/o microemulsions are confined to the water domains. These domains consist in a certain range of the phase diagram of nanometer-sized water droplets. As already mentioned, the comparable dimensions of the polymer molecules and the domains of the complex solvent, which are available to it, may lead to exceptional interactions between them. For clarity, in the following we will discuss the effects of polymers smaller, and those larger, than the droplet dimensions separately.

**Polymers Smaller Than the Droplet Radius.** A series of poly(oxyethylene)s of different molecular weight \( M_w = 600, 1000, 3000, 6000, 8000, \) and 11000 g mol\(^{-1}\) is dissolved in a w/o microemulsion of constant composition. The end-to-end distance of these polymers can be calculated to be always smaller than the droplet diameter. Dynamic light-scattering data reveal that the structure of the microemulsion, i.e., the droplet dimensions, remains almost unaffected upon polymer addition.\(^6\) This coincides with the slight density variation of the aqueous core of the nanodroplets due to dissolved polymer.

However, the phase behavior of the system is influenced by the polymer. For example, the \( L_2 \) droplet phase of the AOT system is broadened and shifted toward higher temperature with increasing concentration of POE (see Figure 2). In contrast, the phase behavior of the \( \mathrm{C}_{12}\mathrm{E}_5 \) system remains unaffected within the same concentration regime of POE. The differences between the two systems can be analyzed regarding a transition which can occur in the droplet phase of microemulsions and is often referred to as "percolation transition" of microemulsions.

As a result of interactions between the individual nanodroplets, temperature variation may cause cluster formation of the droplets, eventually resulting in an infinite, system-spanning droplet cluster at the temperature \( T_c \). This transition can be traced by measurement of the electric conductivity \( \sigma \). At \( T_c \), the conductivity of the whole system increases by several orders of magnitude due to anionic charge transport through the water droplet cluster. \( T_c \) is given by the inflection point of the \( \sigma/T \) curve. This transition is caused by weak interactions between the individual nanodroplets. Therefore, \( T_c \) should respond sensitively to slight variations of the physical properties of the microemulsion system. As a consequence addition of poly(oxyethylene) to a w/o microemulsion can cause a shift of \( T_c \) toward higher temperature (Figure 3) (see also ref 1f). This must be the result of the specific interactions between the surfactants at the oil/water interface and the POE in the water droplets. It is well known that these interactions are attractive for anionic surfactants (here AOT) and repulsive for nonionic surfactants (here \( \mathrm{C}_{12}\mathrm{E}_5 \)). Consequently, for the anionic microemulsion it can be expected that the polymer absorbs to the oil/water interface (Figure 4) whereas for the nonionic microemulsion a depletion effect should occur; the POE is forced into the droplet interior and avoids the interfacial region (see Figure 4). As a result the two systems react differently upon polymer addition.

The adsorption of the polymer, however, must be of significant influence on the properties of the whole

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6. F. Stiebier, private communication.
interface. One can expect mainly two effects: (i) a modification of the spontaneous curvature and (ii) a strengthening of the interface, i.e., an increasing elastic bending constant \( K \).

With the given micromulsion system, one can clearly distinguish between both effects. A variation of the spontaneous curvature and, therefore, the head group area should be a consequence of interactions between monomeric units of the polymer and the surfactant in the interface. Spontaneous curvature effects should therefore depend only on concentration not on the molecular weight of the adsorbed POE (see below).

Furthermore, a variation of the head group area of the surfactant as the oil/water interface leads to a variation of the droplet radius of the nanodroplets. As already mentioned, this is, within experimental accuracy, clearly contradictory to light-scattering measurements. Consequently, we expect the observed shift of \( T_c \) for the anionic system to be the result of the increasing rigidity of the oil/water interface of the system.

From the experimental data \( T_c \) is accessible, the temperature where infinite cluster formation occurs. But how does \( T_c \) depend on the flexibility of the oil/water interface and therefore on the elastic bending constant \( K \)?

For the description of phase boundaries and the structural properties of microemulsions, several phenomenological models have been developed. One essential feature they have in common is the introduction of curvature energy contributions into the free energy of a microemulsion. De Gennes and Taupin calculated for negligible spontaneous curvature a persistence length \( \xi_k \) for the interface which may be defined by

\[
\xi_k = a \exp(\frac{4\pi K}{kT}) \quad (1)
\]

where \( a \) is a molecular size which provides a lower cutoff in the wavelength of the undulations (comparable to the dimensions of the surfactant molecule), \( k \) is the Boltzmann constant, \( K \) the elastic bending constant, and \( T \) the temperature. The oil/water interface remains flat or constantly curved over length scales smaller than \( \xi_k \) but is crumpled at larger length scales. This means for microemulsions containing water domains with \( R_{\text{domain}} < \xi_k \) one has to deal with droplets not far from spherical, and whenever \( R_{\text{domain}} > \xi_k \) the shapes must be strongly nonspherical.

Within the droplet phase of the AOT/isooctane/water system, the temperature dependence of the nanodroplet radius \( R \) is negligible. Simultaneously, \( \xi_k \) depends exponentially on \( 1/T \) according to eq 1, i.e., it should react sensitively upon temperature variation. Temperature variation within the thermodynamically stable one-phasic region may lead from a state with \( \xi_k < R \) to one with \( \xi_k > R \). The formation of an infinite, system-spanning droplet cluster at \( T_c \) is closely related to this transition, i.e., droplet-like \( (\xi_k < R) \)–bicontinuous \( (R > \xi_k) \).

Thus \( \xi_k \approx R \) should hold around \( T_c \).

A quantity directly controlling \( R \) (which is experimentally easily accessible) is \( r_w = w/\xi R \). Then with the help of eq 1, one finds

\[
\ln r_w \approx \frac{4\pi K}{kT}\frac{1}{c} \quad (2)
\]

That is \( \ln r_w \approx 1/T_c \). To test the validity of eq 2, the \( T_c \) dependence on the droplet radius was investigated for the pure microemulsion system without polymer. Figure 5 shows that this relation is well fulfilled for the AOT/isooctane/water system as well as for the AOT/hexane/water system. From the slope of the plot, one finds \( K_{\text{isooctane}} \approx 4.2 \times 10^{-21} \text{J} \) (or about \( kT \)) and \( K_{\text{hexane}} \approx 3.7 \times 10^{-21} \text{J} \) (or about \( 0.9kT \)). These values are in good agreement with literature data\(^\text{a}\) ranging \( K \approx (0.2–5)kT \) thus confirming the validity of our approach.

Nevertheless, eq 2 also provides the relation between \( T_c \) and the bending constant \( K \) of the microemulsion, i.e., for a given size of the nanodroplets \( T_c \approx K \). Consequently, the shift of \( T_c \) with increasing POE concentration in our systems reflects directly the increase of the rigidity of the oil/water interface due to polymer adsorption. This is shown in Figure 6 where \( \Delta T_c = T_c - T_c^0 \) is plotted versus polymer concentration \( T_c^0 \) being the transition temperature for the pure microemulsion without polymer) for several molecular weights of POE. From the plot one can easily see that \( \Delta T_c \) and therefore \( \Delta K \) depends not only on the concentration of POE in the system but also on the molecular weight of the polymer. In contrast, \( \Delta T_c \) for the nonionic system is zero within the whole concentration regime investigated (see Figure 7). In this case the polymer is not adsorbed to the interface, and the flexibility of the interface is not markedly influenced by polymer addition.

A scaling analysis of the rigidity \( K \) for polymer adsorption to a surfactant interface\(^\text{c}\) leads to the following

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Polymers Larger Than the Droplet Radius. Another interesting feature of these systems arises from polymers which are larger than the droplet dimensions of the w/o microemulsion. These polymers do not fit in the compartmental structure of the solvent and, consequently, may create a new water/surfactant environment which is able to dissolve them. Therefore a second series of POE \((M_w = 200 000 \text{ g mol}^{-1})\) was investigated in the microemulsion systems.

\[
\Delta T_c \propto K \propto \text{const} + \text{const}^' \times \ln N + \text{const}^{''} \ln(c_{\text{POE}})
\]  

(3)

assuming all the polymer to be adsorbed to the interface. Hence, the variation of the bending constant depends logarithmically on both the degree of polymerization \(N\) and the concentration \(c_{\text{POE}}\) of the POE in the microemulsion. The individual plots of Figure 6 belong to different molecular weights of POE. As can be seen from Figure 6, a logarithmic fit is able to describe the concentration dependence for fixed \(N\) satisfactorily. At fixed polymer concentration, e.g. \(c_{\text{POE}} = 3 \times 10^{-5} \text{ g L}^{-1}\), eq 6 predicts \(\Delta T_c \propto \ln N\) which is found to hold pretty well, as can be seen from Figure 8, thus confirming the influence of polymer adsorption on interfacial rigidity in microemulsions.

In the microemulsion system under investigation, the bending constant \(K\) is increased by less than 10% for POE adsorption, i.e. in the system investigated the highest concentration of the largest molecular weight POE (11 000 g mol\(^{-1}\)) increases \(K\) from about 1K to about 1.07K. This coincides with the observation that the structure of the microemulsion is qualitatively preserved upon polymer addition. A stronger increase of \(K\) would be expected to induce a phase transition to a liquid crystalline phase (requiring a more rigid interface and therefore a larger persistence length).7

In agreement with the above data, the interactions between the polymer and the surfactant are simpler for microemulsions based on nonionic surfactant, like \(\text{C}_{12}\text{E}_5\). Here, the polymer molecules are repelled from the surfactant containing the oil/water interface. The POE is forced into the water core of the droplet interior (see Figure 4). For the dissolution of the polymer in the droplets mainly sterical considerations are relevant. Consequently, POE larger than the dimensions of the water core of the droplets cannot be dissolved. For these systems the addition of polymer causes a macroscopic phase separation into a lower, water-rich phase which contains the polymer and an upper, oil-rich phase which contains no or very little POE. This is in good agreement with previous observations on a water/\(\text{C}_{12}\text{E}_5\)/decane system.16

For microemulsion systems based on the anionic surfactant AOT, the attractive interactions between polymer and surfactant lead to an adsorption of the polymer at the oil/water interface. That means, in contrast to the nonionic surfactant systems, the POE favors the interfacial region compared to the water core of the droplets (see also Figure 4). Therefore one can easily imagine that the POE molecule is able to penetrate the interface, thus interconnecting different nanodroplets to form a droplet cluster. As a consequence, a POE molecule which does not fit into a single nanodroplet may induce the formation of droplet clusters of a size comparable to the polymer coil (see Figure 9, also ref 1d).

Conductivity measurements display, in agreement with the findings above, a shift of \(T_c\) toward higher temperature...
Deviating from the lower molecular weight POE (see Figure 2), the shift of $T_c$ is not only a consequence of polymer adsorption to the interface but also the result of a polymer-induced cluster formation. Therefore, for higher polymer concentrations the one-phasic region of the microemulsion exists only in the highly conductive state, i.e. in the form of a system-spanning nanodroplet cluster (see Figure 10). This can be compared to the polymer-induced gelation of gelatin-containing w/o microemulsions due to interdroplet cross-linking within the infinite droplet cluster.$^{11}$

A plot of $\Delta T_c$ against polymer concentration (Figure 11) reveals no molecular weight dependence for the high molecular weight POE ($M_w \geq 200 \times 10^5$ g mol$^{-1}$). This is plausible for the following reasons. First, as a result of the logarithmic molecular weight dependence of $\Delta T_c$, for these large polymer molecules $\Delta T_c$ becomes rather insensitive. Second, one has to expect a polymer-induced cluster formation; if the polymer dimensions exceed the droplet dimensions, the formation of droplet clusters occurs. This coincides with the results of dynamic light-scattering studies on these and related systems $^{11}$ with increasing polymer concentration the portion of droplet clusters increases at the cost of singly dispersed nanodroplets.

**Conclusions**

The influence of water soluble polymers, like POE, on the phase behavior of water-in-oil microemulsions could be shown to be the result of specific polymer/surfactant interactions and sterical considerations. Adsorption of the polymer to a surfactant interface built by anionic surfactants leads to an increase of the interfacial elastic modulus. This modulus influences directly the temperature-induced droplet cluster formation in w/o microemulsions. Polymer molecules larger than the droplet dimensions can only be dissolved in the microemulsions with the help of these attractive polymer/surfactant interactions and cause a polymer-induced droplet cluster formation. These results indicate that microemulsions have a great potential as a model system for the study of polymer/colloid interactions. Already a multitude of experimental data on pure microemulsions (without polymer) exist.

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