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Hydrophilic Alcohol Ethoxylates as Efficiency Boosters for Microemulsions

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Highly amphiphilic polyalkane−PEO diblock copolymers drastically increase the solubilization capacity of surfactants in microemulsions if they are used in small quantities as additive to the surfactant. This effect goes along with an additional reduction of the already very low interfacial tension between water and oil. Lamellar phases, which usually develop when the surfactant becomes more efficient, are suppressed to a large extent. In this work we use another type of additive, namely hydrophilic alcohol ethoxylates. These amphiphiles are identical with the previously used block copolymers with respect to the hydrophilic moiety. However, they contain only small hydrocarbon groups ranging from C_8 to C_{18}. A typical example from the hydrophilic alcohol ethoxylates is $C_{12}E_{100}$. Both additive types increase surfactant efficiency equally with respect to mass fraction in the mixture. Because the alcohol ethoxylate additives decorate the surfactant film only on the aqueous side, they influence the curvature of the surfactant membrane or, in other words, the temperature behavior of the microemulsion. Together with nonionic surfactants, however, the shift of the one-phase region to higher temperatures is only a few degrees Celcius. Just as with the polyalkane−PEO block copolymers, the hydrophilic alcohol ethoxylates suppress lamellar phases. This behavior is especially pronounced if the hydrophobic groups are small or the PEO chains are long. We found that hydrophobic units as short as C_8 are sufficient to largely anchor the PEO chains at the interface. If C_{12} or C_{18} hydrocarbon unit are used instead, the PEO chains are fully interfacially active, even if the hydrophilic chain contains up to about 500 EO units. We applied the new additives in bicontinuous and in droplet microemulsions and used nonionic, as well as ionic, surfactants, namely $C_{10}E_4$ and AOT. In contrast to polyalkane−PEO blockcopolymers the new additives are easy to synthesize and are commercially available. Therefore, they might be interesting in applications.

Introduction

Usually large quantities of surfactants are needed to formulate microemulsions. This is especially the case if stability is required over a large temperature range, as it is necessary for applications. A strategy that allows us to obtain one-phase systems at low surfactant concentrations is based on the use of surfactants with longer hydrophobic units. This was investigated in detail for alcohol ethoxylates.[1,2] If, for example, C_8E_3 is used to mix equal amounts of water and octane, at least 20 wt % of surfactant is required to obtain a one-phase system. Replacing C_8E_3 by the equally balanced $C_{10}E_4$ or $C_{12}E_5$ reduces the minimum amount of surfactant needed to 11% and 5%, respectively. The growth of the hydrocarbon chain length increases the bending rigidity of the surfactant film which in turn allows to stabilize larger domain structures. However, the increase in efficiency is accompanied by the disproportionate expansion of a lamellar phase (L_α). In the case of the water−alkane−C_8E_3 system no lamellar phase appears, at least if the surfactant is not the majority component in the mixture. If $C_{10}E_4$ is used, a L_α phase exists at concentrations above about 20%, and for $C_{12}E_5$ almost the whole one-phase region is covered with the lamellar phase.[3,4]

In a different approach to increase the efficiency of surfactants, amphiphilic polymers are used. A first attempt was carried out with hydrophobically modified ethyl hydroxyethyl cellulose, a comb polymer containing a water-soluble backbone and low-molecular-weight, hydrophobic side arms.[5] At low concentrations, this polymer increased in a three-phase system slightly the microemulsion phase at the expense of especially the water excess phase. At higher polymer concentrations the microemulsion phase decreased again. Later it turned out that highly amphiphilic diblock copolymers have a much stronger influence on the phase behavior of microemulsions.[6] Especially polyalkane−polyethylene oxide (PA−PEO) block copolymers were investigated extensively. These polymers can be regarded as polymer analogues to the low-molecular-weight alcohol ethoxylate surfactants. Small quantities of block copolymer added to these surfactants cause a drastic shift of the one-phase region to lower surfactant concentrations. Interestingly, the L_α phase remains largely untouched, compared to the system without polymer additive. However, at higher polymer concentrations an additional lamellar phase can appear.[4,7,8]

Neutron scattering experiments in combination with complex contrast variation experiments showed that the polymer molecules are homogeneously distributed at the surfactant film. They form mushroom conformations with the PA blocks sticking into the oil domains and the PEO blocks sticking into the water domains.[9,10] The polymer decoration increases the bending rigidity of the surfactant film which in turn allows to stabilize

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larger domains or in other words to reduce the surfactant concentration. In this context it is interesting that homopolymers without interfacial activity, which are solubilized in the water and/or oil domains, destabilize microemulsions and strongly shift the one-phase region to higher surfactant concentrations.[11] While PEO does only act repulsively on the nonionic surfactant film,[12] ionic compounds can change the interaction to adsorptive behavior or even complex formation. For nonionic polymers and ionic surfactants the observed effect can be an efficiency increase[13] or the opposite. A detailed discussion of the subject can be found in ref 14.

In this work we will focus on another polymer class, namely water-soluble polymers, which are equipped at one chain end with low-molecular-weight hydrophobic stickers. The simplest representatives having this structure are highly hydrophilic alcohol ethoxylates. Such surfactants are widely used for stabilization of emulsions and dispersions. The analogues with hydrophobic stickers at both chain ends are useful as thickeners. Both types of sticker polymers with one and with two hydrophobic chain ends were used in combination with droplet microemulsions.[15–17] These systems were studied for example with respect to their viscoelastic behavior; however, no influence of the polymer additives on the surfactant efficiency has been reported so far. In this paper we will present results which show how the sticker length and the hydrophilic chain length influence the phase behavior of bicontinuous microemulsions. Additionally, water-in-oil (w/o) and oil-in-water (o/w) microemulsions are investigated.

Experimental Section

Alcohol Ethoxylate Synthesis. All synthetic manipulations except the ethoxylation reactions were carried out under a high vacuum line (pressure = $10^{-4}-10^{-5}$ mbar) or in a glovebox, filled with argon (M Braun, Unilab). The flasks for the manipulations were equipped with Teflon stopcocks, that allowed the transfer of materials between vacuum line and glovebox without being contaminated with air. The flasks which were exposed to overpressure were pressure tested to 4–12 bar, depending on the size of the flask. Ethoxylation reactions were carried out in a double mantle steel reactor (Buchi ecoclave 075). The steel reactor could be connected to the vacuum line but also could be flushed with argon. Temperature control was achieved by using a Huber Unistat 380w thermostat.

Potassium metal (Fluka, >98%) was used as received. 1-Octanol (lot purity 99.5%) and 1-dodecanol (lot purity 99.0%) were purchased from Aldrich. 1-Octadecanol (lot purity 99.7%) was purchased from Fluka. 1-Octanol was stirred at room temperature and 1-dodecanol under slight warming at the vacuum line for 2 h to remove air. Solid 1-octadecanol was degassed overnight. Ethylene oxide (EO) (Fluka, >99.8%) was condensed into a flask at liquid nitrogen temperature and degassed. After being warmed up to room temperature, it was condensed into a second flask which contained calcium hydride and stirred overnight. Toluene (Merck, ≥99.9%) was degassed, distilled into another flask which contained sodium metal, stirred over the sodium for at least 24 h before being degassed again, and heated to 110–115° for 3–4 h.

Alcohol ethoxylates were synthesized by first partially reacting the alcohols with potassium metal in a glovebox. The metalation

Table 1. Characterization of the Alcohol Ethoxylate Additives

	M_n	M_w/M_n	ethoxylation degree
C_8E_{91}	4.130	1.04	91
$C_{12}E_{40}$	2.390	1.04	40
$C_{12}E_{93}$	4.270	1.03	93
$C_{12}E_{189}$	8.490	1.04	189
$C_{12}E_{477}$	21.200	1.07	477
$C_{18}E_{82}$	3.880	1.04	82

degrees were 25% for 1-octanol and 18% for 1-dodecanol. In the case of 1-octadecanol, the metalation degree was 13.5% and the reaction was carried out in toluene. The alcohol−alcoholate mixtures were diluted with toluene and warmed up. Then the mixtures were filled into gastight syringes which were equipped with steel valves and filled into the steel reactor under argon flow. The reactor was cooled to −80° and argon was pumped off via the connection to the vacuum line, which later was used to condense in the needed amounts of EO. The reactor was pressurized with argon, stirred, and slowly heated to temperatures between 90° and 110°. The heating rate was adjusted such that the pressure did not exceed 7 bar. After having reached the maximum temperature, the reaction was continued until no further pressure drop was visible. This took usually 6–12 h. After that time, the reactor was emptied and the product neutralized with acetic acid. The raw products were dissolved in chloroform and washed with water in order to eliminate potassium acetate. The chloroform solutions were concentrated, precipitated in heptane, and dried under vacuum conditions. The products were characterized using a Polymer Laboratories PL 220 SEC instrument together with five Styragel columns with a porosity range from 10^5 to 500 Å at 30°. The solvent was a mixture of THF and *N,N*-dimethylacetamide (DMA) (90:10 by vol) at a flow rate of 1 mL/min. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were calculated using a PEO calibration. Ethoxylation degrees were calculated from the M_n values less the alcohol molecular weight. The results are summarized in Table 1. For the sample names, the same notation is employed as conventionally used for alcohol ethoxylates. C_8E_{91}, for example, stands for *n*-octanol, which was ethoxylated with 91 EO units on average.

Phase Diagrams. Decane (Aldrich) with a purity >99% and water were used for the preparation of the microemulsions. The surfactants were *n*-decyltetraoxyethylene ($C_{10}E_4$) from Bachem (purity 98.1%) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) from Fluka (purity ≥96%). Some investigations were carried out at constant water-to-oil volume ratio of 1. These phase diagrams were recorded by adding successively water and oil to the initial water−oil−surfactant mixture. In a thermostatted water bath at each surfactant concentration the mixtures were investigated visually in transmitted light. Lamellar phases were characterized with the help of cross-polarizers. Other investigations were carried out at constant surfactant-to-water or surfactant-to-decane mass ratios by continuously adding decane or water, respectively. Phase diagrams were recorded in the same way as described above.

Results and Discussion

This work describes the use of highly hydrophilic alcohol ethoxylates as emulsification boosters in microemulsions. With respect to the hydrophilic moiety, the new materials are identical to PA−PEO block copolymers, used so far in this field. Typical molecular weights are in the order of 2000−20 000 g/mol, which correspond to ethoxylation degrees between 50 and 500. The hydrophobic part in the alcohol ethoxylates is formed by a C_8 to C_{18} hydrocarbon chain, whereas in the block copolymers it is a polyalkane chain, usually in the molecular weight range from 2000 to 20 000 g/mol. Those molecular weights translate into 150−1500 C atoms per PA block. From the investigation of block copolymers with different block lengths, it turned out that those polymers with balanced compositions suited best.[4] In such cases the influence of the polymer additive on the temperature behavior of microemulsions was minimal. The structure of the

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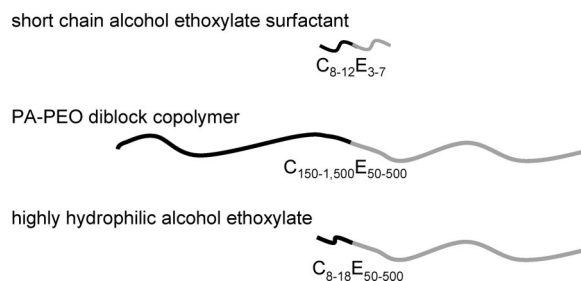(13) Koetz, J.; Andres, S.; Kosmella, S.; Tiersch, B. *Composite Interfaces* **2006**, *13*, 461.

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Scheme 1

short chain alcohol ethoxylate surfactant

$C_{8-12}E_{3-7}$

PA-PEO diblock copolymer

$C_{150-1,500}E_{50-500}$

highly hydrophilic alcohol ethoxylate

$C_{8-18}E_{50-500}$

imbalanced new additives is identical to the structure of alcohol ethoxylate surfactants conventionally used in microemulsions, except that the hydrophilic moiety is 10−100 times larger. Scheme 1 summarizes the structures of the different amphiphiles.

Bicontinuous Microemulsions with $C_{10}E_4$ The hydrophilic alcohol ethoxylate additives were first tested in combination with the conventional surfactant $C_{10}E_4$. Figure 1 shows phase diagrams at water-to-decane volume ratios of exactly 1 in which the overall surfactant mass fraction, γ, is plotted versus temperature. The upper diagram represents the system without additive. At surfactant concentrations above ∼14% a one-phase region appears which expands with respect to temperature at higher surfactant concentrations. The fishtail point is defined by $\tilde{\gamma}$, the lowest surfactant concentration where a one-phase microemulsion is formed, and $\tilde{T}$ the corresponding temperature. At $\gamma > 22\%$ the microemulsion coexists with a lamellar phase or is replaced by a lamellar phase. Below and above the one-phase region, an o/w microemulsion coexists with excess oil ($\underline{2}$) or a w/o microemulsion coexists with excess water ($\bar{2}$). At surfactant concentrations below $\tilde{\gamma}$ two- or three-phase systems exist. This region of the phase diagram was not examined in this work. The second phase diagram in Figure 1 shows the results if the hydrophilic alcohol ethoxylate $C_{12}E_{93}$ is used as additive. For comparison, the lower phase diagram shows the system where the widely investigated PEP−PEO diblock copolymer was used as additive. PEP is a pure polyalkane and consists of alternating ethylene and propylene units. The molecular weights of both blocks are ∼5000 g/mol.
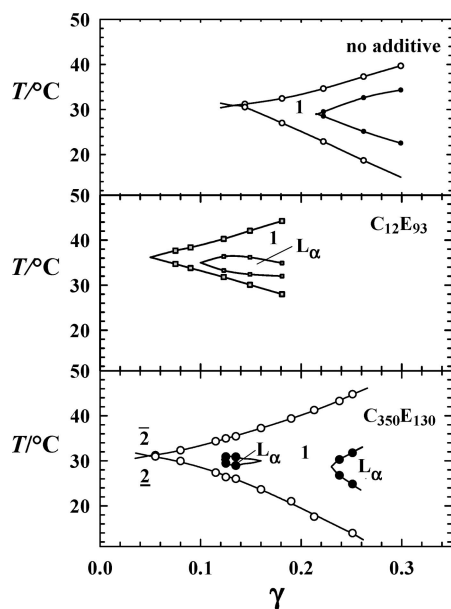
Figure 1. Phase diagrams of water−decane−$C_{10}E_4$ at water-to-decane volume ratios of 1, without additive, with $C_{12}E_{93}$, and with $C_{350}E_{130}$ at $\delta = 0.10$. γ represents the overall surfactant mass fraction, which comprises the surfactant and optionally the polymer additive.

Scheme 2. Temperature-Dependent Film Curvature without and with Additives

no additive   balanced block copolymer   hydrophilic alcohol ethoxylate
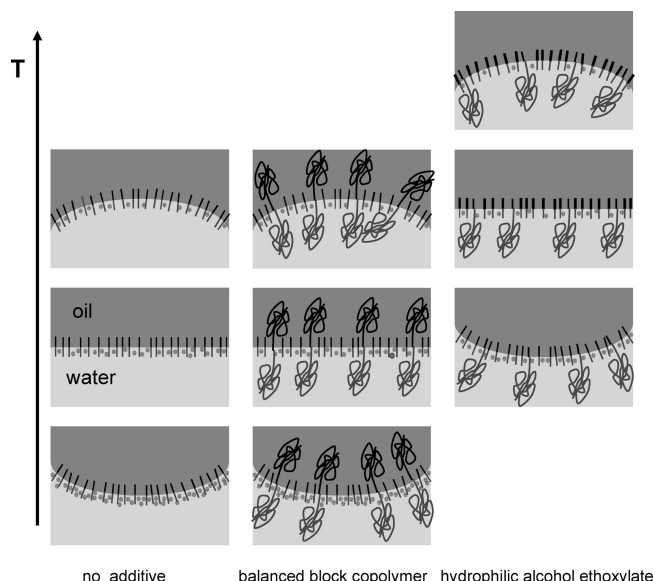
In the notation of alcohol ethoxylates the block copolymer composition can be expressed as $C_{350}E_{130}$. The mass fraction of both additives in the amphiphile mixture (δ) is 10%. Compared to the system without additive ($\delta = 0\%$), the one-phase regions are shifted to smaller surfactant concentrations almost identically for both additive types and at a given surfactant concentration the temperature windows are much wider. Highly amphiphilic PA−PEO block copolymers are quantitatively located at the water−oil interphase, the PA coils extending into the oil domains and the PEO coils into the water domains. The molecular weight of $C_{12}E_{93}$ is approximately half of the $C_{350}E_{130}$ molecular weight. Therefore, at the same δ the number of polymer blocks sticking out of the surfactant film is similar under the assumption that the $C_{12}E_{93}$ chains are largely located at the interface. This in turn must lead to the same efficiency increase what in fact we found. This behavior not necessarily could have been anticipated. Taking into consideration the highly hydrophilic nature of the molecule, monomeric solubilization or micelle formation in the aqueous domains could also be possible. Under the assumption that all polymers are anchored at the surfactant membrane the original picture of Lipowski's theory is fulfilled.[18] Our earlier work circumvented the unsymmetry and the efficient increase was accompanied by a more rigid membrane.[9,10] The increased efficiency on symmetric diblock copolymers is the same for both types of polymers and agrees with the original theory. The current polymer goes along with some unsymmetry which is discussed now.

The striking difference between the two additives is that for $C_{350}E_{130}$ the polymer coils stick out of the surfactant film equally in both directions and so do not influence the mean curvature of the surfactant film; in other words, the temperature behavior is not altered by the block copolymer. In the case of $C_{12}E_{93}$ the orientation of the PEO chains into the water domains causes an additional bending of the surfactant film toward the oil domains. This influence can be compensated by increasing temperature (Scheme 2). It is known for microemulsions containing nonionic surfactants that the average curvature of the surfactant film is zero at $\tilde{T}$. At higher temperatures the film is curved toward the water domains whereas at lower temperatures it is curved toward

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the oil domains. The reason for this behavior is the hydration of EO chains which gets lesser with increasing temperature.[19] Interestingly, only a temperature increase of about 5° is sufficient to compensate the effect of the hydrophilic additives.

A lamellar phase coexists for $\gamma > 23\%$ in the block copolymer case, which is in absolute concentrations equivalent to the lamellar region in the system without additive (Figure 1). Relative to the fishtail point the lamellar phase is shifted back considerably. In addition, the block copolymer system shows a small lamellar island at $\gamma = 12-14\%$. A detailed description of the block copolymer influence on the microemulsion phase behavior can be found in refs 6 and 4. $C_{12}E_{93}$ does not suppress the extension of the lamellar phase as much as the block copolymer additives do. Compared to the microemulsion without additive, the lamellar phase in the $C_{12}E_{93}$ system is nearer at the fishtail point but its temperature extension is smaller. In this context one should keep in mind that without polymeric additives an efficiency increase is accompanied by disproportionate growth of the L_α phase. For example, $C_{12}E_5$ shows approximately the same efficiency as the system $C_{10}E_4$ in combination with $C_{12}E_{93}$ at $\delta = 0.10$, but almost the whole one-phase region is covered with the lamellar phase. Compared to the $C_{12}E_5$ system, the extension of the lamellar phase in the $C_{10}E_4/C_{12}E_{93}$ system is rather small. The center of the lamellar phase for the $C_{12}E_{93}$ system appears slightly below the phase inversion temperature where the spontaneous curvature, c_0, is zero. This dislocation of the L_α phase was seen before for asymmetric block copolymers having much longer PEO than PA blocks.[4] For microemulsions without polymer or with a symmetric diblock copolymer the phase inversion temperature stays rather constant with respect to γ. This is not necessarily the case for the current polymers. As we will discuss below (eq 3) the polymer effect on c_0 depends on the bending rigidity. Due to the spatial renormalization (see ref 11) the bending rigidity increases by ~75% between the fishtail point and the lamellar phase. This effect could be responsible for a shifted c_0.

In the next series of experiments the length of the hydrophobic unit was varied. This is shown in Figure 2. For comparison, the phase diagrams are shown again where $C_{10}E_4$ was used without additive and with $C_{12}E_{93}$. In addition, Figure 2 presents the results for the mixtures containing C_8E_{91} and $C_{18}E_{82}$. In all cases the weight fraction of additive in the additive–$C_{10}E_4$ mixture is $\delta = 0.10$. For all three additives the locations of the one-phase regions on the temperature scale is almost similar as it should be. The shift to smaller surfactant concentrations effected by the additives, is similar for $C_{12}E_{93}$ and $C_{18}E_{82}$, both having the fishtail point at $\gamma = 5\%$. This supports the finding reported before that $C_{12}E_{93}$ is fully interfacially active. The efficiency increase caused by C_8E_{91} is significantly smaller with the fishtail point being located at $\gamma = 7.5\%$. However, compared to the system without additive, where the fishtail point is at 13.5%, the efficiency increasing effect of C_8E_{91} is powerful. This means that the short C_8 hydrophobe leads to a strong but not fully interfacial activity of the additive.

In a simple picture one can expect that additive molecules not being anchored at the water–oil interface are solubilized in the water domains as unimers, assuming that there is no further attractive interaction between the PEO monomer units and the surfactant film.[12] However, free polymer chains reduce the surfactant efficiency.[11] It can be estimated that the efficiency reduction of nonadsorbed polymer is approximately as strong as the efficiency increase caused by polymer located at the water–oil interface. The concentration of nonadsorbed additive in microemulsions can be estimated assuming its concentration to be
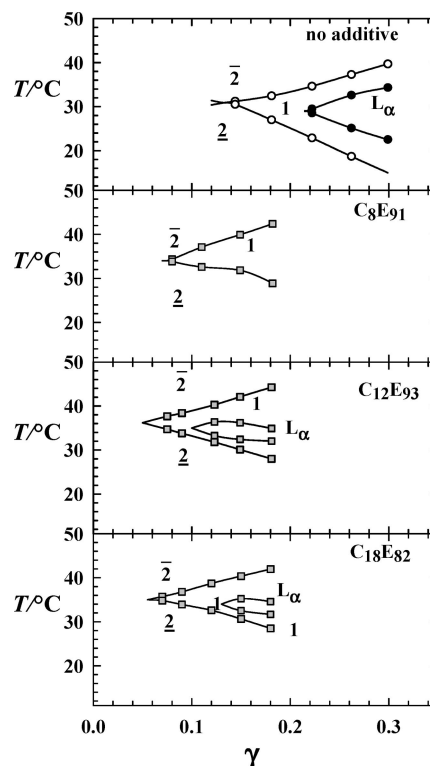
Figure 2. Phase diagrams of water–decane–$C_{10}E_4$ at water-to-decane volume ratios of 1, without additive, with C_8E_{91}, with $C_{12}E_{93}$, and with $C_{18}E_{82}$ at $\delta = 0.10$. γ represents the overall surfactant mass fraction, which comprises the surfactant and optionally the polymer additive.

approximately the same as its critical micelle concentration (CMC) in the binary mixtures with water. For $C_{16}E_x$ CMC values are reported in the literature between $x = 7$ and 21.[20] In this ethoxylation range, the CMC on a molar basis increases linearly with x. The extrapolation to $x = 90$ and conversion to mass values yields CMC = 0.07 g/L. At $\delta = 0.10$ the amounts of $C_{12}E_{93}$ or $C_{18}E_{82}$ in the microemulsions at the fishtail points are about 9 g/L of water. On the basis of this comparison, it is understandable that the additive is largely located at the water–oil interface, if the hydrophobic unit is C_{16} or larger. In the case of shorter hydrophobes, unimer solubility drastically increases. For $C_{12}E_x$ CMC values are reported between $x = 2$ and 12.[21,22] The extrapolation to $x = 93$ yields for $C_{12}E_{93}$ CMC = 3.9 g/L. If one considers the error associated with the extrapolation procedure and that CMC is not identical with unimer solubility in a microemulsion, it might be still assumable that the additive molecules are largely anchored at the water–oil interface. For C_8E_x CMC values are only available until $x = 6$.[23,24] The CMC value for C_8E_{91} estimated on this data basis is 390 g/L. Even if one uses the same molar CMC value for C_8E_{91} as reported for C_8E_6, the mass-based CMC for C_8E_{91} would still be 41 g/L. On the other hand, the C_8E_{91} amount in the microemulsion at the fishtail point at $\delta = 0.10$ is about 14 g/L of water. Knowing this, one would estimate that C_8E_{91} hardly is interfacially active. The phase behavior measurements, however, show that C_8E_{91} is predominantly located at the water–oil interface.

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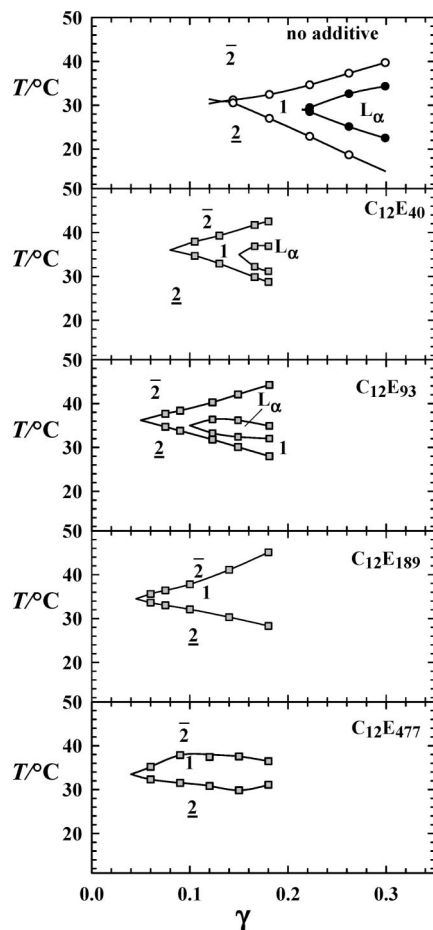(20) Elworthy, P. H.; MacFarlane, C. B. *J. Pharm. Pharmacol. Suppl.* **1962**, *14*, 100.

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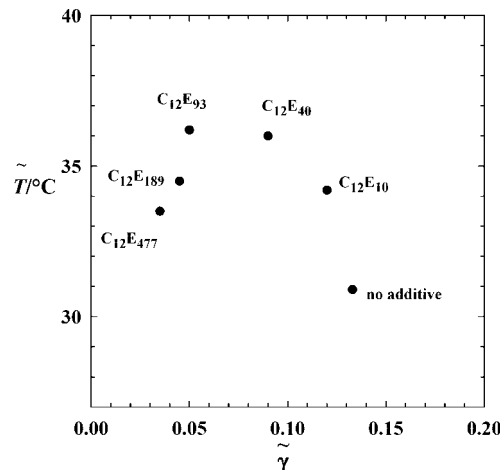(24) Shinoda, K.; Yamanaka, T.; Kinoshita, K. *J. Phys. Chem.* **1959**, *63*, 648.

Figure 3. Phase diagrams of water−decane−$C_{10}E_4$ at water to decane volume ratios of 1, without additive, with $C_{12}E_{40}$, with $C_{12}E_{93}$, with $C_{12}E_{189}$, and with $C_{12}E_{477}$ at $\delta = 0.10$. γ represents the overall surfactant mass fraction, which comprises the surfactant and optionally the polymer additive.

There is also an influence of the hydrophobe's chain length on the existence and extension of the L_α phase. In the case of the additive C_8E_{91}, no L_α phase appears up to $\gamma = 18\%$, whereas if $C_{12}E_{93}$ is used, the L_α phase starts at $\gamma = 10\%$. A further increase of the alkyl chain length to 18 carbon atoms in $C_{18}E_{82}$ slightly shifts back again the L_α phase with a starting point at $\gamma = 13\%$ (see Figure 2). Although it is known that the formation of lamellar phases is strongly enhanced by extending the length of the hydrophobic unit of amphiphiles, it is unlikely that this influences significantly the phase behavior as at $\delta = 0.10$ the molar ratio of surfactant to additive is >100. It seems more likely that the small fraction of noninterfacially active C_8E_{91} is responsible for the suppression of the L_α phase. For homopolymers such behavior was seen before.[25]

In the next step, the length of the hydrophobic unit was fixed at C_{12} and the chain length of the PEO chain was varied. Figure 3 shows the phase diagrams of the systems without additive and with the additives $C_{12}E_{40}$, $C_{12}E_{93}$, $C_{12}E_{189}$, and $C_{12}E_{477}$, all at $\delta = 0.10$. Compared to the mixture without additive, the one-phase region is shifted to smaller γ values the longer the PEO chain of the additive is. The shape of the one-phase region of the system containing $C_{12}E_{477}$ is qualitatively different from the other phase diagrams. Up to $\gamma = 10\%$ the temperature window of the one-phase region widens but stays approximately constant

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Figure 4. Location of the fishtail points of the microemulsions without additive and with $C_{12}E_{10}$, $C_{12}E_{40}$, $C_{12}E_{93}$, $C_{12}E_{189}$, and $C_{12}E_{477}$ at $\delta = 0.10$ for the system water−decane−$C_{10}E_4$ at water-to-decane volume ratios of 1. $\tilde{\gamma}$ is the lowest overall surfactant mass fraction, where a one-phase microemulsion is formed and $\tilde{T}$ is the corresponding temperature.

for higher γ. This behavior gets understandable if one compares the sizes of the microemulsion domains with the extension of the polymer coils. The structural size of the water and oil domains decreases with increasing γ. At $\gamma = 12\%$ the average size of a water domain is 16−17 nm. The size of a PEO chain having the same molecular weight as $C_{12}E_{477}$ in terms of its end-to-end distance, R_{ee}, is 16.5 nm.[26] This means that at surfactant concentrations above about 12% the PEO coil is larger than the size of the water domains. This size match means that the polymer touches the opposite membrane with a certain probability which eventually would disfavor the polymer being in the microemulsion. Such effects could cause a decrease of the efficiency at higher surfactant concentrations or a narrowing of the one-phase region. The R_{ee} values calculated for $C_{12}E_{189}$ and $C_{12}E_{93}$ are 9.5 and 6.3 nm. The sizes of the water domains in the microemulsions exceed these lengths first at surfactant concentrations above 20% and 30%, respectively.

The length of the PEO chain also influences the appearance of L_α phases. In the mixture containing $C_{12}E_{40}$ the location of the L_α phase relative to the fishtail point slightly moves to smaller surfactant concentrations. For the system with $C_{12}E_{93}$, this tendency gets stronger, as well as the drift of the L_α phase to the lower phase boundary. The mixtures containing the longest PEO chains, $C_{12}E_{189}$ and $C_{12}E_{477}$, show no L_α phases up to $\gamma = 18\%$. The similar size of the polymer and the domains might be responsible for this effect. A different viewpoint of phase-separated L_α phases with and without polymer shows that the polymer confinement influences the phase behavior.[7]

In Figure 4 $\tilde{\gamma}$ is plotted vs $\tilde{T}$ for the mixtures described above and additionally for the mixture containing the additive $C_{12}E_{10}$. With increasing PEO chain length of the additive the fishtail points move to smaller surfactant concentrations. It is interesting that already the additive $C_{12}E_{10}$ slightly increases the efficiency of the surfactant although the length of its PEO chains is only 2.5 times larger than the length of the hydrophilic moiety in $C_{10}E_4$ molecules. If $C_{12}E_{10}$ is regarded as surfactant and not as polymer with a long-chain hydrophilic unit, the hydrophilic and the hydrophobic groups influence phase behavior differently. For alcohol ethoxylates it is known that the increase of the EO chain length at constant length of the hydrophobic tail shifts

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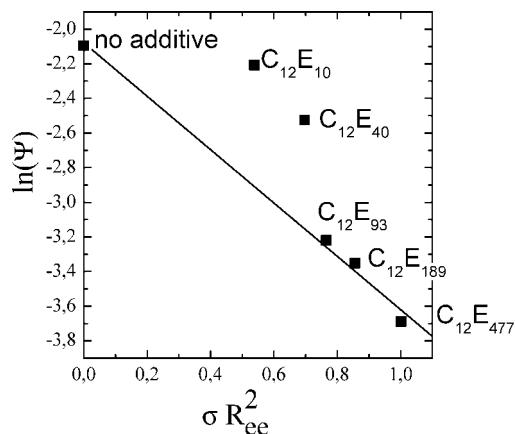
Figure 5. Dependence of the effective surfactant concentration Ψ at the fishtail points as a function of the polymer grafting density σ scaled with the polymer size R_{ee}^2.
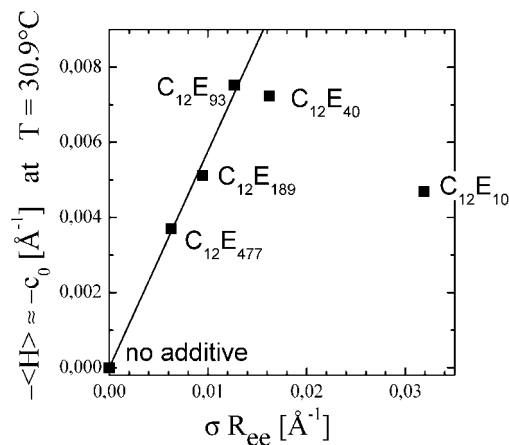

Figure 6. Spontaneous curvature dependence as a function of the polymer density, σ, scaled with the polymer size, R_{ee}.

back the one phase region to higher surfactant concentrations.[2,27] By contrast, elongation of the hydrophobic tail increases surfactant efficiency. This effect was measured for the system water−decane−$C_{10}E_4$ with $C_{12}E_4$ as cosurfactant.[6] If the contributions of both effects are estimated from the data provided in refs 2, 6, and 27, they cancel out each other or even lead to a slight efficiency decrease. This suggests that the nature of the efficiency increase caused by $C_{12}E_{10}$ is due to its commencing polymeric nature.

According to theoretical considerations the effective surfactant concentration at the fishtail point, Ψ, is correlated with the number density of polymer chains per interfacial area, σ, and R_{ee} in the following way

$$\ln(\Psi/\Psi_0) = \Xi\sigma R_{ee}^2 \qquad (1)$$

with the theoretical sensitivity $\Xi = \pi/5$.[28] Ψ corresponds to γ less the fraction of surfactant being solubilized monomerically in oil and water. Ignoring the minimal solubility of $C_{10}E_4$ in water and considering its solubility in decane of 2.0 wt %, Ψ can be easily calculated from γ. Under the condition that δ is constant, σ and R_{ee}^2 are correlated with the molecular weight of the polymer chain, M_w, according to $\sigma \sim M_w^{-1}$ and $R_{ee}^2 \sim M_w^{1.16}$, the latter relation being valid only for PEO.[26] Therefore, the influence of M_w on Ψ should be rather small, i.e., $\ln(\Psi/\Psi_0) \sim M_w^{0.16}$.

In Figure 5 $\ln\Psi$ is plotted against σR_{ee}^2. There is a disagreement for $C_{12}E_{10}$ and $C_{12}E_{40}$, both having short PEO chains. These additives increase the efficiency of $C_{10}E_4$, however, because of the relatively low molecular weights the PEO chains cannot be regarded as ideally swollen coils. It is generally known that low-molecular-weight polymers dissolved in a good solvent form much denser structures than their higher-molecular-weight analogues.[29] For the calculation of R_{ee}, this effect was not taken into account so that the values calculated for σR_{ee}^2 are too large. Hence, the additives $C_{12}E_{10}$ and $C_{12}E_{40}$ were not used for further evaluations. The line shown in Figure 5 represents the fit ignoring the two short chain additives. The measured value for the slope of $\Xi = -1.54$ coincides exactly with the value found for the A−B block copolymers.[28] The small range of σR_{ee}^2 covered with the polymers $C_{12}E_{93}$ to $C_{12}E_{477}$ reflects the weak molecular weight dependence of $\ln(\Psi/\Psi_0)$.

In this context, it should be pointed out that in case of the diblock copolymer half of the polymer coils extend into the water domains and the other half, into the oil domains, both contributing to σ. For the hydrophilic alcohol ethoxylates all polymer coils extend into water domains. At same δ and same block molecular weights, the number of polymer coils per interfacial area and the increase in bending rigidity of the surfactant film is similar for both additive types. As PA−PEO block copolymers are located quantitatively at the water−oil interface, due to the very strong amphiphilicity, the same values found for Ξ additionally demonstrates that the hydrophilic alcohol ethoxylates are quantitatively anchored in the surfactant film, too. This is even the case for $C_{12}E_{477}$ where the hydrophobic tail contributes only 0.8% to the overall molecular weight.

The other important feature shown in Figure 4 is the temperature behavior. For the shorter chain lengths, there is an increase of $\tilde{T}$. Because of the hydrophilic nature of the alcohol ethoxylate additives this intuitively makes sense. The temperature decline for the additives $C_{12}E_{189}$ and $C_{12}E_{477}$ does not fit in this scenario. Experimentally, the relation between film mean curvature $\langle H \rangle$ and temperature was examined by Sottmann and Strey.[30] They found the following equation

$$\langle H \rangle = \mu\Delta T \qquad (2)$$

with the experimental constant $\mu = -1.4 \times 10^{-3}$ Å^{-1} K^{-1} for $C_{10}E_4$. ΔT is the temperature difference between a given temperature and $\tilde{T}$. The relation between $\langle H \rangle$ and the polymer parameters is according to theoretical calculations from Lipowsky and Gompper[18,31] as follows

$$\langle H \rangle = \Upsilon\sigma R_{ee} \qquad (3)$$

with the theoretical sensitivity $\Xi = 0.181/(\kappa/k_BT) \approx 0.43$. The mean bending rigidity was assumed to be $\kappa = 0.42k_BT$. If again the molecular weight is introduced into the relation, it transforms into $\langle H \rangle \sim M_w^{0.42}$. This means that, with increasing molecular weight, the influence on the curvature gets smaller. Exactly this scenario is shown in Figure 4 for higher molecular weights. The reason for the deviations of $C_{12}E_{10}$ and $C_{12}E_{40}$ from the theoretical predictions is the diminishing polymeric nature of the short PEO chains as described before. In Figure 6 $\langle H \rangle$ is plotted against σR_{ee}. The expected dependency is obtained for the higher molecular weights with a sensitivity $\gamma = 0.58$. The mismatch for

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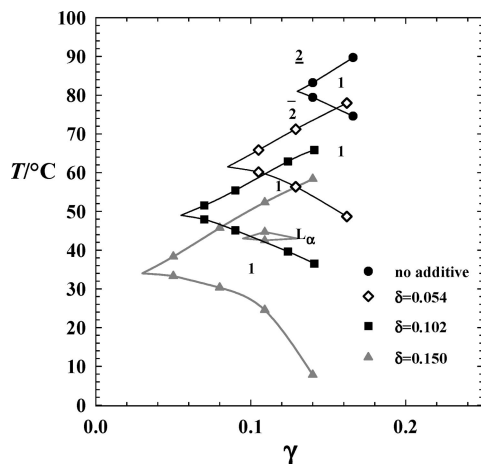
Figure 7. Phase diagrams of water/NaCl (1%)−decane−AOT at water-to-decane volume ratios of 1, without additive and with $C_{18}E_{82}$ at different δ values. γ represents the overall surfactant mass fraction, which comprises the surfactant and optionally the polymer additive.

$C_{12}E_{40}$ is less expressed than for $C_{12}E_{10}$ because of its more polymer-like structure. The dependence of γ on the bending rigidity explains the effect of a surfactant content depending phase inversion temperature where $<H> = 0$. The spatial renormalization leads to an increased bending rigidity which leads to a decreased $|<H>|$ and therefore to a decreased phase inversion temperature.

Bicontinuous Microemulsions with AOT. In order to demonstrate that the efficiency boosting described here is not restricted to nonionic surfactants, an anionic surfactant was also studied. AOT was chosen for this task, as it is known to form microemulsions as single surfactant. Figure 7 shows the results using 1% aqueous NaCl instead of water. The upper phase diagram represents the microemulsion without additive. The efficiency of AOT under these conditions is similar to $C_{10}E_4$, except that the temperature window for the one-phase system is shifted to much higher temperatures. The addition of increasing amounts of $C_{18}E_{82}$ moves the one-phase regions gradually to smaller surfactant concentrations. If 10.2% of the AOT are replaced by the additive ($\delta = 0.102$), the fishtail point is located at $\gamma = 5.5\%$. This is almost the same value as that found for the system $C_{10}E_4/C_{12}E_{93}$ at the same additive concentration. For $\delta = 0.150$ the fishtail point moves further to $\gamma = 3\%$ and a small lamellar phase appears, which was absent in the other AOT microemulsions. The appearance of a lamellar phase at higher additive concentrations is in agreement with the results found for microemulsions containing nonionic surfactants, where the same behavior was found.[4]

The temperature behavior of the AOT systems is qualitatively and quantitatively different from their $C_{10}E_4$ counterparts. With increasing $C_{18}E_{82}$ concentration the one-phase region strongly shifts to lower temperatures. This is understandable if one considers the temperature dependence of the surfactant film curvature. For ionic surfactants this is contrary to alcohol ethoxylates. At higher temperatures the film is curved toward the oil domains, and at lower temperatures it is curved toward the water domains.[19] Accordingly, the addition of hydrophilic alcohol ethoxylate moves the one-phase region to lower temperatures. However, the temperature drop at $\delta = 0.10$ is 32 °C, in the case of the system $C_{10}E_4/C_{12}E_{93}$ at the same δ value, the temperature increase was only 5 °C. This difference can be explained on the basis of the γ dependence of the phase inversion temperature $\tilde{T}$. For $C_{10}E_4$ $\tilde{T}$ is independent of γ. Therefore, the phase diagram is symmetric with respect to $\tilde{T}$. For AOT $\tilde{T}$ strongly drops with
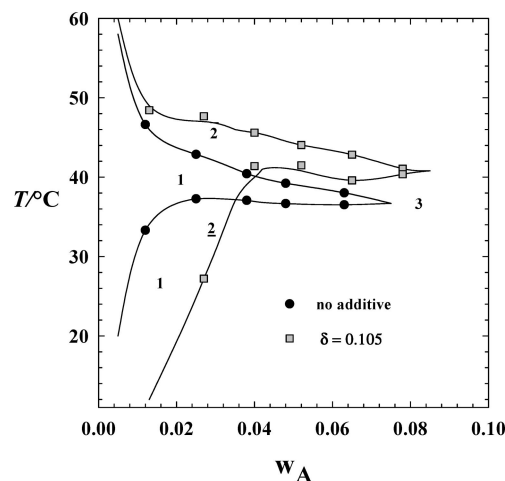
Figure 8. w/o microemulsion of the system water−decane−$C_{10}E_4$ at γ_B = 0.052 without additive and with $C_{18}E_{82}$ at $\delta = 0.105$. w_A represents the weight fraction of water in the overall mixture.

decreasing γ.[27] Therefore, the temperature change in the systems containing $C_{10}E_4$ is uniquely related to the additive, whereas for the mixtures with AOT the surfactant and the additive contribute to the temperature change. There is another significant difference between the microemulsions on the basis of AOT and $C_{10}E_4$. The temperature windows of the AOT-containing one-phase system are much wider than their $C_{10}E_4$ analogues. For example at $\delta = 0.150$ and $\gamma = 12\%$ the temperature range of the AOT microemulsion comprises 35 °C; at $\delta = 0.102$ it is still 22 °C. Under similar conditions for $C_{10}E_4$ at $\delta = 0.10$ the temperature spread is reduced to 6 °C.

Droplet Microemulsions with $C_{10}E_4$ So far we focused on bicontinuous microemulsions, containing equal volumes of water and oil. In the next step the examination was extended to droplet microemulsions. The surfactant used was $C_{10}E_4$. The effect of $C_{18}E_{82}$ on w/o microemulsions is given in Figure 8. In this presentation, the mass fraction of surfactant in the decane−surfactant mixture (γ_B) was held constant at $\gamma_B = 0.052$ and the weight fraction of water in the overall mixture (w_A) was varied. In the system without additive, a microemulsion is formed up to water contents of about 7.5% in a fairly narrow temperature interval around 39 °C. Only at very small water contents below $w_A = 1.5\%$ does the temperature window widen visibly. If $C_{18}E_{82}$ at $\delta = 0.105$ is added, the maximum amount of water that can be incorporated into the microemulsion increases only slightly. The temperature window of the one-phase region at low water contents is extended especially to lower temperatures. If more water is added, the one-phase region is shifted to somewhat higher temperatures but only marginally opens the temperature window.

Figure 9 shows the reverse case, where a microemulsion containing oil droplets in water (o/w) was investigated. Except the exchange of water and oil, the other ingredients were equal to the w/o system. If no additive is used the one-phase region is extended up to a weight fraction of 8.5% of added decane (w_B). The addition of $C_{18}E_{82}$ at $\delta = 0.109$ significantly shifts the one-phase region to higher oil contents. Now up to 17% of decane can be solubilized in the microemulsion. Simultaneously, the stability range is extended strongly to higher temperatures. In the upper part of the one-phase region a lamellar phase coexists with the microemulsion phase.

The experimental findings get comprehensible if one first focuses on the temperature behavior. In both droplet microemulsions the addition of $C_{18}E_{82}$ leads to an increase of the temperature level of the one-phase region due to the hydrophilic
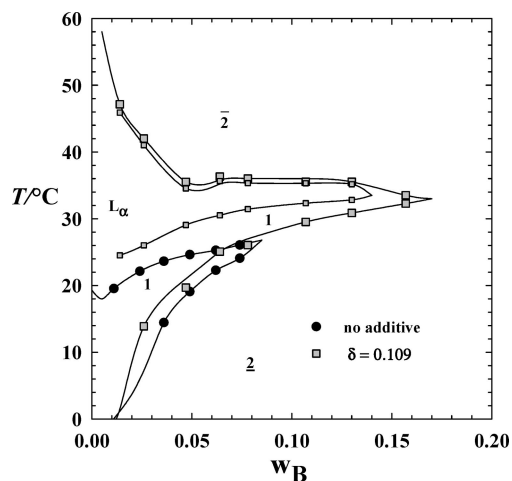
Figure 9. o/w microemulsion of the system water−decane−$C_{10}E_4$ without additive at $\gamma_A = 0.053$ and with $C_{18}E_{82}$ at $\delta = 0.105$ and $\gamma_A = 0.054$. w_B represents the weight fraction of oil in the overall mixture.

nature of the additive. In this respect the droplet and bicontinuous microemulsions behave in the same way. The increased temperature compensates the polymer effect on the spontaneous curvature. In the case of w/o droplets (Figure 8), strong confinement effects play a role, especially at low water contents. At 2% water, for example, the droplet diameter is 4.5 nm and 1.6 PEO chains on average share one droplet. On the other hand, the PEO dimension in terms of R_{ee} is 5.8 nm. Therefore, the polymer requires some space which is expressed by the extension of the one-phase region to lower temperatures. This effect is an entropic volume effect which would not simply be expressed in changes of the bending rigidity. At lower temperatures, droplets are replaced by cylinders, which offer more space for the PEO chains. At 7% water, the droplet diameter is increased to 15.8 nm and each droplet is occupied on average by 5.5 PEO chains. We tend to believe that in this region the polymer effect can be described by effectively changed bending moduli as assumed by the confinement simulations by Auth.[32] The almost-unchanged maximum solubility of water might be due to a degree of confinement between the boosting and reversed boosting behavior.

For the o/w microemulsions the maximum uptake of oil is drastically increased since confinement does not play a role, and the normal boosting effect as described by classical theories[17] explains the increased efficiency. For the o/w microemulsions it is known that at low temperatures spherical droplets form, while at higher temperatures cylinders and possibly networks

form.[33,34] There is no clear-cut phase boundary, since the entropy of mixing allows for a coexistence of both structures.[35] At even higher temperatures a lamellar phase appears,[28] which in our case is only indicated by a two-phase coexistence. The whole scenario is found for our highly efficient microemulsion now as well. The phases $\underline{2}$ and $\overline{2}$ are pushed back, and the droplet phase and the lamellar phase extend more widely.

Conclusions

This work has shown that not only highly amphiphilic block copolymers are useful to increase the efficiency of surfactants in microemulsions drastically but also hydrophilic alcohol ethoxylates. This class of additives offers several advantages compared to block copolymers with long-chain hydrophobes. First, the synthesis is simple and can be carried out for example by ethoxylation of monofunctional alcohols. The synthesis of PA−PEO block copolymers on the other hand is laborious and requires several reaction steps.[36] Second, alcohol ethoxylate additives are interesting candidates from the application standpoint. They are commercially available, readily biodegradable, and in addition, inexpensive. PA−PEO block copolymers so far exist only as research products and are not commercially available. According to our own tests, their biodegradability is very low. Finally, the combination of a long hydrophilic chain with short hydrophobic stickers facilitates comparison with theoretical studies, which usually are based on models where homopolymers are attached to a membrane. This situation additionally gives rise to a changed spontaneous curvature which we observed here in terms of a changed phase inversion temperature. The efficiency increase is the same for symmetric diblock copolymers and the hydrophilic polymers of the present study. Besides the interesting aspects related to applications the alcohol ethoxylate additives offer a broad field of activity from the fundamental research standpoint. Presently we investigate the anchoring behavior of polymers equipped with very short hydrophobic units in the surfactant membrane. In addition, we study the influence of polymer architecture on the membrane properties such as polymers equipped with two hydrophobic end groups[37] or branched architectures.

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