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ORIGINAL CONTRIBUTION

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# Polymerisation of styrene in microemulsion with catanionic surfactant mixtures

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**Abstract** The use of aqueous catanionic surfactant mixtures in the oil-in-water (o/w) microemulsion polymerisation of styrene is reported. Catanionic surfactant mixtures of dodecyltrimethylammonium bromide **1** and sodium dodecylsulfate **3**, or decanediyl-1,10-bis(dimethyldodecylammonium bromide) **2**, a gemini surfactant, and the anionic surfactant **3** were used. Phase behaviour and polymerisation properties of the microemulsions were studied as a function of the total surfactant concentration and the cationic/anionic surfactant ratio. Single-phase o/w microemulsions were only formed if either the cationic or anionic surfactant were present in large excess. Upon $\gamma$-irradiation, polymer nanoparticles were obtained. Using dynamic light scattering, the particle radii were determined to be 10 to 20 nm, the size depending on the total surfactant concentration, the cationic/anionic surfactant ratio and the surfactant/styrene ratio. Size exclusion chromatography indicated molecular weights of polystyrene of between $3\times10^5$ and $1.4\times10^6$ Daltons. Catanionic **1**/**3** and **2**/**3** mixtures differ in their styrene solubilizations. In a **1**- or **3**-rich system, the solubilization efficiency can be improved by increasing the concentration of the oppositely charged minor surfactant component, while in a **2**-rich system the addition of **3** only diminishes the efficiency. Possible reasons for the different behaviours are discussed.

**Keywords** Polymerisation · Microemulsion · Styrene · Catanionic surfactant mixture

## Introduction

In the last two decades the interest in aqueous catanionic (cationic and anionic) surfactant mixtures has grown continuously [1]. Mixing of oppositely charged surfactants can produce interesting microstructures such as vesicles [2], large lamellar sheets [3, 4], or rod-like micelles [4, 5], which are not formed by any of the pure compounds. Due to the strong electrostatic interaction between the head groups, catanionic surfactant mixtures exhibit low critical aggregation concentrations and enhanced surface active properties [3, 6, 7, 8, 9]. Furthermore, variation of the surfactant molecular structure and the stoichiometry of the mixture allows us to tailor specific nano- and microstructures.

Most of the previous studies on catanionic surfactant assemblies have focused on phase behaviour [2, 3, 4, 10, 11, 12, 13], determination of critical aggregation concentration [3, 6, 10, 14], aggregation number and composition of the aggregates [10, 14, 15, 16], while little was reported on the use of the assemblies as a medium for chemical reactions [17]. The incorporation of water-insoluble monomers like styrene in catanionic micellar aggregates will eventually result in the formation of microemulsion droplets, which upon high energy irradiation can be polymerised and surfactant-stabilised nanoparticles are obtained. Depending on whether the cationic or anionic surfactant is present in excess, the particles will exhibit either a positive or negative surface charge.

There are numerous studies on microemulsion polymerisation of styrene and other monomers using either cationic, nonionic or anionic surfactants [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29]. Copolymerisation in microemulsion has also been reported [30]. Most studies have been concerned with the copolymerisation of water-soluble or water-insoluble monomers and surfactant monomers [31, 32, 33, 34, 35, 36, 37, 38]. In order to solubilize water-insoluble monomer more effectively, either divalent organic counterions were introduced [39], or the ordinary single-tail surfactants were replaced by so-called “gemini” surfactants [40, 41]. Gemini surfactants represent dimeric surfactants in which the headgroups of the two amphiphilic parts are connected via a hydrophobic or hydrophilic spacer unit [42, 43].

In catanionic surfactant mixtures, cationic and anionic surfactants are mixed in a non-stoichiometric ratio, the positively and negatively charged surfactants thereby forming pairs, which can be thought of as pseudo-double-tailed, zwitterionic gemini surfactants. Due to the strong electrostatic interaction, the catanionic surfactant mixture forms a rather rigid lipid layer with small effective cross-sectional area of the head groups and reduced surface curvature. As a consequence, the solubilization efficiency for water-insoluble monomers such as styrene will eventually be enhanced. Up to now, only a few articles have been concerned with microemulsions of catanionic surfactant mixtures [44, 45, 46]. A study on the solubilization of styrene has not been reported yet.

In our paper, the preparation and characteristic properties of microemulsions of styrene and catanionic surfactant mixtures in the aqueous phase are described. The polymerisation of styrene in the single-phase o/w microemulsion region was investigated. For the surfactants, we used dodecyltrimethylammonium bromide **1**, decanediyl-1,10-bis(dimethyldodecylammonium bromide) **2**, a gemini surfactant, and sodium dodecylsulfate **3**. The chemical structures of these are shown in Fig. 1. Based on these surfactants, the two quaternary systems water/**1**/**3**/styrene and water/**2**/**3**/styrene were studied. The phase behaviour of the monomeric microemulsions, the size of the final polymer particles, and the molecular weight of the polymer were determined using dynamic light scattering and size exclusion chromatography.

The polymerisation was carried out using $^{60}$Co-$\gamma$-irradiation. High-energy irradiation has several advantages over other polymerisation methods: The samples are homogeneously penetrated, it is possible to initiate the polymerisation at room temperature, and additional initiator compounds are not needed.

## Experimental

### Materials

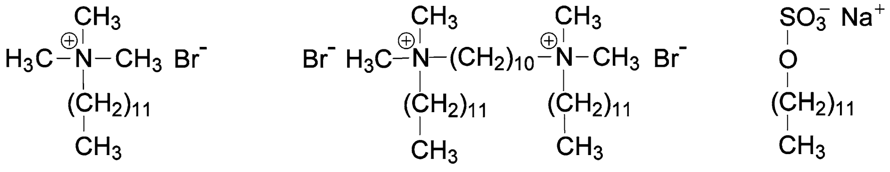
Dodecyltrimethylammonium bromide **1** (Fluka) and sodium dodecylsulfate **3** (Fluka) were used without further purification. Decanediyl-1,10-bis(dimethyl-dodecylammonium bromide) **2** was prepared according to the literature [47, 48]. The purity was checked using 300 MHz $^1$H-NMR and surface tension measurements in aqueous solution (Wilhelmy plate method, Krüss Digital-tensiometer K10T, 25 °C). The cmc value was found to be in the range described in the literature [49]. Styrene (Aldrich) was freshly distilled before use in order to remove the inhibitor and oligomeric products. Milli-Q$_{\mathrm{Plus}}$ water with low conductivity ($R > 18$ MΩ) was used for all experiments.

### Polymerisation

Polymerisation in microemulsion was performed in closed glass vessels at 25 °C. The transparent samples were prepared by titrating the desired amount of freshly distilled styrene into the aqueous surfactant solution. $^{60}$Co-$\gamma$-irradiation was used for the polymerisation. The dose rate was 0.4338 kGy h$^{-1}$. To achieve complete conversion, each sample was subjected to a radiation dose of about 6 kGy.

### Characterisation methods

For the study of the phase behaviour, aqueous solutions with different ratios of cationic and anionic surfactant were prepared. The single phase regions of the micro-



**1** $\mathrm{H_3C{-}\overset{\oplus}{N}(CH_3)(CH_2)_{11}CH_3{-}CH_3\ Br^-}$

**2** $\mathrm{Br^-\ H_3C{-}\overset{\oplus}{N}(CH_3)((CH_2)_{11}CH_3){-}(CH_2)_{10}{-}\overset{\oplus}{N}(CH_3)((CH_2)_{11}CH_3){-}CH_3\ Br^-}$

**3** $\mathrm{CH_3(CH_2)_{11}{-}O{-}SO_3^-\ Na^+}$

**Fig. 1** Chemical structures of surfactants **1**–**3**

emulsions were determined visually by titrating styrene into the aqueous surfactant solution in screw-capped glass tubes. Each sample was thoroughly homogenised using a Vortex mixer and thermostated in a water bath at 25 °C. The added styrene contained a few parts per million of hydroquinone in order to prevent spontaneous polymerisation.

Particle sizes were determined at a temperature of $25 \pm 0.1$ °C using a goniometer system (ALV GmbH, Langen) equipped with an ALV 5000e correlator (Ar ion laser, $\lambda = 488$ nm). Data were evaluated according to the cumulant method, and values were checked using a constrained regularisation procedure (CONTIN, ALV).

Molecular weights were measured using gel permeation chromatography (Waters 501) equipped with a UV detector. A set of two Styragel columns (HR1, HR5, Waters) and a Eurogel column (GPC 1000, Knauer) was used after calibration with polystyrene standards (Polyscience). Freshly distilled tetrahydrofurane (THF) was used as eluant; the flow rate was 1 mL $\mathrm{min}^{-1}$. Prior to the measurement, the polymer was separated from the surfactant by precipitation in methanol and filtration using a pressure filtration apparatus.

## Results and discussion

### Phase behaviour

### *System water/**1**/**3**/styrene*

The phase behaviour of the system water/**1**/**3**/styrene was studied for different total surfactant concentrations, different weight ratios of **1** to **3**, and different amounts of styrene added to the system. We found that clear solutions could only be prepared if either **1** or **3** were present in large excess. At weight fractions of **1** between 31–73%, a crystalline complex was formed, which precipitated from the solution as a white solid. In Fig. 2, a partial phase diagram is shown. If **1** (Fig. 2a) or **3** (Fig. 2b) are present in large excess, a clear, single-phase (1Φ) microemulsion region is found near to the water edge of the phase triangle. This is remarkable, as for the ternary water/**3**/styrene system no microemulsion exists. Up to now, microemulsions with **3** were only obtained if a nonionic cosurfactant such as pentanol was added [20]. Obviously, **1** has a similar effect on the stability: the electrostatic repulsion between the negatively charged head groups of **3** is diminished and the interfacial layer is stabilised. In contrast, a microemulsion with pure **1** is stable. For comparison, its single phase region is also indicated in Fig. 2a.

The phase triangle shows that the size of the single phase region depends on the total surfactant concentration and the cationic/anionic surfactant ratio in a complex manner. Let us first discuss the effect of the surfactant concentration. In Fig. 3a and b, the weight percentage of solubilized styrene is plotted versus the weight percentage of the total surfactant concentration for different catanionic mixing ratios **1**/**3**. One expects that the amount of solubilized styrene increases with the surfactant concentration simply because the number of micelles available for the styrene solubilization increases as well. This is in fact observed for the sample with mixing ratio **1**/**3** of 5:95 (Fig. 3a). However, for a sample with mixing ratio of 10:90, the amount of solubilized styrene only increases with the surfactant concentration until a limit of 10 wt% surfactant is reached. At a higher surfactant concentration, the solubility of styrene drops again. A similar behaviour is found for the mixing ratio of 15:85. For the mixing ratio of 20:80, the limiting surfactant concentration has even moved to 6 wt%. Below this concentration, up to 2 wt% of styrene is

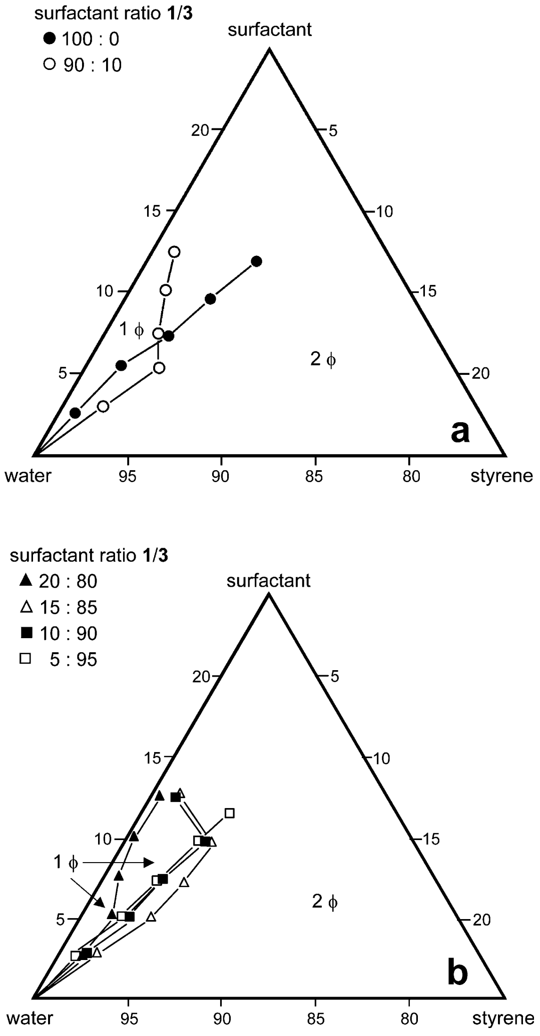


**Fig. 2** Partial phase diagram of the water/**1**/**3**/styrene system for **a** **1**-rich and **b** **3**-rich catanionic mixtures

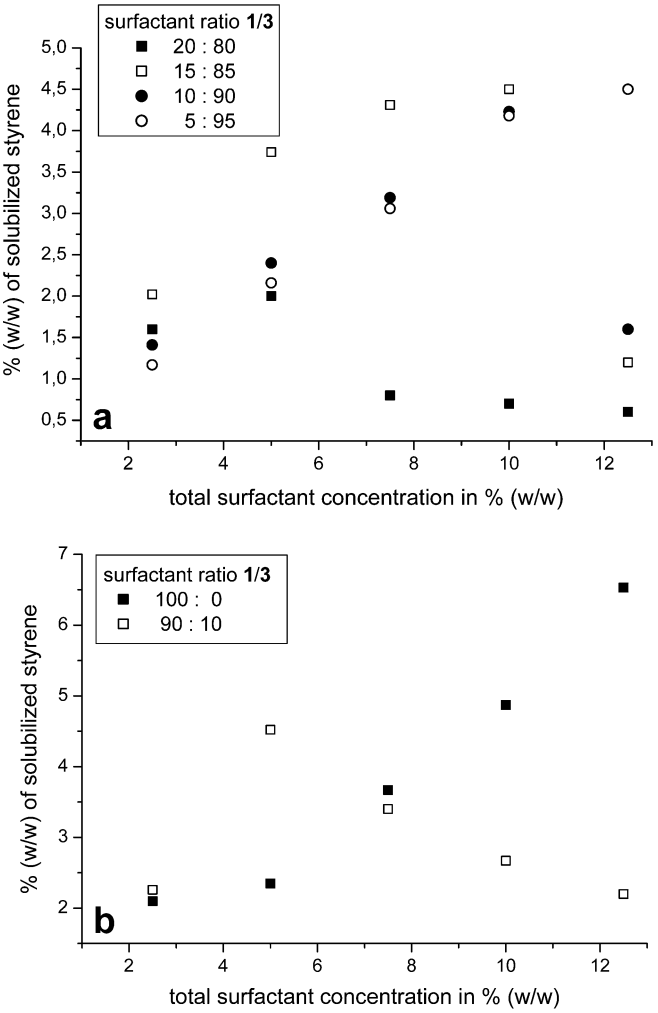


**Fig. 3** Plot of solubilized amount of styrene versus total surfactant concentration for **a** **3**-rich and **b** **1**-rich catanionic mixtures

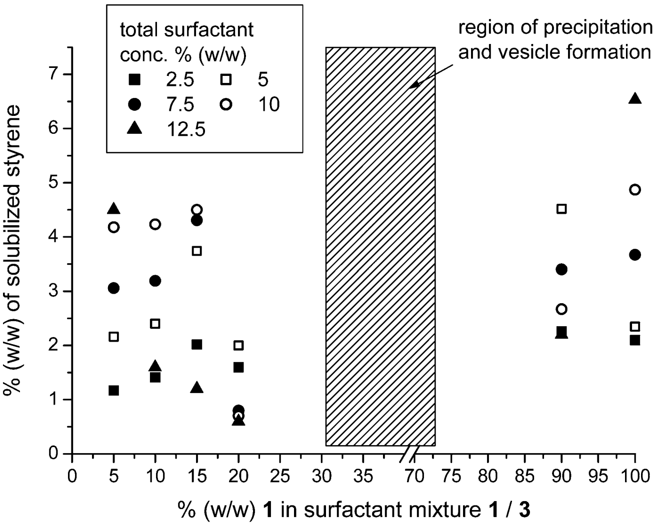


**Fig. 4** Plot of solubilized amount of styrene versus weight fraction of **1** in the catanionic surfactant mixture **1**/**3** for different total surfactant concentrations

dissolved; above this concentration less than 1 wt% is dissolved. We ascribe this effect to a structural transition in the micellar aggregates. Phase transitions in aqueous mixtures of catanionic surfactant systems have already been studied by several authors [2, 3, 4, 10, 11, 12, 13]. Using small-angle neutron scattering, Bergström and Pedersen [12] studied the aqueous **1**/**3** system comprehensively. Vesicles only occur in the very diluted system with a surfactant concentration of 1 wt% or less, while micelles are formed at higher concentrations, as they were used in our study. If the catanionic mixing ratio is changed toward equimolarity and the total surfactant concentration is kept constant, the transition series rod-shaped micelles → disk-shaped micelles → large lamellar flakes is found. The transition series is almost symmetrical with respect to the equimolar composition. A similar transition series is found if the surfactant concentration is increased [12]. The phase transitions are driven by a reduction of the surface curvature and the molecular mobility in the surfactant aggregates caused by salt formation between the two oppositely-charged surfactants. At more equalized surfactant ratios, the formation of flat, disc-shaped bilayer-type structures is favoured, which represent precursors for the crystalline precipitate occurring at the equimolar surfactant ratio and high total surfactant concentration. While the rod-like aggregates are able to swell and solubilize large amounts of styrene, this is much less the case for the bilayer-type structures or the crystalline precipitate. Therefore, in our system the phase transition is accompanied by the sudden drop in styrene solubilization.

Catanionic mixtures containing **1** in excess show similar effects on the styrene solubilization (Fig. 3b) as the **3**-rich samples. In samples with pure surfactant **1** the solubilized amount of styrene increases fairly linearly with the surfactant concentration. However, in samples with mixing ratio 90:10 the solubilization efficiency only increases until a surfactant content of 5 wt% is reached and then it decreases. Again, the decrease in styrene solubilization can be ascribed to a structural transition in the micellar aggregates.

In Fig. 4, the influence of the **1**/**3** surfactant ratio on the styrene solubilization is represented for various total surfactant concentrations. At a very small content of **1** (mixing ratio 5:95) and high surfactant concentration of 10 or 12.5 wt%, up to 4.5% of styrene is solubilized. However, at a higher content of **1** in the surfactant mixture, say at a mixing ratio of 20:80, the styrene solubility has decreased to less than 2% due to the micellar transition discussed above. Between 31–73 wt% of **1**, precipitation occurs. No micelles are formed, no styrene is solubilized. For **1**-rich samples, say at a mixing ratio of 90:10, again 4–4.5% of styrene is solubilized provided that the surfactant concentration is only low and does not exceed 5 wt%. At higher surfactant concentrations, the styrene solubilization drops to 2.2%, again due to the phase transition discussed above.

### *System water/**2**/**3**/styrene*

In order to better understand the influence of the molecular structure of the surfactants on phase behaviour and microemulsion stability, we also investigated a system consisting of water, cationic gemini surfactant **2**, anionic surfactant **3** and styrene. The dimeric surfactant **2** is generally less mobile in micellar aggregates than **1** because of the presence of the spacer unit connecting the two amphiphilic parts. The mobility will be further decreased if one of the two positively charged parts forms a salt with the anionic surfactant **3**. Therefore a catanionic mixture of **2** and **3** can be expected to form more rigid surfactant layers than a corresponding mixture of **1** and **3**, for example. At first glance, the phase behaviour of the water/**2**/**3**/styrene system resembles the one discussed in the previous section. Clear solutions were only obtained if either **2** or **3** were present in large excess. However, the precipitation region was considerably more extended than in the water/**1**/**3**/styrene system. The surfactants precipitated at weight fractions of **2** between 23–85%. As indicated in the phase triangle, a single-phase (1Φ) microemulsion region exists near to the water edge, if either surfactant **2** (Fig. 5a) or **3** (Fig. 5b) are present in large excess. Again, microemulsions with **3** as the main surfactant become stable upon addition of small amounts of **2** (like 1 wt%); in other words the gemini surfactant acts as a cosurfactant stabilising the aggregates by lowering the charge density at the interface. In contrast, microemulsions containing only **2** are stable and exhibit a rather large single-phase region. However, if **3** is added, the size of the single-phase region only decreases (Fig. 5a).

As in the previous system, the styrene solubilization depends on the total surfactant concentration and the catanionic mixing ratio. We first discuss the effect of the total surfactant concentration. If the mixing ratio is only 5:95, the amount of solubilized styrene (in wt%) increases nearly linearly with the surfactant concentration (in wt%) (Fig. 6a). At a surfactant concentration of 12.5%, up to 5.2% of styrene is solubilized in a clear microemulsion. This value is about 10% higher than for the **1**/**3** system of equal composition. For the 10:90 mixture, the styrene solubilization again increases with the surfactant concentration, but in this case a limit of 10 wt% surfactant exists, above which the amount of solubilized styrene drops again. The phase behaviour is very similar to the **1**/**3** system and so we conclude that again a phase transition into flat bilayer structures occurs, which diminishes the solubilization efficiency.

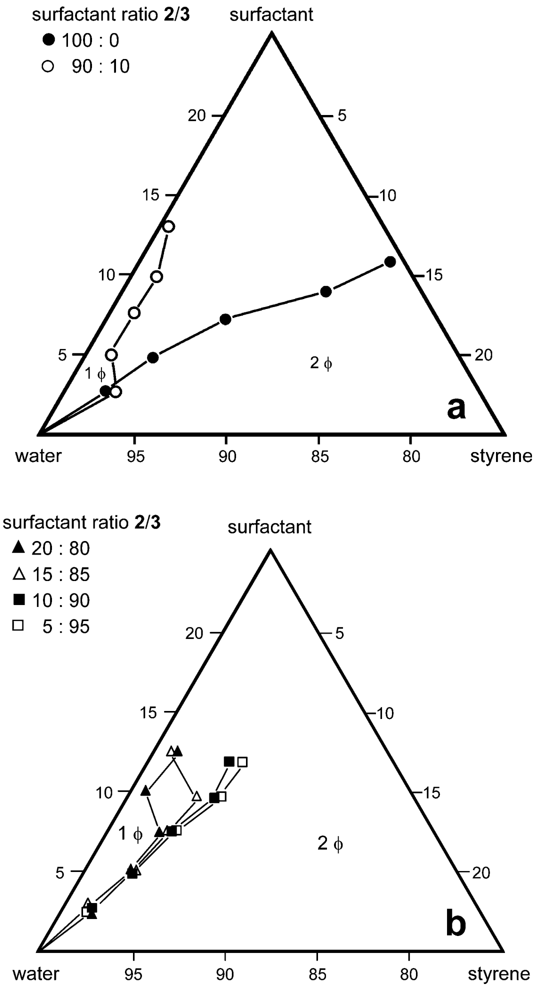


**Fig. 5** Partial phase diagram of the water/**2**/**3**/styrene system for **a** **2**-rich and **b** **3**-rich catanionic mixtures

For a mixing ratio of 20:80, the limiting surfactant concentration is even lower. While at 5% surfactant content 2.6% of styrene is dissolved, only 0.6% is dissolved at 10% surfactant content. The solubilization efficiency of the **2**-rich system is plotted in Fig. 6b. For the pure water/**2**/styrene system with a surfactant content of 12.5%, we find a high efficiency of up to 13.8% styrene in a clear microemulsion. The reason is that the hydrophobic spacer units of **2** are able to arrange parallel to the oil/water interface, which favours the uptake of large amounts of styrene in the micelle [36]. As also shown in Fig. 6b, the addition of **3** is very unsuitable for the solubilization efficiency of the system. If the mixing ratio is 90:10, only 1.3% of styrene is dissolved at total surfactant concentrations higher than 3%. Although phase transitions in catanionic aggregates **2**/**3** have not been studied yet, one can infer similar structural changes to those in the **1**/**3**-system. Single phase o/w microemulsions of the water/**2**/styrene system are known to

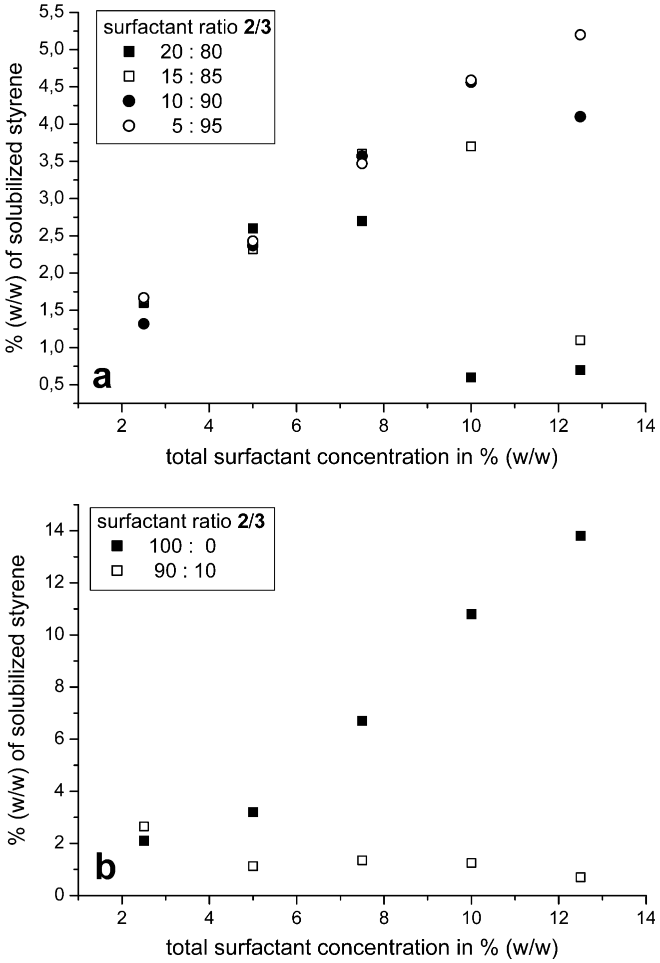


**Fig. 6** Plot of solubilized amount of styrene versus total surfactant concentration for **a** **3**-rich and **b** **2**-rich catanionic mixtures

contain rather spherical, slightly ellipsoidal micellar droplets [50]. If **3** is added, the salt formation with **2** lowers the charge density at the interface as well as the surfactant mobility within the micelle and between adjacent micelles. The surface curvature is reduced, and a rearrangement into flat bilayer structures with much lower efficiency in styrene solubilization is favoured.

## Polymerisation

### *System water/***1***/***3***/styrene*

**Table 1** Hydrodynamic radius $R_h$ of polymer particles and weight average molecular weight $M_w$ of polymer obtained upon $\gamma$-irradiation of the water/**1**/**3**/styrene system with various weight ratios of **1**/**3** and weight ratios (WR) of surfactant to styrene (total surfactant concentration: 10 wt%)

| Weight ratio **1**/**3** | WR | $M_w$ ($10^6$ g mol$^{-1}$) | $R_h$(nm) | $\sigma$ [a] |
|---|---|---|---|---|
| 100:0 [b] | 1 | 1.09 | 20.2 | 0.35 |
| | 2 | 0.65 | 16.5 | 0.28 |
| | 3 | 0.47 | 14.6 | 0.25 |
| | 4 | 0.46 | 14.2 | 0.23 |
| | 5 | 0.35 | 12.7 | 0.30 |
| 90:10 | 1 | 0.56 | 18.4 | 0.14 |
| | 2 | 0.78 | 16.7 | 0.18 |
| | 3 | 0.72 | 15.6 | 0.18 |
| | 4 | 0.36 | 13.0 | 0.18 |
| | 5 | 0.29 | 12.6 | 0.12 |
| 15:85 | 1 | 0.64 | 19.3 | 0.15 |
| | 2 | 1.20 | 18.3 | 0.20 |
| | 3 | 0.96 | 17.7 | 0.18 |
| | 4 | 0.83 | 16.9 | 0.16 |
| | 5 | 0.52 | 14.4 | 0.17 |
| 10:90 | 1 | 0.83 | 19.0 | 0.17 |
| | 2 | 1.30 | 17.6 | 0.13 |
| | 3 | 1.20 | 17.2 | 0.18 |
| | 4 | 0.94 | 17.1 | 0.13 |
| | 5 | 0.75 | 16.7 | 0.14 |
| 5:95 | 1 | 0.69 | 18.6 | 0.16 |
| | 2 | 0.84 | 16.6 | 0.17 |
| | 3 | 0.94 | 16.8 | 0.13 |
| | 4 | 0.89 | 16.2 | 0.18 |
| | 5 | 0.68 | 15.4 | 0.12 |

[a] Standard deviation of $R_h$; [b] data taken from [50]

Samples with total surfactant concentration of 10 wt% and catanionic weight ratios **1**/**3** of 5:95, 10:90, 15:85 and 90:10 were studied for polymerisation. A rather high surfactant concentration of 10 wt% was chosen, because comparable data on polymer particles from microemulsions of pure cationic surfactants **1** or **2** are only available for this concentration [50]. Samples were always subjected to a $\gamma$-irradiation dose of 6 kGy, which was sufficient to completely polymerise the styrene monomer in the mixture. Besides the catanionic mixture composition, we also varied the weight ratio of surfactant to styrene, WR, from 5 to 1. Because of the high styrene content, samples with a WR of 1 were turbid initially and remained turbid during the entire reaction process. In these samples, the styrene content was probably too high to become completely solubilized in the micellar aggregates. As a consequence, the formation of a two-phase structure with microemulsion and emulsion droplets was likely. Samples with a mixing ratio of 90:10 and WR between 2–4 were turbid initially, but turned into clear solutions during $\gamma$-irradiation. The same was true for the sample with a mixing ratio of 5:95 and a WR of 2. All of the other samples were clear initially and remained clear during the entire irradiation process.

The size of the latex particles obtained after $\gamma$-irradiation was determined using dynamic light scattering. The hydrodynamic particle radii $R_h$ are compiled in Table 1. For comparison, the size of particles obtained from microemulsions with pure surfactant **1** is also listed [50]. The particle radii were between 13–19 nm, quite similar to those from microemulsions with pure **1**. The size of the particles increased with decreasing WR. This is because the added styrene was accommodated in the micellar aggregates and led to a swelling. For the samples with a WR of 1, a much higher $R_h$ value was expected because the styrene content is so high that a two-phase system with microemulsion and emulsion droplets should exist, and the polymerisation should occur in either of the droplets. However, the data in Table 1 indicate that the large number of small particles still dominates the dynamic light scattering. The average particle size for the weight ratio 90:10 with a WR of 1 is practically the same as for the weight ratio 15:85 and a WR of 2. Only the molecular weight is different, as will be discussed below. Table 1 also indicates that the size of the particles from **3**-rich samples was less dependent on the addition of styrene than the size of particles from **1**-rich samples. Obviously the **3**-rich micelles are less able to swell due to a more rigid structure of the interlayer.

In Fig. 7, the $R_h$ values are plotted versus the weight fraction of **1** in the catanionic surfactant mixture of the parent microemulsion. If **3** is the major component and WR is constant, a change in the mixing ratio toward equimolarity leads to slightly larger particles. The reason might be that upon the addition of **1** the interfacial curvature of the parent micellar aggregates is decreased. Less, but larger aggregates are formed, which are able to solubilize more styrene. Consequently, the final polymer particles are larger too. An admixture of small amounts of **3** to excess **1** in the parent microemulsion has no clear effect on the final particle size. Depending on the WR surfactant/styrene, the particles are either of the same size, or slightly larger or smaller than the particles from microemulsions of pure **1** (Fig. 7).

The molecular weight of polystyrene was determined using size exclusion chromatography. As indicated in Table 1, the molecular weights (weight average) are in the range from $3\times10^5$ to $1.3\times10^6$ Daltons. The polydispersity was in the range 2–4. The relation between $M_w$ and the WR surfactant/styrene is more clearly shown in the plots of Fig. 8a and b. If the WR is decreased from 5 to 2, the molecular weight is increased, simply because the monomer content in the micelles is increased. This can be taken as proof that the polymerisation takes place entirely in the micellar droplets. However, at a surfactant/styrene WR ratio of 1, the resulting molecular weight was much lower. In that case, a two-phase structure was present; in other words, parts of the styrene formed large monomer droplets. In the large droplets the concentration of growing polymer chains is high and a variety of termination processes can occur so that the resulting molecular weight is low. In microemulsion droplets, only a single chain is growing at a time, and the most frequent chain termination is chain transfer to the monomer. Hence the lower molecular weight indicates that the polymerisation at least partially

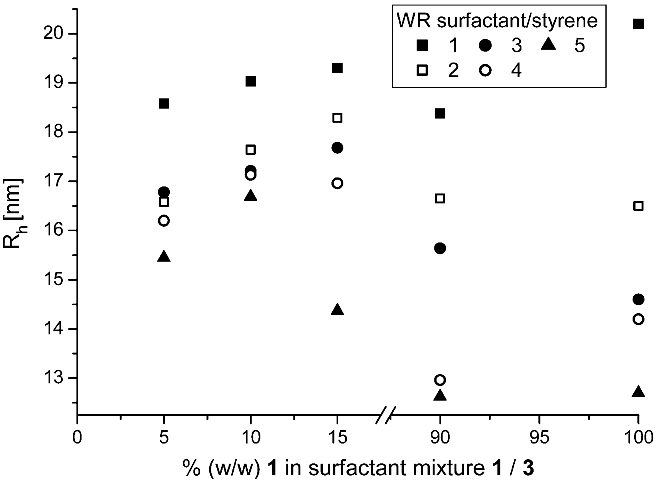


**Fig. 7** Plot of hydrodynamic radius $R_h$ of polymer particles versus weight fraction of **1** in catanionic surfactant mixture **1**/**3** with different WR of surfactant/styrene

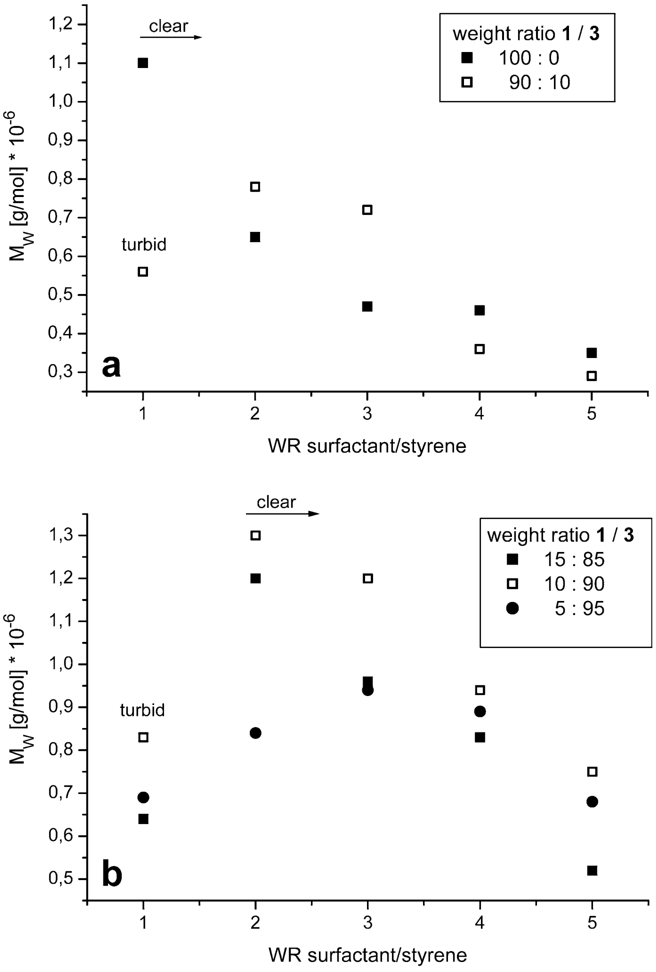


**Fig. 8** Plot of weight-average molecular weight $M_w$ versus WR of surfactant/styrene for **a** **1**-rich and **b** **3**-rich catanionic mixtures **1**/**3**

took place in larger droplets. The high polydispersity of the molecular weight further supports this conclusion. From the molecular weight and the hydrodynamic radius, the average number of chains per particle can be calculated. For samples with WR between 2–5, it was about 10 – slightly higher than the values of 1–5 frequently observed in microemulsion polymerisation of styrene in the ternary water/**1**/styrene system [50]. The higher number of chains per particle may have its origin in the presence of the more voluminous, non-spherical aggregates discussed above. However, for the sample with a WR of 1, the number of chains was about 30. This high value is a further indication that parts of the polymer were formed in emulsion rather than in microemulsion droplets.

### *System water/**2**/**3**/styrene*

The polymerisation was studied for samples with the same cationic/anionic surfactant ratio and the same total surfactant concentration of 10 wt% as in the water/**1**/**3**/styrene system. **2**-rich samples with a mixing ratio of 90:10 were always turbid after styrene addition and a precipitate formed during $\gamma$-irradiation independent from the total surfactant concentration. **3**-rich samples with a WR surfactant/styrene of 1 were turbid initially and remained turbid upon polymerisation. Samples with a WR of 2 were turbid initially, and turned into bluish-clear solutions upon $\gamma$-irradiation. All other samples were bluish-clear initially and remained clear during the entire reaction process.

The size of the polymer particles and the molecular weight of the polymer are listed in Table 2. Let us first discuss the hydrodynamic particle radius $R_h$, which is plotted against the composition of the catanionic surfactant mixture in Fig. 9. For **3**-rich samples, particles with radii between approximately 15–18 nm were obtained. The particle sizes were very similar to those from the previous system of the same composition. This indicates that the polymerisation properties were mainly determined by compound **3**. Unlike this, the particles from **2**-rich samples were much larger, especially if the WR surfactant/styrene was only 1 or 2. Particles with radii up to 160 nm were obtained. As mentioned above, the samples remained turbid during polymerisation or the polymer even precipitated. It therefore seems likely that parts of the styrene were not solubilized in the micellar aggregates and formed large droplets. Consequently, the polymerisation no longer followed the kinetics of microemulsion polymerisation [27] and instead a heterogeneous mixture of particles with a broad size distribution was obtained. The large standard deviation of 0.4–1.2 obtained for the sample with a 90:10 ratio may be taken as an indication of the broad size distribution (see Table 2).

**Table 2** Hydrodynamic radius $R_h$ of polymer particles and weight average molecular weight $M_w$ of polymer obtained upon $\gamma$-irradiation of the water/**2**/**3**/styrene system with various weight ratios of **2**/**3**and weight ratios (WR) of surfactant to styrene (total surfactant concentration: 10 wt%)

| Weight ratio **2**/**3** | WR | $M_w$($10^6$ g mol$^{-1}$) | $R_h$(nm) | $\sigma$ [a] |
|---|---|---|---|---|
| 100:0 [b] | 1 | 0.73 | 29.9 | 0.19 |
| | 2 | 0.93 | 21.1 | 0.22 |
| | 3 | 0.89 | 20.4 | 0.29 |
| | 4 | 0.65 | 17.9 | 0.22 |
| | 5 | 0.40 | 16.2 | 0.28 |
| 90:10 | 1 | 0.28 | 163.1 | 1.19 |
| | 2 | 0.24 | 67.1 | 0.51 |
| | 3 | 0.32 | 30.7 | 0.43 |
| | 4 | 0.46 | 51.7 | 0.89 |
| | 5 | 0.33 | 33.0 | 0.48 |
| 15:85 | 1 | 0.72 | 19.3 | 0.16 |
| | 2 | 0.89 | 17.9 | 0.27 |
| | 3 | 1.20 | 17.0 | 0.13 |
| | 4 | 0.81 | 15.0 | 0.13 |
| | 5 | 0.55 | 14.9 | 0.16 |
| 10:90 | 1 | 0.64 | 17.7 | 0.15 |
| | 2 | 0.94 | 17.0 | 0.22 |
| | 3 | 0.88 | 17.0 | 0.13 |
| | 4 | 0.62 | 15.0 | 0.12 |
| | 5 | 0.37 | 14.9 | 0.13 |
| 5:95 | 1 | 0.69 | 17.9 | 0.18 |
| | 2 | 1.10 | 17.6 | 0.16 |
| | 3 | 1.40 | 17.0 | 0.12 |
| | 4 | 0.64 | 15.8 | 0.11 |
| | 5 | 0.56 | 13.0 | 0.16 |

[a] Standard deviation of $R_h$; [b] data taken from [40, 50]

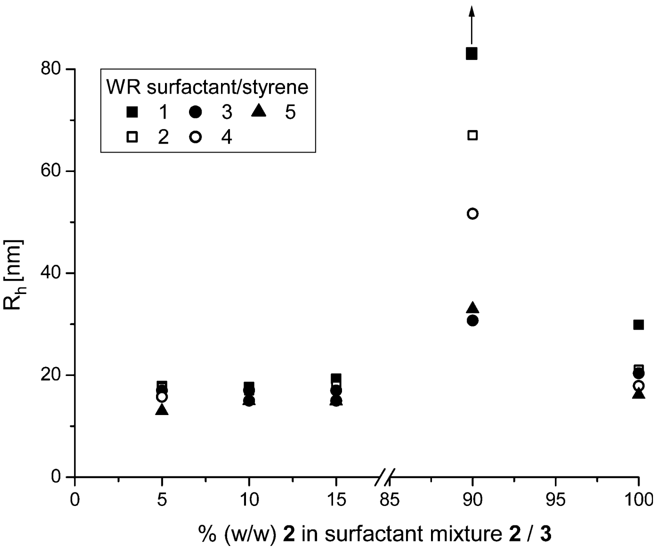


**Fig. 9** Plot of hydrodynamic radius $R_h$ of polymer particles versus weight fraction of **2** in catanionic surfactant mixture **2**/**3** with different WR of surfactant/styrene

In Fig. 10, the molecular weight of the polymer is plotted versus the WR value. For the catanionic mixtures with a **2**/**3** ratio of 90:10, only fairly low molecular

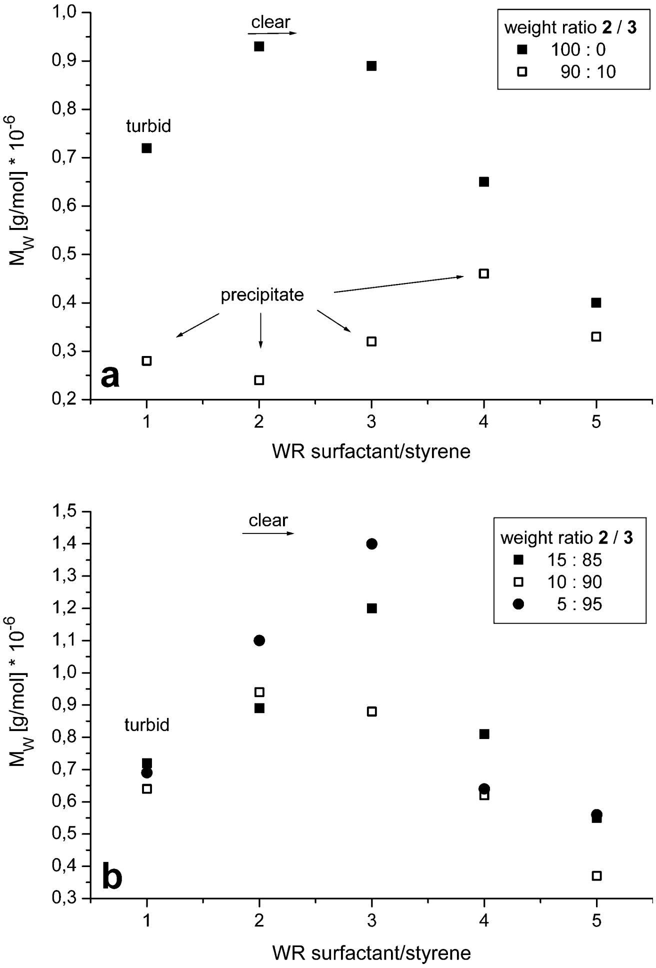


**Fig. 10** Plot of weight average molecular weight $M_w$ versus WR of surfactant/styrene for **a** **2**-rich and **b** **3**-rich catanionic mixtures **2**/**3**

weights of about $3 \times 10^5$ Daltons were obtained independent from WR (Fig. 10a). As mentioned above, the samples were turbid initially, precipitated upon polymerisation, and had the largest particle sizes, up to 160 nm. The low molecular weight can be taken as further indication that a heterogeneous system was formed, in which no real microemulsion polymerisation took place. The situation is quite different if **3**-rich samples are considered. Except for a WR of 1, the samples were bluish-translucent during the whole polymerisation process. This indicates that styrene was completely solubilized in the micellar aggregates. The fact that polymer particles with small size, low standard deviations of 0.1–0.2, and high molecular weights of up to $1.4 \times 10^6$ Daltons were obtained indicates that the polymerisation took place exclusively in the single phase region of the microemulsion. In Fig. 10b, two different effects on $M_w$ are indicated. First, a decrease of WR from 5 to 3 leads to a swelling of the micelles, because more styrene is solubilized per particle and chains grow longer until termination occurs. The $M_w$ increases with decreasing WR. Secondly, beginning at a high WR of 2, the system becomes heterogeneous. Polymerisation takes place in micellar aggregates and in large monomer droplets, where chain termination occurs more frequently. As a result, lower molecular weights are obtained. The $M_w$ decreases, if WR is further decreased.

## Conclusions

Our studies indicate that aqueous micellar solutions of catanionic surfactant mixtures are suitable for solubilizing styrene under the formation of microemulsions. However, clear, single-phase microemulsions are only formed if either the cationic or anionic surfactant is present in large excess. The study also shows that microemulsions of sodium dodecylsufate, which are normally quite unstable, can be stabilised very effectively upon the addition of a few percent of a cationic surfactant.

Styrene can be polymerised in the microemulsion droplets upon $\gamma$-irradiation. A clear dispersion of polymer particles is obtained provided that the initial weight ratio of surfactant to styrene is not smaller than 2. The final polymer particles exhibit radii between 10–20 nm. Depending on whether the cationic or anionic surfactant is present in excess, the surface charge of the particles is either positive or negative. While in **1**- and **3**-rich samples the addition of the oppositely-charged surfactant increases the styrene solubility, this is not the case for **2**-rich samples. None of the **2**-rich catanionic mixtures exhibits the high styrene solubilization of the microemulsions with pure **2** as surfactant. The reason is probably that the charge density at the interface and the molecular mobility in the aggregates are lowered so much upon the addition of **3** that the micellar droplets become instable and rearrange into flat bilayer-type structures, which are much less able to solubilize the oil component. Similar structural rearrangements were also observed for the other samples at higher surfactant concentration and when the surfactant mixing ratio was shifted toward equimolarity.

Nevertheless, our studies indicate that microemulsions with catanionic surfactant mixtures are suitable for the preparation of polymer nanoparticles with diameters between 20–40 nm and with either cationic or anionic surface charge. The size of the particles and the molecular weight of the polymer can be tailored by varying the catanionic surfactant ratio and the total surfactant concentration.

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