

Phase Behavior of a “Clouding” Nonionic Polymer in Water. Effects of Hydrophobic Modification and Added Surfactant on Phase Compositions

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Cloud point curves and conjugate coexistence curves for the quasi-binary water systems of ethyl(hydroxyethyl)-cellulose (EHEC) and its hydrophobically modified analogue (HMEHEC) have been determined. The cloud point curves are remarkably independent of the polymer concentration up to as high as 20 wt % polymer, and they are clearly different from the coexistence curves. This is interpreted as an effect of the multicomponent nature of the polymer. Hydrophobic modification of EHEC lowers the cloud point by approximately 15 °C. On heating above the cloud point, EHEC redistributes to the concentrated phase, but, however, a substantial amount of the polymer remains in the dilute phase even far above the cloud point. For HMEHEC, essentially all polymer is found throughout in the concentrated phase. Addition of the anionic surfactant, sodium octylbenzenesulfonate (SOBS), affects the phase behavior. Small amounts of SOBS cause a swelling of the concentrated phase for both EHEC and HMEHEC, due to an electrostatic repulsion between polymer–surfactant aggregates. On further addition of SOBS, a dissolution of polymer from the concentrated phase is observed for EHEC. For HMEHEC, the surfactant binding swells the concentrated phase until the one-phase region is reached.

Introduction

The solubility of a polymer in a solvent is from simple thermodynamic arguments predicted to increase on heating. However, for many nonionic polymers in water the opposite behavior is observed; i.e., the solubility of the polymer becomes worse as the temperature increases. At some point it is more favorable for the system to separate into two phases, one polymer-rich and one polymer-poor. This phase separation temperature is referred to as the lower consolution temperature, LCST, or often simply the cloud point. Examples of the LCST phenomenon includes the poly(ethylene oxide)–water system^{1,2} and some cellulose ether–water systems.^{3,4}

One common way to study the phase behavior of polymer systems is to determine the *cloud point curve*, where a set of samples with different compositions is phase separated by slowly altering the temperature and where the cloud point is taken as the point where the solution becomes turbid. Another approach is to let samples with a given global polymer concentration phase separate at a temperature above their cloud point and determine the composition of the phases. This procedure gives a *coexistence curve* (or conjugate coexistence curves, making a distinction between the dilute and concentrated branches).

Cloud point curves are commonly found in the literature, whereas there are quite few determinations of the coexistence curves, due to the experimental difficulty and workload needed to obtain the compositions of the phases. For a truly binary system the coexistence curve and cloud point curve coincide.^{5–7} Polymers, however, are generally polydisperse and must therefore be considered as multicomponent systems, which implies that the coexistence curves should be dependent on the global composition and not coincide with the cloud point curve.

Polymer–solvent systems are therefore normally referred to as *quasi-binary*. Adding another chemically different component, for example a surfactant, to a quasi-binary system gives a *quasi-ternary* system, etc.

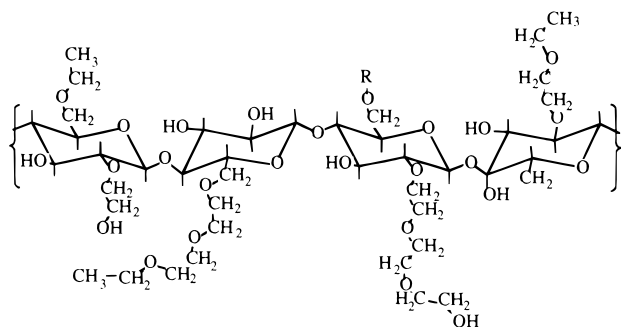
In the present study we have investigated the phase behavior of an LCST polymer, the cellulose ether ethyl(hydroxyethyl)-cellulose, EHEC, and its hydrophobically modified analogue, HMEHEC. We have determined cloud point and coexistence curves for the quasi-binary water systems as well as for the quasi-ternary system, by adding small amounts of the anionic surfactant, sodium octylbenzenesulfonate, SOBS. Despite the diverse collection of cloud point curves available for these systems,^{3,4,8–11} coexistence curves have never been determined.

It is well-known that above a critical aggregation concentration, *cac*, ionic surfactants cooperatively bind to the slightly hydrophobic EHEC molecules, forming mixed aggregates.^{4,11–15} A related cooperative binding is also observed for HMEHEC, but in addition a noncooperative binding region of surfactant is seen at surfactant concentrations below the *cac* of EHEC.^{14,16} In this region, the surfactants bind to the hydrophobic domains originating from the polymer hydrophobic tails. Earlier investigations have shown that the binding of ionic surfactant to the nonionic EHEC has a pronounced influence on the phase behavior.^{4,10,11,15,17}

Experimental Section

Materials. EHEC and HMEHEC (Figure 1) were supplied by Akzo Nobel Surface Chemistry AB. They have the same molecular weight ($M_w \approx 100\,000$) and degrees of ethyl and hydroxyethyl substituents ($DS_{\text{ethyl}} = 0.6–0.7$ and $MS_{\text{EO}} = 1.8$, respectively, where the numbers refer to the average substitution per glucose unit of the cellulose), as given by the manufacturer. The only structural difference between the polymers is the

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EHEC: R = -H
HM-EHEC: R = -(CH₂CH₂O)_x-C₆H₄-C₉H₁₉

Figure 1. Structure of EHEC and HMEHEC.

introduction of a few hydrophobic grafts onto the EHEC backbone, forming HMEHEC. The hydrophobic modification of branched nonylphenol was 1.7% relative to the number of glucose units, as determined by UV absorbance using phenol in aqueous solution as reference. Before use, the polymers were purified as described elsewhere.¹⁸ The surfactant SOBS was obtained from Tokyo Kasei, except for the 12, 15, and 20 mM samples, which were mixed from another batch of SOBS. This was synthesized and supplied as a kind gift by Prof. Peter Stilbs' group at KTH, Stockholm. SOBS was used without further purification. Water of Millipore quality (resistivity ~ 4 MΩ/cm) was used in all sample preparations.

Methods. Samples for the cloud point determinations were prepared by mixing stock solutions of polymer (2.5 wt %), surfactant (200 mM), and water to the desired concentrations in glass tubes, which were sealed. The high-concentration samples (>3 wt %) were prepared by osmotic compression against a roughly 30 wt % dextran solution. The final EHEC concentration of these samples was determined by optical rotation.

The cloud point temperatures, T_{cp} , were measured by visual detection. The precision in the T_{cp} determination for samples of low concentration (<3 wt %) was usually within ± 1 °C, while for higher concentrations the determination was more inaccurate (± 3 – 5 °C).

Samples for the macroscopic phase separation studies were prepared by mixing stock solutions of polymer (2.5 wt %), surfactant (100, 200 mM) and water in 10 mL glass tubes with Teflon tightened screw caps to the desired concentrations. The samples were made in three series: the quasi-binary system, the quasi-ternary system (global SOBS concentration from 0.5 to 10 mM), and an additional quasi-ternary series at 80 °C (global SOBS concentration from 12 to 20 mM). The samples were rotated end over end at room temperature for several days before being phase separated and analyzed. Each sample was phase separated by equilibration (tilting) at the phase separation temperature for 2 h, followed by centrifugation (1500 g) at the same temperature for an additional 2 h. The low-viscous transparent supernatant was then separated from the dense high-viscous slightly turbid concentrated phase. The concentrated phase fraction was determined by weighing the glass tube with the phase and subtracting the glass tube tara.

The polymer concentrations in the quasi-binary system were determined by optical rotation, by first diluting them to a convenient polymer concentration (optical rotation measuring range 0.1–1 wt %). The compositions of the phases for the surfactant containing samples were determined spectrophotometrically and by weighing the solid content after freeze-drying a known amount of the sample. The absorbance was measured

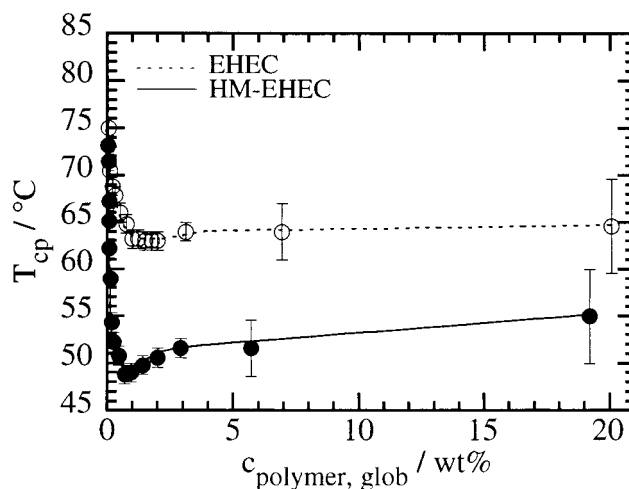


Figure 2. Cloud point curves of the EHEC–water (dotted line, open circles) and HMEHEC–water (full line, filled circles) systems.

at 261 nm on a Perkin-Elmer Lambda 14 UV/vis spectrometer. From the measured specific absorbances of SOBS and the polymers at the applied wavelength, the respective phase concentrations were calculated by a compound equation combining both spectrophotometric and gravimetric data.

Results

Phase Behavior of the Quasi-Binary Systems. The cloud point curves of EHEC and HMEHEC (Figure 2) show that the hydrophobically modified polymer consistently has a lower cloud point than the unmodified analogue (differing by ca. 15 °C), which indicates an increased polymer–polymer attraction.^{19–21} Previous phase investigations of aqueous solutions of related EHECs have shown a remarkably weak concentration dependence of the cloud point curves at higher polymer concentrations.^{11,22} In agreement with a study by Cabane et al.²² on a differently substituted EHEC, our study shows that even at a polymer concentration as high as 20 wt % the cloud point is only slightly higher than the threshold temperature (the minimum of the cloud point curve). Note, however, that the uncertainties in the cloud point determination can be large for the highly concentrated samples (± 5 °C), due to the very high viscosity and slow growth of the phase-separated droplets at high polymer concentrations, which makes it difficult to determine a distinct cloud point.

The coexistence curves for the EHEC and HMEHEC quasi-binary water systems, obtained from three different global compositions for each polymer, are shown in Figure 3 a. Clearly, the coexistence curves are very different from the cloud point curves. Interestingly, a substantial amount of polymer remains in the dilute phase even at temperatures far above the cloud point, especially for EHEC. The positions of the curves are clearly dependent on the global compositions (they are shifted toward higher polymer concentrations as the global concentration is increased), which reflects the multicomponent nature of the system. Figure 3b shows that, at any given phase separation temperature, the concentration of the dilute phase is linearly dependent on the global polymer concentration. For a truly binary system, the coexistence curve is independent of the global composition.

Comparing the two polymers, HMEHEC phase separates at lower temperatures than EHEC, resulting in a dip in the conjugate coexistence curves. At any given phase separation temperature and global polymer concentration, the right-hand branches of the coexistence curves show that the concentrated

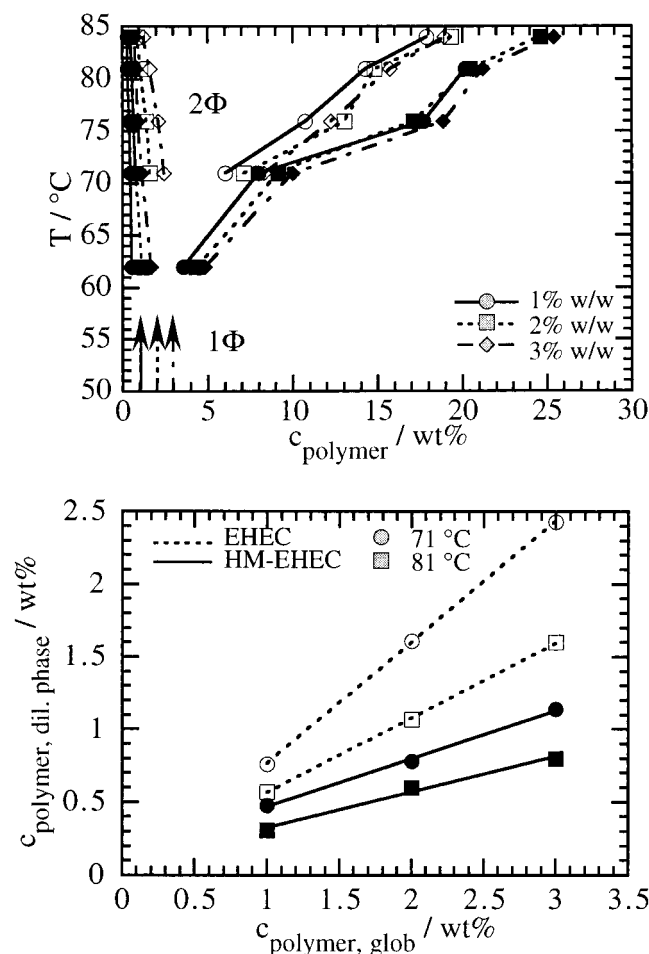


Figure 3. (a) Conjugate coexistence curves of the EHEC–water (open symbols) and HMEHEC–water (filled symbols) systems. Curves from three global compositions are shown for each polymer. Circles correspond to 1 wt %, boxes to 2 wt %, and diamonds to 3 wt % global polymer concentration. Arrows show the global compositions. (b) The dilute phase polymer concentration as a function of the global polymer concentration of the EHEC–water (open symbols) and the HMEHEC–water (filled symbols) systems. Circles and boxes correspond to 71 and 81 °C phase separation temperature, respectively.

phase of the HMEHEC system is consistently more concentrated than the corresponding EHEC phase. Comparing the dilute phase curves reveals an evident difference between the polymers. The water content of the HMEHEC dilute phase is higher than for the EHEC dilute phase, showing that HMEHEC prefers the concentrated phase to the dilute phase to a larger extent than EHEC.

Phase Behavior of the Quasi-Ternary System. Figure 4 shows the influence of SOBS on the cloud points of 2 wt % polymer solutions. At a SOBS concentration higher than approximately 8 mM, the cloud point increases rapidly for both polymer systems, and the difference between the systems becomes smaller.

Figure 5 shows the coexistence curves when a small amount of SOBS is added to a system of 2 wt % polymer solution. Curves for two global surfactant concentrations are shown, but the intermediate curves follow the same monotonic trends. On surfactant addition, the concentrated branches of the coexistence curves are shifted toward lower polymer concentrations, while the dilute branches of the coexistence curves of the respective polymer show no or insignificant changes. At a given temperature, the concentrated phase swells with increasing SOBS concentration, indicating polymer–surfactant association. As

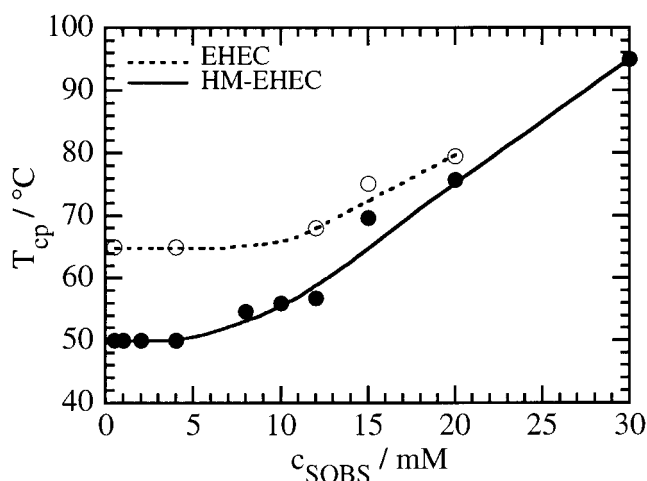


Figure 4. Influence of SOBS on the cloud point of 2% EHEC (open circles) and HMEHEC (filled circles).

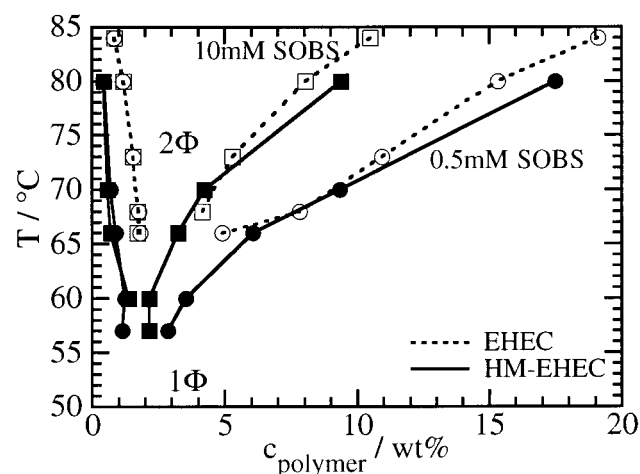


Figure 5. Conjugate coexistence curves of the EHEC–water–SOBS (open symbols) and HMEHEC–water–SOBS (filled symbols) systems. Two global SOBS concentrations are shown: 0.5 mM SOBS (circles) and 10 mM SOBS (boxes).

the surfactant binds to the polymer, the system responds to the increased electrostatic repulsion by expanding the mixed aggregate-rich concentrated phase at the expense of the water-rich dilute phase. Figure 6 shows this dilution of the concentrated phase with increasing global SOBS concentration for two phase separation temperatures. The decrease in concentration is quite similar for the two polymer systems. This agrees with the previous finding that covalently cross-linked EHEC and HMEHEC gels show very similar swelling behavior on SDS addition.^{23,24}

On addition of SOBS, the concentrated phase increases in volume, but for EHEC the phase volume goes through a maximum at ca. 15 mM SOBS (Figure 7a). For the HMEHEC system (Figure 7b), the concentrated phase expands until it reaches the one-phase region. At a given global surfactant concentration the phase volume for the EHEC system does not change significantly on heating, while in the case of HMEHEC, the phase volume decreases drastically when the temperature is increased.

Figure 8 shows how much of the total amount of the polymer that is found in the concentrated phase. The greater part of HMEHEC is always found in the concentrated phase and shows only a weak temperature dependence (passes through a minimum at ca. 60–65 °C). In contrast, EHEC redistributes to the concentrated phase on heating. Only above 80 °C ($T_{\text{cp}} + 15$

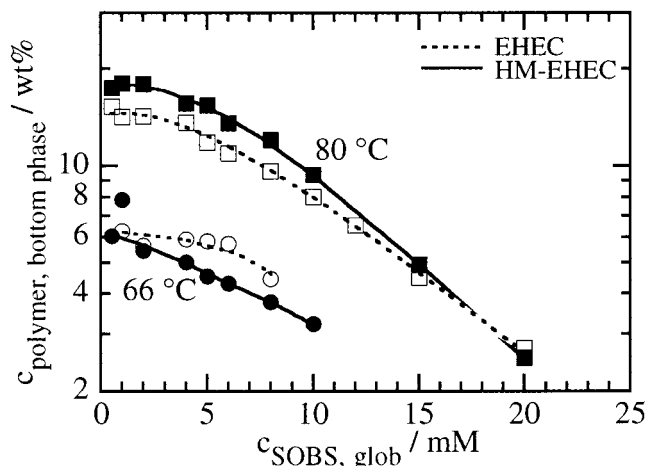


Figure 6. Concentrated phase polymer concentration of the EHEC–water–SOBS (open symbols) and HMEHEC–water–SOBS (filled symbols) systems as a function of global SOBS concentration. Circles and boxes correspond to 66 and 80 °C phase separation temperature, respectively.

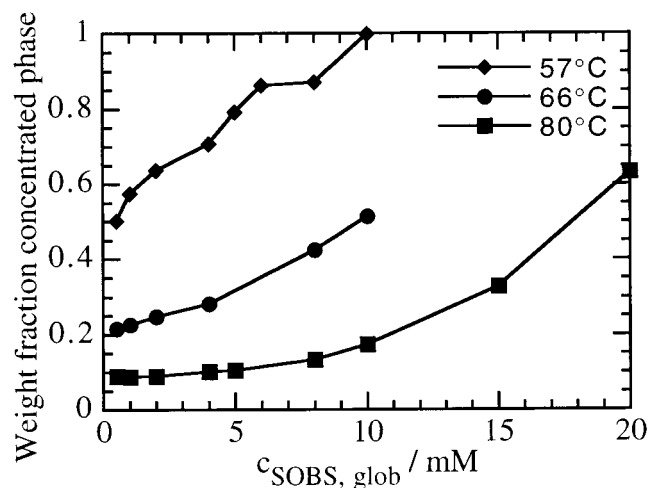
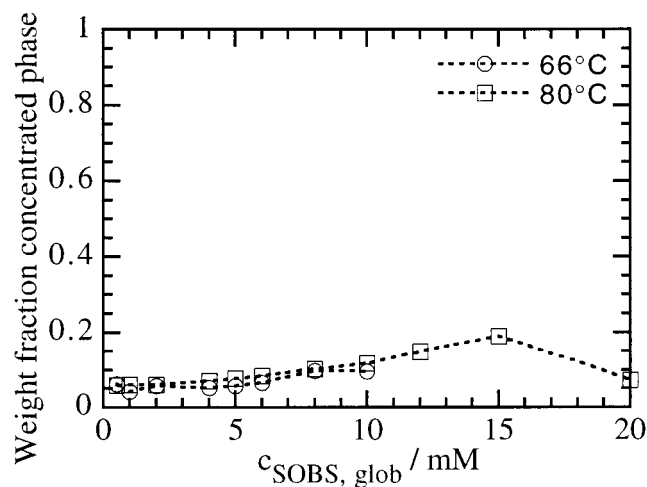


Figure 7. (a) Weight fraction of the concentrated phase of the EHEC–water–SOBS system. Circles and boxes correspond to 66 and 80 °C phase separation temperature, respectively. (b) Weight fraction of the concentrated phase of the HMEHEC–water–SOBS system. Diamonds, circles, and boxes correspond to 57, 66, and 80 °C phase separation temperature, respectively.

°C) is the dominant part of EHEC found in the concentrated phase. For both polymers, low amounts of SOBS (≤ 10 mM) seem to promote a polymer redistribution to the concentrated

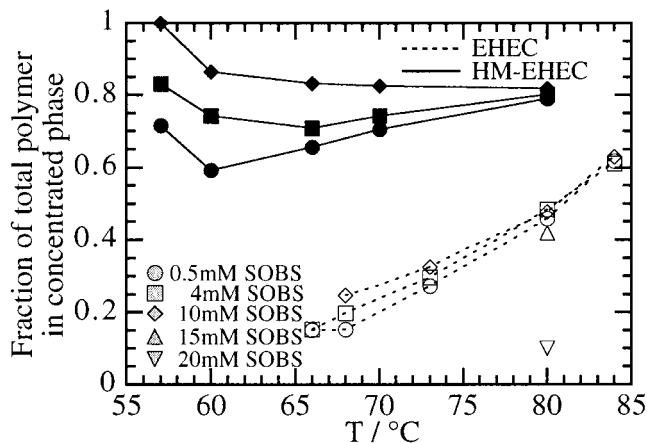


Figure 8. Fraction of the polymer that is found in the concentrated phase of the EHEC–water–SOBS (open symbols) and HMEHEC–water–SOBS (filled symbols) systems as a function of phase separation temperature. Circles, boxes, and diamonds correspond to 0.5, 4, and 10 mM global SOBS concentration. For 80 °C phase separation temperature, triangles show 15 and 20 mM global SOBS concentration (the symbols for the HMEHEC system are overlapping the other SOBS concentrations in the same spot at 0.8, 80 °C).

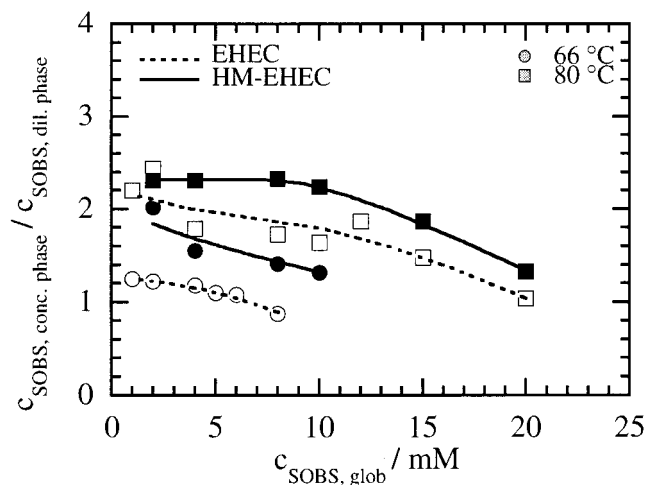


Figure 9. Distribution of SOBS between the concentrated and dilute phase of the EHEC–water–SOBS (open symbols) and HMEHEC–water–SOBS (filled symbols) systems as a function of global SOBS concentration. Circles and boxes correspond to 66 and 80 °C phase separation temperature, respectively.

phase at temperatures in the vicinity of the cloud point. At temperatures well above the cloud point, addition of low amounts of surfactant has small or insignificant influence on the polymer mass distribution between the phases. However, at the highest investigated global SOBS concentration (20 mM, 80 °C) only a small fraction of EHEC is found in the concentrated phase, while no influence is observed on the mass distribution for the corresponding HMEHEC point.

Figure 9 shows that the value of the distribution coefficient of SOBS between the concentrated and the dilute phase generally is between 1 and 2.5 and decreases slightly with increasing global SOBS concentration. Comparing the two polymer systems, SOBS is to a greater extent enriched in the HMEHEC concentrated phase than in the corresponding EHEC phase. Both polymer systems favor SOBS redistribution to the concentrated phase on heating.

Discussion

In the literature, a large collection of phase diagrams of quasi-binary or quasi-ternary systems, relevant for this study, is found.

The cloud point curve or conjugate coexistence curves are sometimes taken as the two-phase border for a true binary or ternary system. However, we have in our investigation shown that for some systems there may be very large differences between the cloud point and coexistence curves (cf. Figures 2 and 3a), which suggests that for these systems interpretation of the phase diagrams must be done with great caution.

The multicomponent nature of the polymer most certainly plays a great role in the clouding behavior of EHEC–water systems (the number of possible EHEC components roughly equals 10^{190}).²⁵ The most commonly investigated parameter is the effect of a molecular weight distribution. It has been shown theoretically that the shape and position of the cloud point curve are strongly dependent on both the broadness and the shape of the molecular weight distribution.^{7,26} However, it is known that the cloud point curve of EHEC in water is only slightly affected by degradation of the polymer,⁴ which suggests that the strong multicomponent feature of the cloud point and coexistence curves mainly originate from fluctuations in the substitution pattern, rather than from a broad chain length distribution. The remarkably flat feature of the cloud point curves at high polymer concentration, Figure 2, and the dependence of the coexistence curves on the global concentration (Figure 3a) is plausibly a result of a fractionation of the multicomponent system. We found that the approximately linear dependence of the dilute phase concentration on the global polymer concentration (Figure 3b) could easily be reproduced by Flory–Huggins calculations for a simple ternary system, where, in addition to water and the clouding polymer, also a nonclouding (or more soluble) polymer fraction is present. If the difference in polymer–solvent χ -parameter of the two polymer fractions is large enough (typically $\Delta\chi > 0.3$), the dominant polymer mass in either phase originates from one of the two fractions, and thus the concentration in the dilute phase would approximately be linearly dependent on the global polymer concentration. The concentrated phase composition should also follow the same behavior, but the relative concentration shift is here comparable to the experimental errors.

The increase of the amount of EHEC in the concentrated phase at higher temperatures (Figure 8) can be explained in terms of an increased hydrophobicity of the polymer at elevated temperatures. It is more difficult to explain the nonmonotonic temperature behavior of the amount of polymer in the concentrated phase for HMEHEC. Let us consider a multicomponent system with nonclouding components that distribute roughly evenly between the phases. In the vicinity of the cloud point, a slight increase in temperature has great effect on the phase volume, as evidenced by Figure 7b. A significant amount of nonclouding polymer distributing evenly throughout the system might explain the initial decrease of the HMEHEC content in the concentrated phase.

The influence of SOBS on the cloud point of EHEC and HMEHEC (Figure 4) shows the same features as known for other ionic surfactants.^{4,10,11,15,17} At surfactant concentrations well above the cac, the cloud point increases steeply, due to electrostatic repulsion and/or solubilization of interpolymer cross-links. Information about the dominating mechanism for the cloud point increase is obtained from the analysis of the coexisting phase.

If no exchange of polymer between the two phases occurs on addition of surfactant, one would expect the more concentrated phase to expand at the expense of the dilute phase on ionic surfactant binding. This simple view holds for the HMEHEC system since, due to the efficient hydrophobic cross-

linking, essentially all HMEHEC is found in the concentrated phase, independent of the surfactant concentration at temperatures well above cloud point (Figure 8). The binding of SOBS is too small to allow a breakdown of the network, but large enough to swell the concentrated phase until the one-phase region is reached, at sufficiently large global SOBS concentrations. Analogous swelling of the concentrated phase is also observed for a hydrophobically modified cationic cellulose derivative and SDS, at higher SDS concentrations than the charge neutralization point.²⁷

In contrast to HMEHEC, EHEC does not form a strongly associated infinite network in water, which gives the possibility to transfer polymer between two phases more easily than for HMEHEC. Figure 7a and Figure 8 indicate that, at above ca. 15 mM SOBS, EHEC is solubilized from the concentrated phase. This illustrates the difference in phase behavior of the two polymer systems. On extensive binding of SOBS the polymers become more soluble, which for the EHEC system implies that individual polymer molecules may be solubilized from the concentrated phase, while in the case of HMEHEC the binding is too low to break down the network and solubilize individual polymer molecules.

At a given temperature in the vicinity of the cloud point, the surfactant influence on polymer redistribution is larger in the case of HMEHEC, due to the network formation in the associating system. We believe that, initially, an increasing surfactant concentration is strengthening the aggregate cross-links of the network, due to formation of more developed mixed aggregates. Eventually, at higher surfactant concentrations, i.e., when the surfactant-to-polymer hydrophobe ratio is high, the network is destabilized, due to solubilization of the cross-links. However, in this investigation we do not seem to reach this region, since at higher surfactant binding the electrostatic repulsion and/or individual polymer solubilization prevents phase separation.

Concerning the binding of ionic surfactant to EHECs, discussed above, it is important to point out that there are no conditions when all surfactant is bound to the polymer; i.e., there is always a monomeric (free) fraction of the surfactant present in solution. Direct measurements of the SOBS concentration in the phases do not give information about the bound vs free SOBS concentration. However, we can easily estimate the binding isotherm from the data in Figure 9 by assuming that the free SOBS concentration is equal in the two phases, and the distribution of binding sites between the phases follows the distribution of polymer. The binding isotherms thus obtained for the binding of SOBS to EHEC and HMEHEC for 80 °C are shown in Figure 10, as a function of the free surfactant concentration, presented as the number of bound SOBS molecules per glucose residue of the polymer. The HMEHEC isotherm shows the characteristic steep increase in binding around 8 mM free SOBS (the cmc for SOBS in the investigated temperature range varies only slightly around 15–16 mM).²⁸ However, the bound amount of SOBS at the highest free SOBS concentration investigated is still quite low (one SOBS per 10 glucose residues or six per hydrophobic graft on HMEHEC), which indicates that we only observe the beginning of the cooperative region of the binding isotherm. At higher bound amounts, the solubility of the polymer–surfactant complex is enhanced so that phase separation does not occur (cf. Figure 4). It is known from investigations on the SDS–EHEC system that at saturation the number of bound surfactants per glucose residue is around 1 at 25 °C.¹⁴

Up to 10 mM free SOBS, the EHEC–SOBS binding isotherm

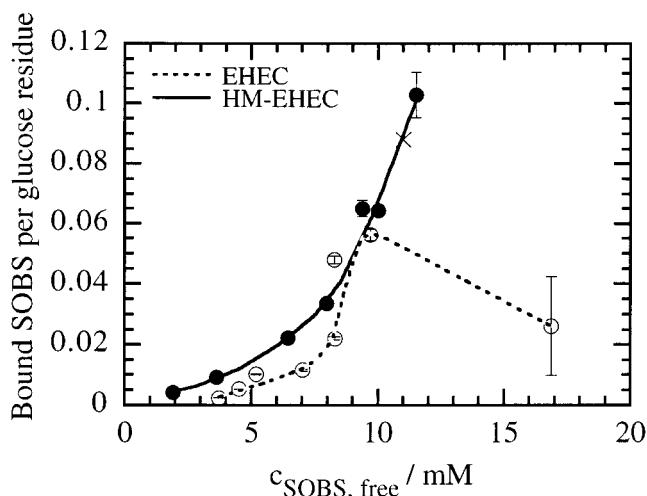


Figure 10. Binding isotherm of SOBS to EHEC (open circles) and HMEHEC (filled circles) calculated with the assumption that the distribution of binding sites is equal to the polymer concentration distribution. The cross sign marks the resulting point, adjusting the binding site distribution from 1.39 (polymer distribution, last point of EHEC isotherm) to 1.09. The error bars is estimated from errors in weighing (± 0.5 mg) and absorbance (± 0.001 absorbance units).

shows the same feature as for HMEHEC. The bound amount is slightly higher for the HMEHEC system at lower free SOBS concentration, which is reasonable, due to the more hydrophobic nature of the HMEHEC polymer and the feature of the binding isotherm discussed above. However, the last point in the EHEC isotherm is unphysical; the bound amount should not decrease when the surfactant concentration is increased. We suggest that this is a result of a dissolution of EHEC molecules from the concentrated phase to the dilute phase (see Figure 8), as a result of extensive binding of SOBS to EHEC, so that at high surfactant concentration the degree of surfactant binding is actually higher for the polymer in the dilute phase. If this is the case, our assumption that the distribution of sites follows the polymer distribution between the phases becomes invalid. The distribution of sites (concentrated/dilute phase) needs to be adjusted from 1.39 (the polymer distribution) to 1.09 to follow the HMEHEC isotherm (cross in figure). This would mean that the degree of surfactant binding is a factor of 1.28 larger, on average, for the polymers in the dilute phase.

Conclusions

The cloud point curves of the quasi-binary EHEC and HMEHEC–water systems show a remarkably weak concentration dependence up to very high polymer concentrations. This feature together with the global concentration dependence of the coexistence curves for the systems has been interpreted as a result of the multicomponent nature of the polymers.

An evident difference between the two investigated polymer systems is the polymer content in the phases. The associating HMEHEC forms a hydrophobically cross-linked network, essentially involving all of the polymer in semidilute solutions. Therefore, when the solvent conditions are worsened, almost all HMEHEC is found in the concentrated phase. In contrast, comparable amounts of the nonassociating EHEC are distributed between the phases.

The polymer concentration in the concentrated phase increases rapidly with increasing temperature, due to the worsening of the solubility conditions. However, the increase is achieved in

different ways for the two polymers. For EHEC the concentration increase in the concentrated phase originates from a redistribution of polymer to the concentrated phase, while for HMEHEC, where almost all of the polymer is already found in the concentrated phase, the increase is mainly due to a shrinkage of the phase.

On addition of SOBS, a low amount of the surfactant binds to the polymer causing an expansion of the concentrated phase, due to the electrostatic repulsion between the mixed micellar aggregates. For EHEC, further binding increases the solubility of the polymer, which results in a dissolution of the EHEC from the concentrated phase. For HMEHEC the hydrophobic cross-links are still strong at low surfactant binding, which means that individual molecules are not dissolved but, rather, the entire network swells until the one-phase region is reached.

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