Colloid Polym Sci 279: 340–347 (2001)

ORIGINAL CONTRIBUTION

M. Tsianou
K. Thuresson
L. Piculell

Phase separation in aqueous mixtures of hydrophobically modified cellulose derivatives with their nonmodified analogues

Received: 6 July 2000
Accepted: 6 September 2000

M. Tsianou · K. Thuresson (✉)
L. Piculell
Physical Chemistry 1
Center for Chemistry and
Chemical Engineering
Lund University
P.O. Box 124, Lund 22100, Sweden
e-mail: krister.thuresson@fkem1.lu.se
Fax: +46-46-2224413

Abstract Mixtures of hydrophobically graft-modified cellulose derivatives and their nonmodified analogues have been studied in aqueous solution. A qualitatively similar behavior was found in the phase behavior of nonionic as well as of cationic polymer systems. Over a large range of total polymer concentrations and mixture ratios the solutions phase separated into two phases of similar polymer concentration, with one of the phases enriched in the hydrophobically modified polymer. From the manufacturing process the cellulose derivatives investigated are likely to contain polymer chains with a rather continuous distribution in degrees of substitution and, possibly, substitution patterns. This causes a complex phase behavior that cannot be adequately described by a ternary representation. The multicomponent nature became apparent from composition analyses of the phases in equilibrium. It may thus be more appropriate to view the phase separation as a fractionation. A phase of small relative volume with a highly enhanced hydrophobe content (compared to the original hydrophobically modified polymer sample) was created. This was particularly obvious in more dilute solutions. Sometimes the phase separation was difficult to observe because the phases in equilibrium had similar polymer concentrations and, therefore, similar refractive indices. The observations presented here call for the attention of producers and users of these types of polymers.

Key words Cellulose ether · Hydrophobically modified polymer · Phase behavior · Segregation · Fractionation

Introduction

Reversibly associating water-soluble polymers are of considerable interest to both industrial chemists and chemists working in academia [1, 2, 3, 4]. Hydrophobically modified (HM) polymers are often used for rheology control and stabilization, and in many applications they are found to be superior to traditional (unmodified) polymers. A HM polymer has a low number of hydrophobic moieties (less than 5 mol %) attached either as end groups to the hydrophilic backbone (in an end-capped HM polymer) or as side groups, or grafts, along the backbone (in a graft-modified HM polymer). HM polymers are thus amphiphilic and have a tendency to self-associate in aqueous solutions, forming clusters or networks.

The intermolecular links of a HM polymer give rise to an effective attraction that should have consequences for its miscibility with water. Evidence of this attraction has indeed been found, both in simulation studies [5, 6] and in experiments. The experimental evidence includes a lower osmotic pressure than that expected from the corresponding nonmodified polymer and also a lower solubility [7, 8, 9]. The decreased solubility is particularly pronounced in an intermediate concentration range, where the association can be expected to bring the polymer chains closer together than the average distance given by the global concentration [9]. As a result, the solution separates into two phases, one that contains essentially all the HM polymer and another that contains virtually pure solvent [10].

The two-phase region may also be approached by dilution of a semidilute single-phase HM polymer solution. The polymer-containing phase is then seen to have finite "swelling" in excess water. It is useful to compare this situation with that in a covalently bonded polymer gel. Here intermolecular associations are permanent and when the gel is contacted with excess solvent macroscopic swelling is limited. This analogy suggests that the phase separation of the HM polymers involves network formation, where different hydrophobes of the same polymer end up in different cross-links. This network formation, in turn, requires HM chains that contain at least two hydrophobes. The latter point is illustrated by the following observations [9]. The lower consolute temperature, or cloud point, T_{cp}, of a poly(ethylene glycol) (PEG) with $M_{\mathrm{w}} \approx 6500$ is almost unaffected by modification by a C_{18} hydrophobic moiety at one end of the chain ($T_{\mathrm{cp}} > 100$ °C). However, when the headgroups of two such diblock molecules, which form micelles, are chemically connected, the situation becomes different. In a certain concentration range the attractive potential between micelles [10] lowers the solubility significantly and a minimum of T_{cp} of about 25 °C was found.

Nevertheless, not all HM polymers display phase separation on dilution with water. The reason is that HM polymers – in contrast to chains in a permanent gel – can rearrange so that intramolecular cross-links, or clusters composed of a finite number of chains, are formed. In this way, dilution can occur essentially without any bonds being broken. For soluble end-capped HM polymers, dilution thus leads to a transition from an infinite network to (for highly dilute systems) aggregates of "flowerlike" micelles, where both ends of a given polymer are attached to the same hydrophobic core. Annable and Ettelaie [11] have argued, however, that there is an entropic cost associated with such a dilution under the constraint of complete association of the hydrophobes. A chain with one end attached to a given micelle can have its other end attached either to the same micelle or to any neighboring micelle situated at a distance of the order of the polymer end-to-end distance from the first micelles. The number density of neighboring micelles decreases on dilution, and thus the number of configurations for the HM polymer chains decreases.

An interesting situation arises when the HM polymer is mixed with its nonmodified analogue in water. As has been shown in a few recent experiments [11, 12], the presence of the nonmodified polymer promotes the phase separation of the HM polymer. This effect can be understood in terms of the Flory–Huggins analysis. The derivation of the Flory–Huggins expression for the entropy of mixing [13] shows that a flexible polymer derives its solubility mainly from an increase in configurational entropy at each link of the flexible polymer as the polymer is diluted. In a concentrated system, the number of accessible directions for a chain to turn at a link is severely reduced by the presence of other chains. In this way the tendency for phase separation in a single polymer solution is reduced. In contrast, the phase separation in a mixed polymer solution generates two phases, where both have a similar polymer concentration. Here, the gain in polymer configurational entropy by forming a single phase vanishes. The only remaining entropy gain on mixing is the much smaller translational entropy associated with a uniform distribution of both types of polymer molecules in the entire system.

In their pioneering study, Annable and Ettelaie [11] found, experimentally as well as theoretically, a segregation of an end-capped HM polymer from its nonmodified analogue in aqueous solutions. The experiments were performed on mixtures of end-capped and nonmodified PEG. The theoretical analysis used a simple Flory–Huggins approach, but with the added constraint that an end of a HM polymer had to be attached to a hydrophobic cross-link. Given this constraint, the phase separation between HM polymers and nonmodified polymers was found to be caused by the entropic mechanism mentioned previously, i.e., the gain in the number of possible termination points of a given chain outweighed the loss in translational entropy on mixing different chains. The mechanism for phase separation in this mixture was thus found to be different from the normal segregative phase separation of two polymers in a common solvent, which is caused by preferential interactions among the components, as described by the Flory–Huggins χ parameters. The approach of Annable and Ettelaie is different in that in mixtures of a HM polymer and its unmodified analogue, the repeating units of main chains of the two polymer components are identical, making the HM polymer–polymer interactions athermal and the polymer–solvent interactions identical for both polymers.

The segregation of HM polymers from their nonmodified analogues in solution could be of considerable practical importance. One particular concern is the possible consequences of a heterogeneity in the degree of modification of technical quality HM polymers. This heterogeneity could be large, especially for graft-modified polymers that are obtained by a grafting reaction in a heterogeneous medium and/or by modifying "parent" polymers that are already quite heterogeneous. A case in point would be hydrophobically modified cellulose derivatives. The question arises if a sufficiently broad – or perhaps bimodal – distribution in the degree of substitution in such a sample could give rise to a phase separation. Another source of possible heterogeneity is, of course, deliberate mixing. In many applications, a common strategy to obtain properties within certain specified limits is to use polymer mixtures.

In the present study, we have investigated aqueous solutions of commercial graft-modified cellulose derivatives mixed with their unmodified analogues. Moreover, we have looked at nonionic as well as cationic cellulosic polymers. The study was performed with the following questions in mind: 1. Is the same type of segregative phase behavior found with graft-modified as with end-modified HM polymers? A study on mixtures of nonmodified and hydrophobically modified sodium polyacrylate (HM-PA/PA mixtures) [12] suggests that there are, indeed, significant differences in the phase diagrams. 2. To what extent does the expected heterogeneity of technical HM polymer samples appear in the phase behavior?

Experimental

Materials

Nonionic ethyl(hydroxy ethyl)cellulose (EHEC) and HM-EHEC were supplied by Akzo Nobel Surface Chemistry, Stenungsund, Sweden. Apart from a substitution with nonylphenol groups at 1.7 mol% of the anhydroglucose units of HM-EHEC, the HM-EHEC and EHEC samples were very similar. Cationic derivatives of hydroxyethylcellulose (HEC) were obtained from Amerchol, Union Carbide Chemicals and Plastics Company, USA. Both the nonmodified polymer (catHEC; trade name Ucare JR400) and the hydrophobically modified derivative (catHM-HEC; trade name Quatrisoft LM200) are positively charged owing to quarternary trialkylammonium residues. In the catHEC polymer the quarternary nitrogen is substituted with three methyl groups, while in the catHM-HEC one, it is substituted with two methyl groups and one dodecyl group. Apart from the hydrophobic modification, the two latter polymers differ in their molecular weights and also in their charge densities, with the catHEC polymer having about 4 times higher charge density [14]. The characteristic parameters of the polymers used in the present study are given in Table 1. The cat(HM)-HECs were used after purification by dialysis against MilliQ-treated water as described elsewhere [14], followed by lyophilization. To obtain polymer samples virtually free from nonreacted reactants and simple salts, the EHECs were subjected to a more elaborate purification, as described in detail elsewhere [15]. Sodium dodecyl sulfate (SDS) of specially pure grade was obtained from BDH Laboratory, UK.

Sample preparation and methods

Stock solutions of the four cellulose derivatives were prepared by weighing the components (polymer and water of MilliQ quality) into glass tubes that were sealed with Teflon-tightened screw caps. Samples of desired compositions were prepared by mixing appropriate amounts of polymer stock solutions into glass tubes which were subsequently flame sealed. The samples were carefully mixed by turning end-over-end for several days and were then left to stand for at least 1 week to ensure equilibrium conditions. After equilibration the samples were centrifuged for at least 24 h and the phase behavior was determined by visual inspection. In the samples that phase separated, two liquid phases were formed. The phase volumes were determined by measuring their heights in the tubes. Under some circumstances the phase boundaries were difficult to detect since the two phases in equilibrium had similar polymer concentrations and refractive indices. This became especially noticeable in catHM-HEC/cat-HEC mixtures at low concentrations and at high fractions of catHM-HEC.

For some of the EHEC mixtures, the phases were separated from each other and weighed. By assuming a specific weight of $\rho = 1$ g/ml the volume of the bottom phases could be calculated. The two determinations (weighing or using a ruler) show the same trends, while the absolute values differed by up to 20%, with the gravitational determinations giving a larger volume (cf. Fig. 4). The difference, which is larger in the viscous samples (high polymer concentration), is likely to stem from the fact that part of the top phase remains in the test tube together with the bottom phase. Thus, this separation of the two phases is not complete.

The compositions of the phases in equilibrium in the (HM)-EHEC systems were determined by light absorbance combined with gravitational methods. By weighing the samples before and after lyophilization the total polymer concentration could be obtained. The ratio between EHEC and HM-EHEC in the top phases was obtained from the absorbance of light at a wavelength of 275 nm using a Perkin Elmer Lambda 14 UV–vis spectrophotometer. At this wavelength the two polymers present the largest difference in their absorbance spectra since HM-EHEC is chemically modified with nonylphenol (Fig. 1). The variation of the absorbance with polymer concentration gave straight lines in a calibration curve (Fig. 2). No absorbance measurements were performed on the bottom phases owing to their small volumes (cf. Fig. 4).

All experiments in this investigation were performed at 25 °C.

Table 1 Characteristic parameters for the polymers used in the present investigation

	EHEC	HM-EHEC	catHEC	catHM-HEC
Molecular weight	100,000 (as given by the manufacturer)	100,000 (as given by the manufacturer)	500,000 [23]	100,000 [23]
MS_{EO} (molar substitution)	2.1 [15]	2.1 [15]	~2.5 (typical value for a HEC polymer [24, 25])	~2.5 (typical value for a HEC polymer [24, 25])
Degree of substitution (ethyl)	0.8 [15]	0.8 [15]	0	0
Charge	Nonionic	Nonionic	Positive	Positive
Concentration of charges (mM) in 1 wt% solution	0	0	12	3
Degree of hydrophobic modification (mol%)	0	1.7	0	~8 (calculated assuming $MS_{EO} = 2.5$)

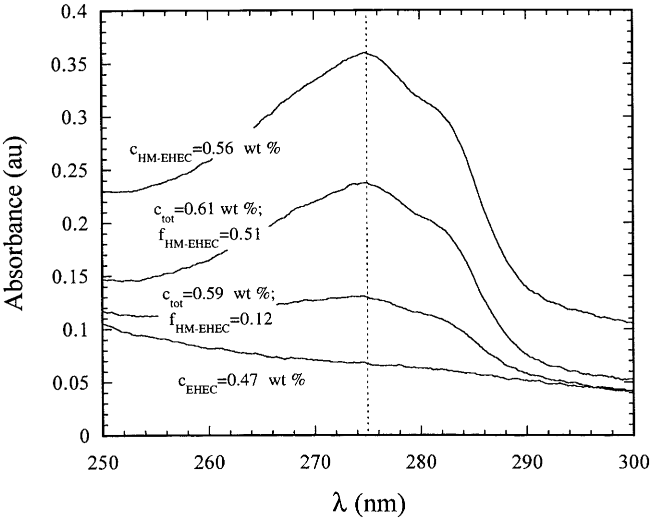

Fig. 1 Light absorbance spectra of aqueous solutions of hydrophobically modified (*HM*)-ethyl(hydroxy ethyl)cellulose (*HM-EHEC*) or EHEC, and of mixed solutions of HM-EHEC and EHEC. The total polymer concentration is approximately 0.5 wt%

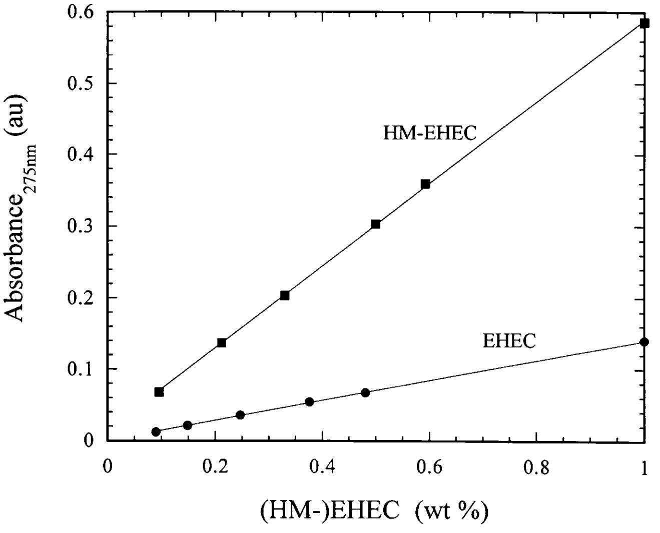

Fig. 2 The absorbance at 275 nm plotted as a function of polymer concentration for HM-EHEC and EHEC aqueous solutions. At this wavelength the absorbance difference between EHEC and HM-EHEC is maximum

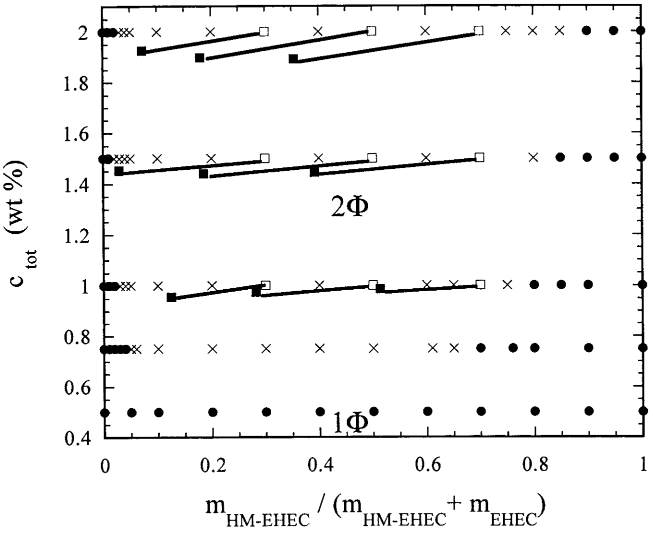

Fig. 3 A phase diagram describing the behavior of aqueous EHEC/HM-EHEC mixtures. *Filled circles* correspond to one-phase samples (*1Φ*), while *crosses* represent two-phase (*2Φ*) samples. The *open squares* are 2Φ samples that were subjected to composition analysis. Corresponding top phases are represented by *filled squares*. *Open* and *filled squares* belonging to the same sample are joined together by a line

Results and discussion

HM-EHEC/EHEC mixtures

A phase map for EHEC/HM-EHEC mixtures in aqueous solution is shown in Fig. 3. The points indicated in the diagram show the macroscopic appearance of the compositions investigated, which were either monophasic (filled circles) or biphasic (crosses). In order to enable direct comparisons with previous studies [11, 12] we used as composition variables the global polymer concentration, c_{tot}, and the weight fraction (out of the total mass of polymer) of HM-EHEC. At low total polymer concentrations ($c_{\mathrm{tot}} \leq 0.5$ wt%), the EHEC/HM-EHEC mixtures were monophasic at all mixing ratios, but a large two-phase region (2Φ) appeared at and above 0.75% polymer. The features of the map of Fig. 3 are distinct from those of the PEG/HM-PEG mixtures of Annable and Ettelaie [11] but similar to those observed for HM-PA/PA mixtures [12]. The aqueous PEG/HM-PEG mixtures gave a remarkably simple phase map, with a rectangular two-phase area delimited by three straight lines: Below c_{tot} ~2%, the aqueous mixed solutions were monophasic at all mixing ratios. Similarly, a single phase was found at all c_{tot} (in the range investigated, i.e., below 10 wt%) once the weight fraction of HM-PEG exceeded 0.65. In contrast, virtually all contents of HM-PEG below this value resulted in phase separation. The phase diagram in Fig. 3 is more classical, with rounded phase boundaries, a finite miscibility of the minority component in both phases and a widening of the two-phase area with increasing c_{tot}.

On the phase map in Fig. 3, we have also indicated a few partial tie-lines. These join point-pairs representing compositions of top phases and their corresponding mother solutions. The tie-lines show that the phase separation is indeed of the segregative type (i.e., both phases have similar c_{tot} but differ in the polymer composition), with top phases enriched in EHEC. It is interesting to see that the polymer concentration in the top phase is only slightly lower than c_{tot}. In addition, the tie-lines show that the compositions of the top phases do not fall on the boundary between the 1Φ and 2Φ regions, as they would for a truly ternary mixture. All top phases display a large hydrophobe content, and this hydrophobe content increases with increasing $f_{\text{HM-EHEC}}$ in the mother solution. At a given mixing ratio of the two polymers (constant $f_{\text{HM-EHEC}}$), the hydrophobe content of the top phase decreases with increasing c_{tot}, but also at the highest polymer concentration investigated ($c_{tot} = 2$ wt%) the segregation is far from complete. The multicomponent nature of the polymer component(s) is thus clearly evident. The explanation is likely to be the heterogeneous manufacturing process of (HM)-EHEC. This gives rise to a distribution in the hydrophobic substitution pattern and in the degree of hydrophobic modification of the HM-EHEC chains [15, 16]. Furthermore, weakly associating ethyl groups assembled in blocks along the EHEC chains may give a significant hydrophobic attraction also between EHEC chains. Thus, in the present systems EHEC and HM-EHEC chains are not expected to be distinctly different. The phase separation should therefore be viewed as a fractionation rather than as a strong segregation between EHEC and HM-EHEC. The most strongly associating polymer chains, with a hydrophobic substitution pattern and structure such that they fit in the network structure, are expected to collect in the bottom phase.

Annable and Ettelaie [11] also investigated the relative volumes of the separating phases in aqueous HM-PEG/PEG mixtures. They found that the relative volume of the bottom phase, $v_{rel,b}$ (i.e., the volume of the bottom phase divided by the total sample volume) increased nearly linearly with the global HM-PEG fraction according to the relation $v_{rel,b} = 1.54 f_{\text{HM-PEG}}$ to reach unity at $f_{\text{HM-PEG}} = 0.65$, where the single-phase region was reached (cf. earlier). Moreover, the relative phase volumes in the two-phase region were found to only depend on $f_{\text{HM-PEG}}$, irrespective of the total polymer content. Both these features were in excellent agreement with the simple theory they proposed.

The relative phase volumes of the HM-EHEC/EHEC mixtures of our study displayed a more complex variation, as shown in Fig. 4. First, $v_{rel,b}$ was consistently (much) smaller than $f_{\text{HM-EHEC}}$, again indicating a large fraction of modified polymers in the top phase. (The hypothetical case $v_{rel,b} = f_{\text{HM-EHEC}}$ is indicated as a thick line in Fig. 4. This case would result from, for example, a complete segregation of HM-EHEC into two "pure" phases of equal concentration.) Second, in the HM-EHEC/EHEC mixtures the variation of $v_{rel,b}$ with $f_{\text{HM-EHEC}}$ depended strongly on the global polymer concentration. At any given value of $f_{\text{HM-EHEC}}$, $v_{rel,b}$ was found to increase with increasing total polymer concentration. Moreover, the shapes of the $v_{rel,b}$ versus $f_{\text{HM-EHEC}}$ curves depended on c_{tot}. At $c_{tot} = 2$ wt% there was a stronger-than-linear increase in $v_{rel,b}$ within the entire range of $f_{\text{HM-EHEC}}$ investigated, while at $c_p = 1$ and 1.5 wt% the corresponding curves display maxima. The latter behavior again demonstrates the multicomponent nature of the present mixtures and calls for a more detailed analysis. We propose that the maximum is created by the following mechanisms. Imagine that the two-phase region is approached from the right, i.e., by successively replacing HM-EHEC by EHEC. We propose that this eventually results in a fractionation, where only the most highly substituted fraction of HM-EHEC separates out into a small phase. A large number of the HM-EHEC chains that are not sufficiently different from nonmodified EHEC chains stay in the top phase. As the EHEC content increases, EHEC will preferably go to the top phase, allowing slightly fewer substituted fractions of HM-EHEC to go to the bottom phase. This mechanism would give rise to the initial increase in the bottom phase volume on going from right to left in the phase map. The eventual decrease encountered at sufficiently high EHEC contents (low $f_{\text{HM-EHEC}}$) must eventually take place as a trivial result of the overall decrease in the content of HM-EHEC.

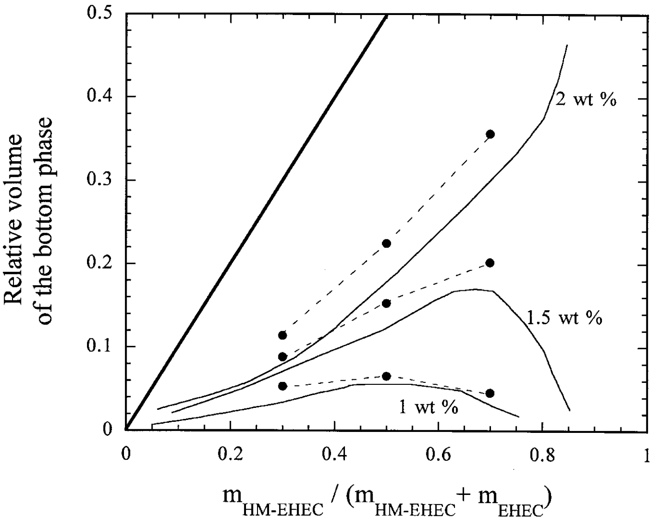

Fig. 4 The variation of the relative volume of the bottom phase with the fraction of HM-EHEC in the sample. Data for three different polymer concentrations (1, 1.5 and 2 wt%) are shown. The *full curves* represent data obtained from the phase heights, while the *dots* (and *dashed curves*) represent data obtained by weighing the phases. The *thick line* represents the phase volume for the hypothetical case with a complete segregation of the two polymer components into two coexisting phases with the same concentration

A fractionation according to this mechanism is expected to be stronger for a more dilute mixture: then only the most modified HM-EHEC polymers are sufficiently hydrophobic to separate out. This is consistent with the observed variation in the phase volumes with c_{tot}. The qualitative behavior of this model can easily be checked with the help of the data in Figs. 3 and 4. From mass balance, and assuming that the overall polymer concentration is equal to c_{tot} in both phases, we immediately arrive at the following equation for the apparent fraction of HM-EHEC in the bottom phase:

$$f_{\text{HM-EHEC,b}} = [f_{\text{HM-EHEC}} - (1 - v_{\text{rel,b}}) f_{\text{HM-EHEC,t}}]/v_{\text{rel,b}},$$

where the indices t and b represent the top and bottom phases, respectively, and $f_{\text{HM-EHEC,t}}$ corresponds to the measured hydrophobe content in the top phase (Fig. 3). When we apply this relation to our data we arrive at values of $f_{\text{HM-EHEC,b}}$ in the range 1.3–4.5 in the bottom phases corresponding to the tie-lines in Fig. 3. Values above 1 would appear unphysical at first, but the interpretation is that the bottom phase is strongly enriched in hydrophobes, even compared to the original HM-EHEC sample. As we predicted, this enrichment is stronger for the more dilute overall mixtures.

It is worth pointing out that the observations and interpretations of the present data are in agreement with a recent investigation where it was found that aqueous HM-EHEC solutions may phase separate if the HM-EHEC sample is chemically heterogeneous from the manufacturing process [16]. It was suggested that the phase separation observed in the latter investigation was due to a fractionation of the polymer material into two phases on grounds of the degree of hydrophobic substitution and the availability of hydrophobic tails for intermolecular associations. The tendency for phase separation of the HM-EHEC solutions was found to increase with the hydrophobicity of the pendant groups.

HM-EHEC/EHEC mixtures with added surfactant

Earlier investigations on the (HM)-EHEC system indicate that the interchain interactions are modulated by addition of the anionic surfactant SDS, and in a certain low SDS concentration range the interchain attractions are believed to be significantly enhanced [17, 18]. Indeed, we have found here that addition of 1 mM SDS to a solution with $c_{\text{tot}} = 0.5$ wt% and $f_{\text{HM-EHEC}} = 0.5$ induced phase separation (at this particular composition the solution was 1Φ without SDS, see Fig. 3). At such a low surfactant concentration, SDS is only expected to bind to the hydrophobic moieties on the HM-EHEC molecules since the critical aggregation concentration of the SDS/EHEC system is approximately 3.5 mM [17]. The phase separation resulted in a bottom phase with a relative volume of 0.1. A simple salt effect of SDS can be ruled out since the HM-EHECs are nonionic polymers and much higher salt concentrations are normally needed to obtain any noticeable effect on the phase behavior [18]. Addition of the same concentration of SDS to a sample already within the two-phase region ($c_{\text{tot}} = 1$ wt% and $f_{\text{HM-EHEC}} = 0.5$) increased the relative volume of the bottom phase from 0.07 to 0.24. This may also be taken as an indication of that the segregation is promoted by stronger attractions between the HM-EHEC chains. However, another factor expected to contribute to the phase volume is the larger osmotic pressure of a phase enriched in the ionic surfactant [19], which might result in a higher water content than in the absence of SDS.

catHM-HEC/catHEC mixtures

It is often found that polyelectrolyte systems have a lesser tendency to phase separate than systems containing nonionic polymers. The contribution to the mixing entropy from the small counterions is large, and collecting them in one phase is highly unfavorable. However, in systems containing two polyelectrolytes with the same charge sign and charge density the situation is different. A segregative phase separation can readily take place without creating a vastly uneven counterion distribution. Such systems thus behave similarly to mixtures of two uncharged polymers [20, 21, 22].

The results obtained from the catHEC/catHM-HEC systems are presented in Figs. 5 and 6, and the resemblance to Figs. 3 and 4 is indeed striking. However a closer examination reveals some, mainly quantitative, differences. The immiscibility of cat-HEC and catHM-HEC is more pronounced, and at higher c_{tot} a phase separation occurs even when a minute fraction of either of the pure polymers is replaced by the other (Fig. 5).

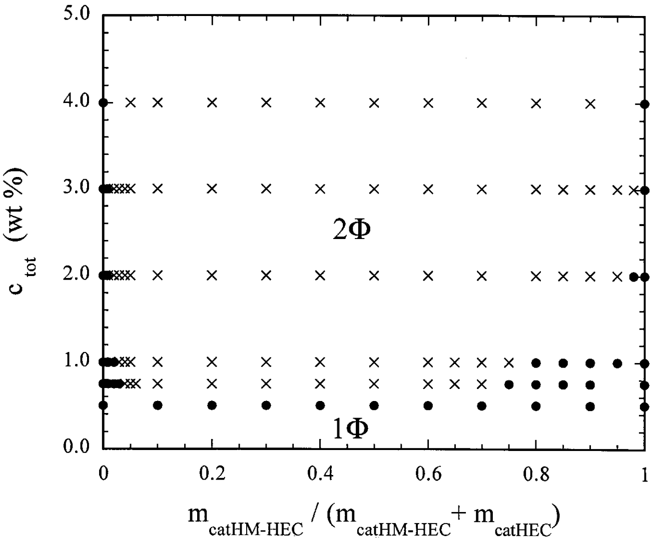

Fig. 5 A phase diagram describing the behavior of catHEC/catHM-HEC mixtures in aqueous solution. *Filled circles* correspond to 1Φ samples, while *crosses* represent 2Φ samples

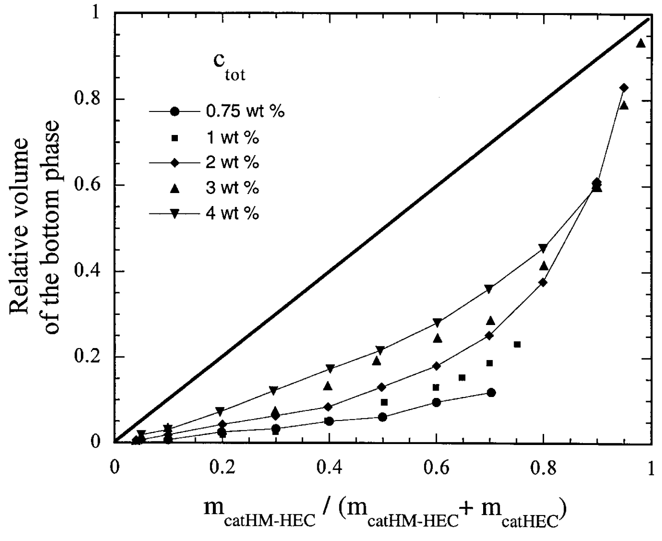

Fig. 6 The variation of the relative volume of the bottom phase with the fraction of catHM-EHEC in the sample. Data are given for five different polymer concentrations, 0.75 wt% (*filled circles*), 1 wt% (*squares*), 2 wt% (*diamonds*), 3 wt% (*up triangles*) and 4 wt% (*down triangles*). The *thick line* represents the phase volume expected from a complete segregation of the two polymer components into two coexisting phases with the same concentration

Figure 6 shows data of the volumes of the bottom phase as a function of $f_{\mathrm{catHM\text{-}HEC}}$ at different polymer concentrations, c_{tot}. At the highest polymer contents, $v_{\mathrm{rel,b}}$ approaches unity for biphasic mixtures approaching pure catHM-HEC. (This was never seen for HM-EHEC/EHEC, but these mixtures were not investigated at such high c_{tot} because of their high viscosities.) At the lower polymer concentrations, $v_{\mathrm{rel,b}}$ increased more slowly (as in the HM-EHEC/EHEC mixtures) but the final approach to single-phase systems was difficult to observe at low c_{tot} in the ionic mixtures. This is because the two phases became very similar in appearance. For this reason, even the reported phase boundaries at high $f_{\mathrm{catHM\text{-}HEC}}$ and low c_{pol} in Fig. 5 should be viewed with some caution. It seems that the refractive indices of the two phases became increasingly similar. As a result, we could not determine which of the phases disappeared on approach to a single phase. A third possibility, which seems difficult to discard a priori, would be that the mixtures approached a critical point. (Unfortunately, the phase compositions of the ionic mixtures are not so easy to measure by spectrophotometry, since the hydrophobes do not absorb light strongly in the UV range.) Nevertheless, our observation of two phases with similar refractive indices presents a caveat for producers and users of this type of polymer: a seemingly clear and uniform solution of HM polymers may in fact contain two phases that can separate macroscopically under gravity upon storage.

Conclusions

As for the simpler end-modified HM polymers, graft-modified cellulose ethers phase separate segregatively, into two phases of closely similar overall polymer contents, when mixed with their unmodified analogues. However, the multicomponent nature of the latter polymers is clearly apparent, resulting in a complex phase behavior that cannot be adequately described in a ternary representation. The phase separation may more appropriately be viewed as fractionation in a mixture containing a rather continuous distribution of degrees of substitution and, possibly, substitution patterns. The following features of the phase separation (all of which might be relevant in applications) were observed.

- Over a large range of polymer compositions the phase separation results in the creation of a phase of a small relative volume with a highly enhanced hydrophobe content – even compared with the original HM polymer sample.
- The phase separation depended strongly on the overall polymer concentration. More dilute mixtures, within the two-phase area, gave a smaller relative volume of the hydrophobe-enriched phase, but a higher enrichment.
- Some phase-separated mixtures, especially at relatively high dilution and high HM polymer contents, gave separating phases that were difficult to distinguish from each other, having a similar refractive index and a not-too-obvious difference in viscosity.

Acknowledgement This work was supported by the Centre for Amphiphilic Polymers, Lund University.

References

1. Glass JE (ed) (1989) Polymers in aqueous media. Advances in chemistry series, vol 223. American Chemical Society, Washington, DC
2. McCormick CL, Bock J, Schulz DN (1989) In: Mark HF, Bikales NM, Overberger CG, Menges G (eds) Encyclopedia of polymer science and engineering, vol 17. Wiley-Interscience, New York, pp 730–784
3. Schulz DN, Glass JE (eds) (1991) Polymers as rheology modifiers. American Chemical Society, Washington, DC
4. Dubin P, Bock J, Davies RM, Schulz DN, Thies C (eds) (1994) Macromolecular complexes in chemistry and biology. Springer, Berlin Heidelberg New York
5. Baljon-Haakman ARC, Witten TA (1992) Macromolecules 25:2969–2976
6. Groot RD, Agterof WGM (1994) J Chem Phys 100:1649–1656

7. Thuresson K, Joabsson F (1999) Colloids Surf A 151:513–523
8. Freyssingeas E, Thuresson K, Nylander T, Joabsson F, Lindman B (1998) Langmuir 14:5877–5889
9. Thuresson K, Nilsson S, Kjøniksen A-L, Walderhaug H, Lindman B, Nyström B (1999) J Phys Chem B 103:1425–1436
10. Semenov AN, Joanny J-F, Khokhlov AR (1995) Macromolecules 28:1066–1075
11. Annable T, Ettelaie R (1994) Macromolecules 27:5616–5622
12. Petit F (1996) PhD thesis. Université Pierre et Marie Curie, Paris
13. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca
14. Tsianou M, Kjøniksen A-L, Thuresson K, Nyström B (1999) Macromolecules 32:2974–2982
15. Thuresson K, Lindman B (1999) Colloids Surf A159:219–226
16. Karlson L, Joabsson F, Thuresson K (2000) Carbohydr Polym 41:25–35
17. Thuresson K, Söderman O, Hansson P, Wang G (1996) J Phys Chem 100:4909–4918
18. Thuresson K, Nilsson S, Lindman B (1996) Langmuir 12:2412–2417
19. Rose'n O, Sjöström J, Piculell L (1998) Langmuir 14:5795–5801
20. Bergfeldt K, Piculell L (1996) J Phys Chem 100:5935–5940
21. Warren PB (1997) J Phys II 7:343–361
22. Gottschalk M, Linse P, Piculell L (1998) Macromolecules 31:8407–8416
23. Dhoot S, Goddard ED, Murphy DS, Tirrell M (1992) Colloids Surf 66: 91–96
24. Tanaka R, Meadows J, Phillips GO, Williams PA (1990) Carbohydr Polym 12:443–459
25. Karlström G, Carlsson A, Lindman B (1990) J Phys Chem 94:5005–5015