ELSEVIER

Carbohydrate Polymers 50 (2002) 219–226

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

A rheological investigation of the complex formation between hydrophobically modified ethyl (hydroxy ethyl) cellulose and cyclodextrin

L. Karlson[a,*], K. Thuresson[b], B. Lindman[b]

[a]Akzo Nobel Surface Chemistry AB, SE-444 85 Stenungsund, Sweden
[b]Physical Chemistry 1, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Received 1 October 2001; revised 26 November 2001; accepted 26 January 2002

Abstract

The thickening effect of a hydrophobically modified polymer in an aqueous solution is dependent on intermolecular hydrophobic associations, and if the polymer concentration is significantly above the overlap concentration also on chain entanglements. In this investigation we have added different cyclodextrins (CD) in order to decouple hydrophobic polymer–polymer associations via inclusion complex formation with the polymer hydrophobic tails. Both size and hydrophobicity of the cavity of the CD-molecules were found to have an effect on the process. In addition, the influence of chemical structure of the polymer hydrophobic tails was investigated. Either a linear C_{14}-chain or a more bulky nonylphenol group was used. The viscosity as a function of CD-concentration first decreased strongly, and then attained a constant value. At excess CD the viscosity became virtually the same as in a solution of the unmodified parent polymer, provided that complex formation was not sterically hindered. This suggests that all hydrophobic links, originating from the hydrophobic modification process, which influence the rheology could be deactivated. On the other hand, with combinations where the complex formation was hindered to a certain degree the initial decrease was less accentuated, and also, the viscosity leveled out at a significantly higher value.

In an attempt to rationalize the data a simple model based on the assumption that each complex formed deactivates one rheologically active link was used. In combination with the Langmuir adsorption model the number of complexes as a function of CD concentration could be obtained. This model also gave a value of the complex formation constant. Furthermore, in solutions where all hydrophobic links could be deactivated the results from the model suggested that all polymer hydrophobic tails were originally active in forming the network. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclodextrin; Ethyl (hydroxy ethyl) cellulose; Hydrophobically modified polymers

1. Introduction

Hydrophobically modified polymers (HM-P), or water-soluble associative polymers, are now routinely used in technical formulations. (Glass, 1989, 1996). They are added with the purpose to modify the rheology of a solution or to increase the stability of a dispersion. Such formulations contain, as a rule, a wide range of components that may interact with the polymer molecules in various ways. In some cases such an interaction results in a lower viscosity than what was expected from tests in simpler solutions, while in other cases synergism may increase the thickening effect in the final formulation. Sometimes, which is worse, it may happen that the solution becomes thermodynamically unstable, resulting in a phase separation. Although complications also occur in solutions based on conventional (non-hydrophobically modified) thickeners such phenomena are more frequent in formulations containing the hydrophobically modified version of the polymer. One reason can be traced to that many compounds have a preferred tendency to interact with the polymer hydrophobic moieties. Therefore molecularly specific information has been invaluable in the understanding of macroscopic properties that such solutions possess. Such data, like binding of surfactant molecules to the polymers, has been obtained by self-diffusion measurements with NMR, fluorescence probe measurements, etc. (Bokias, 2001; Burke & Palepu, 2001; Chronakis & Alexandridis, 2001; Colby, Plucktaveesak, & Bromberg, 2001; Griffiths, Fallis, Teeraporncharsit, & Grillo, 2001; Hoff, Nyström, & Lindman, 2001; Jiménez-Rigaldo, Selb, & Candau, 2000; Miguel, Burrows, Formosinho, & Lindman, 2001; Piculell, Thuresson, & Ericsson, 1995; Piculell, Guillermet, Thuresson, Shubin, & Ericsson, 1996; Schillen, Anghel, Miguel, & Lindman, 2000; Thuresson, Soderman, Hansson, & Wang, 1996). For instance it has been possible to rationalize differences in phase behavior and rheology between

---

* Corresponding author. Fax: +46-303-839-21.
E-mail address: leif.karlson@akzonobel.com (L. Karlson).

PII: S0144-8617(02)00036-X

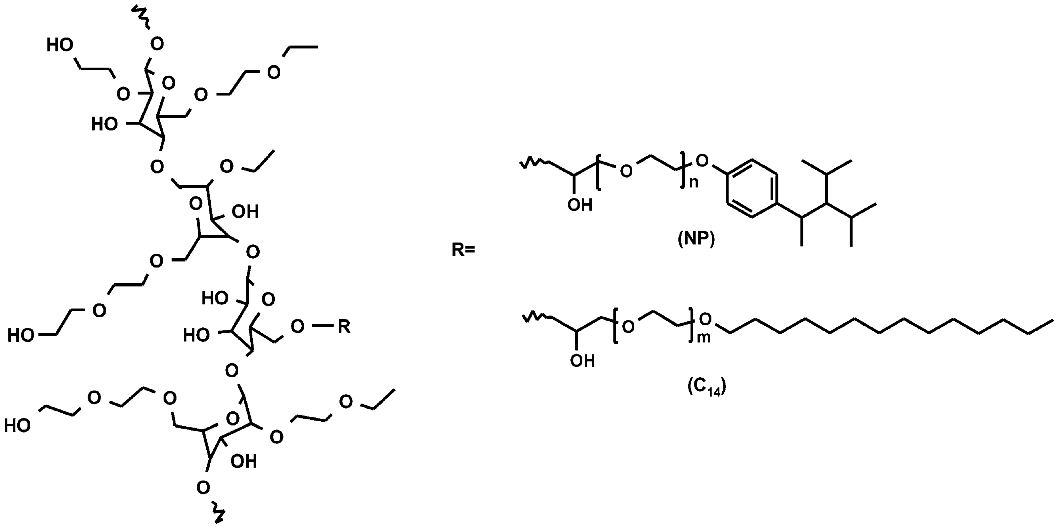

Fig. 1. Possible structural segment of HM-EHEC. R = (C_{14}) for HM(C_{14})-EHEC while for HM(NP)-EHEC R = (NP).

solutions based upon a HM-P or upon the unmodified parent polymer. It is now generally accepted that in semi-dilute aqueous solutions of a water-soluble polymer a hydrophobic modification leads to an increased viscosity due to a formation of a three-dimensional network that is physically held together by inter-polymeric hydrophobic associations. It is also recognized that the strength of the associations and the stoichiometry of the junctions can be modified by addition of surfactant (Thuresson et al., 1996; Thuresson, Karlson, & Lindman, 1999). Although tedious to obtain, such detailed knowledge about one system can later be used in similar systems to interpret macroscopic properties in terms of molecular mechanisms.

A normal route to elucidate the effect of a hydrophobic modification is to compare properties of solutions containing the HM-P with those of the unmodified parent polymer. However, besides that it is time-consuming to synthesize and to investigate both the HM-polymer and the unmodified analogue, it should be born in mind that by making two polymers fractions it is possible, or even likely, that these differ by more than just the hydrophobic modification. A way to circumvent this, and to obtain knowledge about the effect of the hydrophobic modification, is to decouple the hydrophobic associations. This could be done by for instance adding surfactant in excess (so that each hydrophobic tail is decorated by a micelle) or by adding excess amount of diethyleneglycol monobutyl ether, BDG, to the aqueous solution of the HM-P (Karlson, Joabsson, & Thuresson, 2000). At such conditions the HM-P solution has a behavior resembling that of the unmodified parent polymer under the same conditions. A complication is that by following this route also other hydrophobic associations like those originating from the polymer backbone of the parent polymer are lost. Such associations are now known to be responsible for many characteristic properties, among which the thickening effect is one, of for instance certain cellulose-based polymers (Akiyoshi, Sasaki, Kuroda, & Sunamoto, 1998).

A more specific way is offered by cyclodextrin (CD) which is a cyclic oligomer of alpha-D-glucose. The CD molecule has a toroidal shape and contains a hydrophobic cavity within an otherwise hydrophilic molecule (Connors, 1997; Immel & Lichtenthaler, 1996). The cavity has non-polar properties because the glucose-units in the CD-ring arrange in a way such that the hydrophilic parts, the hydroxyl groups, are oriented towards the outside of the ring. Thus, a less polar guest molecule, with dimensions to fit within the cavity, readily substitutes polar water molecules. This hydrophobic attraction drives a complex formation, which has for instance frequently been studied in surfactant/CD systems. Various methods, e.g. calorimetry or surfactant selective electrodes, have been used to determine complex constants (Amiel & Sebille, 1996; Funasaki, Yodo, Hada, & Neya, 1992; Junquera, Tardajos, & Aicart, 1993; Mwakibete, Bloor, & Wyn-Jones, 1994; Mwakibete, Bloor, Wyn-Jones, & Holzwarth, 1995; Park & Song, 1989; Sasaki, Christian, & Tucker, 1989). Since bolt-and-nut (or host–guest inclusion) complexes form between CD-molecules and hydrophobic, or partly hydrophobic, compounds, like long-chained alcohols, or surfactants, complexes are also anticipated between HM-P and CD. By hiding the hydrophobic moieties of a HM-P within the cavities of CD molecules the HM-P solutions are expected to virtually behave like solutions formed from their unmodified analogues. In contrast to what was discussed above, by following this latter route, effects from hydrophobic associations via the polymer backbone are expected to prevail since the hydrophobic segments of the polymer backbone do not fit into the CD cavity. This concept to reduce hydrophobic interactions was used for the first time in the beginning of the nineties (Eisenhart & Johnson, 1992; Lau & Shah, 1994). During the last years CD has been used to decouple hydrophobe–hydrophobe interactions and thereby controlling the

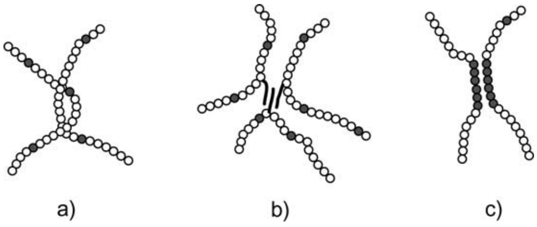

Fig. 2. Schematic presentation of the thickening mechanisms of HM-EHEC. (a) Entanglements of polymer chains, (b) associations between grafted hydrophobic chains, and (c) associations between hydrophobic segments of the backbone. An open circle represents a hydrophilic glucose unit and a filled circle represents a glucose unit that is hydrophobic due to a high substitution degree of ethyl groups.

associations in HM-P solutions (Akiyoshi et al., 1998; Zhang, Hogen-Esch, Boschet, & Margaillan, 1998), and recently the idea was used to shield hydrophobic tails with CD in order to characterize a sample of a hydrophobically modified alkali-soluble emulsion (HASE) (Islam, Jenkins, Bassett, Lau, & Ou-Yang, 2000). Since this inhibits aggregate- and clusters-formation it became possible to use techniques such as gel permeation chromatography and static light scattering to characterize individual molecules.

In another approach the concept of bolt-and-nut complex formation has been used to *increase* the viscosity in a solution of an amphiphilic polymer that contained short and bulky hydrophobic moieties that showed low tendency to self-associate. Instead the HM-P chains were connected via agglomerates of covalently linked CD-molecules (Amiel & Sebille, 1996, 1997, 1999; Sandier, Brown, Mays, & Amiel, 2000).

In this paper we have focused on the interaction between hydrophobically modified ethyl (hydroxy ethyl) cellulose (HM-EHEC) (Fig. 1) and CD, and a range of combinations of polymer hydrophobes and CD molecules have been used. Properties that have been varied include size and hydrophobicity of the CD cavity as well as structure of the polymer hydrophobic tails.

2. Experimental

2.1. Materials

Hydrophobically modified ethyl (hydroxy ethyl) cellulose (HM-EHEC) was synthesized and purified from salt and glycol impurities as described elsewhere (Karlson et al., 2000). The hydrophobic moieties were either nonylphenol (NP) or tetradecyl (C_{14}). The HM(NP)-EHEC and HM(C_{14})-EHEC samples were chemically characterized with respect to modification degree of hydrophobic moieties as described in a paper by Karlson et al. (Karlson et al., 2000), methyl-α-cyclodextrins (M-α-CD), β-cyclodextrins (β-CD), and methyl-β-cyclodextrins (M-β-CD), were supplied by Wacker-Chemie (under the trade names Alpha W6 M1.8, Beta W7, and Beta W7 M1.8, respectively). The dimensions of the central cavity β-CD, which has seven glucose units, has been reported to be about 6–7 Å, while α-CD, which has six glucose units, has a smaller cavity (4.7–5.3 Å) (Loftsson & Brewster, 1996) The degree of methylation per glucose unit was 1.6–1.9 for both M-α-CD, and M-β-CD as given by the supplier. The CDs were all of pharmaceutical quality and were used without any further purification. To all samples water of Millipore quality was used.

2.2. Methods

Aqueous stock solutions containing HM-EHEC (1% w/w) or HM-EHEC (1% w/w) and cyclodextrin (1% w/w) were prepared by weighing the components in test tubes before sealing with Teflon tightened caps. These solutions were let to equilibrate for several days before proceeding. In order to facilitate preparation of solutions with cyclodextrin concentration below 0.1% w/w a dilution of the concentrated stock solution was made. The concentrated stock solution (1% w/w CD and 1% w/w HM-EHEC) was adjusted with the 1% w/w HM-EHEC solution to obtain a new stock solution with 0.1% w/w CD and 1% w/w HM-EHEC. From these three stock solutions, samples with desired compositions were prepared by weight. All contained a polymer concentration of 1% w/w, while the CD-concentration varied in the range 0.02–1% w/w (0.15–9 mmolal). Before any measurements, the final samples were left to equilibrate at room temperature for at least 12 h.

The rheological measurements were performed with a StressTech rheometer from Rheologica, Sweden. The rheometer was equipped with a 4 cm, 1° cone and plate system, and the temperature in the measuring geometry was controlled to within ±0.1 °C by an external water bath. The rheometer was put in the continuous shear mode, and the viscosity, η, was determined as a function of the shear rate, $\dot{\gamma}$. The reported η values are obtained from the Newtonian plateau where η is independent of $\dot{\gamma}$.

2.3. Model considerations

Our results were interpreted in a simple model where CD-molecules are regarded to bind to the hydrophobic tails of the polymer chains with a complex formation constant K. It is assumed that 1:1 bolt-and-nut complexes are formed, and we have chosen to represent this complex formation within a Langmuir adsorption model. The concentration of 'adsorption sites', B, in the model is expected to correlate to the concentration of polymer hydrophobic tails (in fact an almost quantitative agreement is found). To obtain the K and B values from our rheological data we have assumed that $\eta \propto G_{\infty}\tau \propto nk_bT\tau \propto n$ (Annable, Buscall, Ettelaie, & Whittlestone, 1993; Green & Tobolsky, 1946). I.e. a change in viscosity at the Newtonian plateau is only dependent on the concentration of rheologically active chains, n (k_b is the Boltzmann constant, and T the

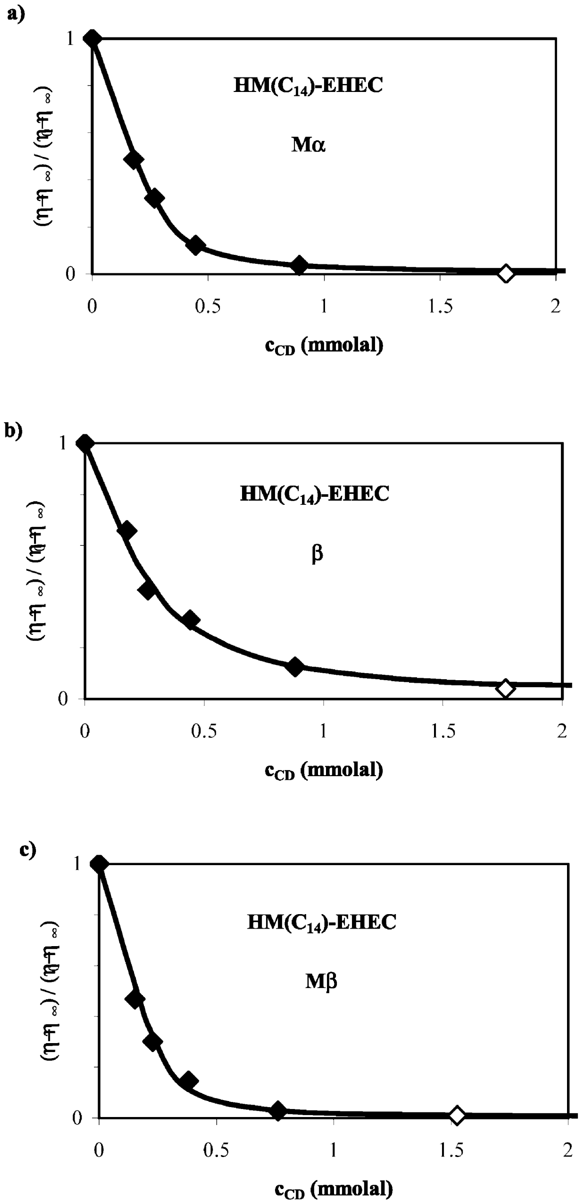

Fig. 3. Relative viscosity of HM(C14)-EHEC solutions (1% w/w) as a function of the cyclodextrin concentration, c_{CD}. The full lines represent a fit of Eq. (1) to the data. Open symbols were excluded from the fit. (a) M-α, (b) β, and (c) M-β.

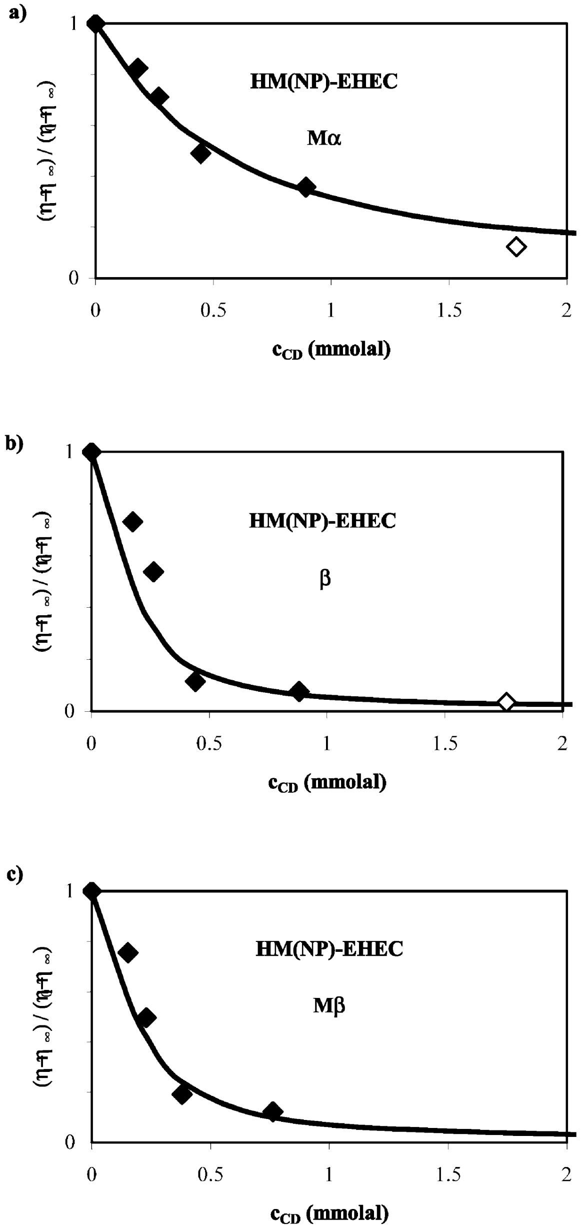

Fig. 4. Same as Fig. 3, but for HM(NP)-EHEC solutions (1% w/w).

temperature). Furthermore, the characteristic time, τ, of the relaxation process, that is important for the viscosity at the Newtonian plateau, is also regarded as independent of the CD-concentration, c_{CD}. By this latter assumption the main contribution to the viscosity in these HM-EHEC solutions is regarded to stem from associations via the polymer hydrophobic tails, and the effect from entanglements of the EHEC backbone is insignificant (Fig. 2(a) and (b)). An estimate of the overlap concentration, taken as the reciprocal intrinsic viscosity, $c^* = 1/[\eta] \approx 0.2\%$ w/w, justifies this assumption, since at the polymer concentration used (1% w/w) reptation is not likely to be a dominant relaxation process. From this follows that (see Appendix A)

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = 1 - \Theta$$

$$= 1 - \frac{\dfrac{B + c_{\mathrm{CD}} + 1/K}{2} - \sqrt{\dfrac{(B + c_{\mathrm{CD}} + 1/K)^2}{4} - Bc_{\mathrm{CD}}}}{B} \qquad (1)$$

Here η_0 and $\eta_\infty$are the viscosity without CD and at excess CD, respectively, and Θ is the fraction of occupied binding sites in the Langmuir model. In the following we have fitted this equation to our experimental

Table 1
Viscosity of HM-EHEC solutions (1% w/w) in water, η_0, and with 20% diethyleneglycol monobutyl ether (BDG), η_{BDG}. $c_{hydrophobe}$ is the concentration of polymer hydrophobic tails in the polymer solution (1% w/w). η_0 and η_{BDG} are given relative to the viscosity of water and 20% BDG in water, respectively

HM-EHEC	η_0	η_{BDG}	$c_{hydrophobe}$ (mmolal)
NP	440	36	0.28
C_{14}	1439	42	0.29
0[a]	45	36	0

[a] Refers to the unmodified parent polymer, EHEC. Data from Karlson et al. (2000).

data points $((\eta - \eta_\infty)/(\eta_0 - \eta_\infty)$ vs. $c_{CD})$ with K and B as fitting parameters.

3. Results

The two different HM-EHEC polymers were combined with the three different CD molecules and the viscosity was followed as a function of the CD-concentration, c_{CD}. Thus, six combinations have been investigated. Fig. 3 shows the influence the three different CD-molecules have on the HM(C_{14})-EHEC solution, while the results obtained from the HM(NP)-EHEC solutions are presented in Fig. 4. Independent of the CD and of the hydrophobic tail of the polymer the general trends are the same. At low c_{CD} the viscosity decreases rapidly and when c_{CD} approaches the concentration of polymer hydrophobic tails, $c_{hydrophobe}$ (see Table 1), the decrease becomes less pronounced. At higher c_{CD} η levels out at a more or less constant level, η_∞. The full lines in each figure represent a fit of Eq. (1) to the data (filled symbols). The agreement is good and the K and B values obtained from the fit are given in Table 2. We note that the concentration of 'adsorption sites', B, correlates well to the concentration of hydrophobic tails in the solution (compare Tables 1 and 2). Hence B varies only slightly between chemically different CD-molecules, while the difference is somewhat bigger between the two sets of data from the two different polymers. From this analysis it follows that the concentration of (available) 'adsorption sites' is about 10% larger in solutions of HM(C_{14})-EHEC than in solutions of HM(NP)-EHEC (Table 3).

In the HM(C_{14})-EHEC solutions the complex formation constant K is large when methylated CDs are used, while with HM(NP)-EHEC the situation is different. Here the binding instead seems to be dependent on the size of the hydrophobic cavity. The binding is promoted by a large cavity and a stronger binding is found for β-CD than for α-CD. Another interesting observation is that the viscosity at excess CD is lower for solutions containing HM(C_{14})-EHEC than for solutions containing HM(NP)-EHEC. This suggests that CD can deactivate a larger fraction of the hydrophobic associations in the former solutions. However, also in the HM(C_{14})-EHEC solutions a small fraction of hydrophobic associations (from polymer hydrophobic tails) remains also at excess CD, since the viscosity of the unmodified EHEC in an aqueous solution has an even lower value, Table 1.

Table 2
Complex formation constant, K, and concentration of adsorption sites, B, obtained by fitting Eq. (1) to the experimental data. η_∞ is the viscosity at excess CD

HM-EHEC	CD	K (mmolal^{-1})	B (mmolal)	η_∞ (mPa s)
NP	M-α	2.7	0.27	115
	β	22.6	0.25	105
	M-β	17.0	0.26	105
C_{14}	M-α	44.0	0.32	50
	β	11.2	0.31	80
	M-β	66.0	0.30	80

4. Discussion

In line with earlier observations on HM-P/CD systems (Zhang et al., 1998), we find that the viscosity of HM-EHEC solutions decreases on addition of CD (Figs. 3 and 4). The reason to the decreased viscosity is that the hydrophobic moieties of the polymer chains become hidden within the CD-molecules. This deactivates hydrophobic associations between polymer chains, and network formation is opposed (Fig. 5) (Akiyoshi et al., 1998; Zhang et al., 1998). At high c_{CD} the solution is likely to contain individual polymer chains with the hydrophobic tails capped with CD molecules, while at intermediate CD-concentrations probably clusters of HM-polymers (and CD-molecules) exist.

To further increase our knowledge about the mechanism we have used a simple model to describe our data. Since this model is based on a Langmuir adsorption isotherm the complex formation constant between a CD-molecule and a polymer hydrophobic tail is obtained, as well as the concentration of 'adsorption sites' (polymer hydrophobic tails) that are available for complexation with CD-molecules. The simple model describes the data well, and the concentration of adsorption sites, B, attains numerical values close to the total concentration of polymer hydrophobic tails, $c_{hydrophobe}$ (Tables 1 and 2). This means that almost all of the HM-EHEC hydrophobic tails are available for capping with CD, and that they contribute to the network forming process (Fig. 2(b)). Following this discussion the viscosity at excess CD, η_∞, is expected to be close to that of an aqueous solution of the corresponding polymer without hydrophobic tails. This is indeed what we find (Fig. 3(a)). The best example is given by the combination of M-α and HM(C_{14})-EHEC. Here the viscosity at excess CD, η_∞, is close to that of the parent polymer (EHEC) in an aqueous solution, Table 1. The reason to that η_∞ is higher for some HM-EHEC/CD combinations is that all polymer hydrophobic

Table 3
Complex formation constant, K_1 (mM^{-1}), for β-CD in combination with tetradecyl trimethyl ammonium bromide (TTAB) and tetradecyl sulphate (TDS)

Surfactant	K_1	Reference
TTAB	39.8	Mwakibete et al. (1995)
TDS	48.2	Park and Song (1989)

tails are not available for complex formation with CD in these cases. This steric hindrance becomes especially obvious with the HM(NP)-EHEC, which has been modified with a bulky nonylphenol-group. Judging from a comparison between B and $c_{\text{hydrophobe}}$, which has been determined independently by chemical analysis, it seems that about 10% of the hydrophobic tails are not accessible to the CD-molecules in this case. Within experimental error this corresponds to what can be estimated from the η_∞ values. Such considerations, by using Eq. (1), suggest that about 16% of the hydrophobic tails are not accessible to the CD-molecules in this case. We also note that technical NP used for the synthesis of HM(NP)-EHEC contains nonylphenol isomers with the nonyl group either in *ortho* or *para* position and also a small fraction of phenol bearing two nonyl groups, dinonylphenol. It is likely that dinonylphenol- and the orto-nonylphenol-isomers constitute the fraction of hydophobic tails have that too large dimensions to fit within the cavity of the CD-molecules. About 10% of the NP consist of dinonylphenol and nonylphenol with the nonyl group in *ortho* position.

With HM(C_{14})-EHEC the η_∞ value is slightly higher with β-CDs as compared to M-α-CD, Table 2. We may speculate that this again has steric reasons, but this time the overall dimensions of the CD-molecule is suggested to be too large for it to come in close contact with the polymer chains. This would imply that there is an optimum size of the CD-molecules.

In this context we note that the parent polymer by itself is slightly associating. This is due to that the manufacturing process results in polymer chains with a blocky structure (Fig. 2(c)). In an aqueous solution the more hydrophobic blocks (likely to contain a high substitution degree of ethyl-groups) associate. This is expected to influence the viscosity, and furthermore, these hydrophobic patches are also regarded to interact with hydrophobic compounds. Surfactants are for instance believed to associate with these parts of the polymer chains (Cabane, Lindell, Engström & Lindman, 1996; Lindell & Cabane, 1998). As discussed in Section 1 an excess amount of diethyleneglycol monobutyl ether, BDG, can be added to decouple such hydrophobic associations (Karlson et al., 2000). This is the reason why viscosity decreases when BDG is added to a solution of the unmodified EHEC polymer, Table 1. CD, on the other hand, is not expected to be able to inhibit such hydrophobic associations between polymer chains. Indeed, there is no detectable influence of CD on the viscosity of a solution of the parent polymer EHEC (results not shown).

The complex formation constant, K, depends on the combination of CD and HM-EHEC hydrophobic tails. The two polymer hydrophobic tails that we have investigated differ by their structure, and the nonylphenol tail is much more bulky than the C_{14} hydrophobic tail. From the observations for the HM(NP)-EHEC systems it seems clear that the relative dimensions of the CD-cavity and the hydrophobic tail are important for the complex formation constant. The β-CD, with the largest cavity, has the highest K-value, while the smallest K-value, with the NP-hydrophobe, is obtained with the M-α-CD, where the bulky nonylphenol groups seem to fit less well. It is known that methylation increases the height of the cavity but at the same time the inner diameter of the cavity is decreased (Immel & Lichtenthaler, 1996). We found that K is smaller for M-β-CD than for β-CD which shows that the bulky nonylphenol group fits less well into the cavity of M-β-CD. This is probably the effect of the decreased inner diameter of the cavity.

Comparing the two HM-EHEC polymers it seems that a straight C_{14} hydrophobic tail more readily substitutes water molecules within the CD-cavity, than a branched nonylphenol group does. β-CD, which has the largest cavity, is an exception since K has a larger value with the nonylphenol hydrophobe. This may be due to a too large cavity of the CD to fit the C_{14} hydrophobic tail in combination with a steric hindrance from large overall dimensions of the CD molecule, as speculated above. It seems that M-β-CD and the C_{14} hydrophobic tail have

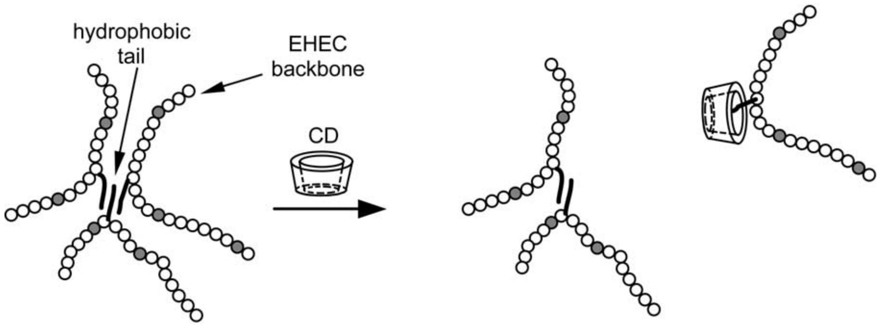

Fig. 5. Schematic representation of the disruption of the polymer network following complex formation between cyclodextrin and polymer hydrophobic tails.

relative sizes that fit well together since this combination has the largest K-value that we observe.

Finally we note that the K values we find for HM(C_{14})-EHEC are lower, but in the same range, as those obtained with surfactants containing a C_{14}-alkyl group as hydrophobic tail (Mwakibete et al., 1995; Park & Song, 1989). This may be due to that the polymer backbone is a large and bulky 'head-group'.

5. Conclusions

In this investigation CD have been added to solutions of hydrophobically modified ethyl hydroxy ethyl cellulose, HM-EHEC. When the CD concentration increased it was found that the viscosity first decreased rapidly and then attained a constant value. This is ascribed to deactivation of the polymer hydrophobic tails since these form inclusion complexes with the CD-molecules. The data could be well represented by a simple model based on the Langmuir adsorption model with the assumption that each polymer hydrophobic tail/CD-complex deactivates one rheologically active link in the polymer network. A close agreement was found between the concentration of active links that could be deactivated and the concentration of polymer hydrophobic tails. We also found that the complex formation constant, K, was dependent on relative sizes of the polymer hydrophobic tail and the cavity of the CD-molecule. For instance, a more bulky hydrophobic tail gave a lower K than a linear polymer hydrophobic tail, and provided geometry does not oppose complex formation the K-value increased by a methylation of the CD.

It was also argued that the CD only deactivates hydrophobic associations originating from polymer hydrophobic tails. This is an important observation in the present system since both hydrophobic tails and hydrophobic patches of the backbone contribute to the cross-linking density.

Acknowledgements

This work was sponsored by the Centre for Amphiphilic Polymers (CAP) at Lund University.

Appendix A

The viscosity at the Newtonian plateau, η_0, can be expressed as the product of the storage modulus in the limit of high frequencies times the characteristic time of the relaxation process, $\eta_0 = \Gamma_\infty \tau$. Since G_∞ is proportional to the cross-linking density ($G_\infty = nkT$), and the characteristic time of the relaxation process is regarded constant (independent of the CD concentration) the viscosity becomes proportional to the cross-linking density, $\eta_0 \propto n$.

Furthermore, we assume that each CD that binds to a polymer hydrophobic tail decreases n by deactivating one active link. Without added CD the viscosity is η_0 while when all hydrophobic tails are deactivated (complexed with a CD) the viscosity is η_∞. The following relationship is obtained:

$$\Theta \propto \frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} \tag{A1}$$

Here Θ is the fraction of hydrophobic polymer tails that are capped with CD. We note that this equation is expected to be valid in the polymer concentration range where the solution is percolated but where effects of entanglements are negligible. Eq. (A1) can be rewritten to obtain:

$$1 - \Theta \propto 1 - \frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} = \frac{\eta_0 - \eta_\infty - \eta_0 + \eta}{\eta_0 - \eta_\infty} = \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \tag{A2}$$

By rewriting the expression for the Langmuir adsorption isotherm (K is the complex constant. c_f,c_b, and c_{CD} are the free, bound, and total concentrations of CD, respectively. B is the concentration of polymer hydrophobic tails):

$$\Theta = \frac{Kc_f}{1 + Kc_f} = \frac{K(c_{CD} - c_b)}{1 + K(c_{CD} - c_b)} = \frac{K(c_{CD} - \Theta B)}{1 + K(c_{CD} - \Theta B)},$$

since $\Theta = \dfrac{c_b}{B}$

we obtain:

$$\Theta = \frac{1}{B}\left(\frac{KB + Kc_{CD} + 1}{2K} \pm \sqrt{\left(\frac{KB + Kc_{CD} + 1}{2K}\right)^2 - Bc_{CD}}\right) \tag{A3}$$

Eqs. (A2) and (A3) give

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = 1 - \Theta$$

$$= 1 - \frac{\dfrac{B + c_{CD} + 1/K}{2} - \sqrt{\dfrac{(B + c_{CD} + 1/K)^2}{4} - Bc_{CD}}}{B} \tag{A4}$$

References

Akiyoshi, K., Sasaki, Y., Kuroda, K., & Sunamoto, J. (1998). Controlled association of hydrophobized polysaccharide by cyclodextrin. *Chemistry Letters*, *1998*, 93–94.

Amiel, C., & Sebille, B. (1996). New associating polymers system involving water soluble beta-cyclodextrin polymers. *Journal of Inclusion Phenomena Molecular Recognition in Chemistry*, *25*, 61–67.

Amiel, C., & Sebille, B. (1997). New associating heteropolymers involving water soluble beta-cyclodextrin polymers. *Revue de L'Institut Francais du Petrole*, *52* (2), 248–250.

Amiel, C., & Sebille, B. (1999). Association between amphiphilic poly (ethylene oxide) and beta-cyclodextrin polymers: Aggregation and phase separation. *Advances in Colloidal Interface Science*, *79*, 105–122.

Annable, T., Buscall, R., Ettelaie, R., & Whittlestone, D. (1993). The rheology of solutions of associating polymers: Comparison of experimental behavior with transient network theory. *Journal of Rheology*, *37* (4), 695–726.

Bokias, G. (2001). Association of hydrophobically modified positively charged *N*-isopropylacrylamid copolymers with nonionic surfactant Triton X-100. *Polymer*, *42*, 3657–3664.

Burke, S. E., & Palepu, R. (2001). Interaction of a hydrophobically modified cationic cellulose ether derivative with amphiphiles of like charge in an aqueous environment. *Carbohydrate Polymers*, *45*, 233–244.

Cabane, B., Lindell, K., Engström, S., & Lindman, B. (1996). Microphase separation in polymer + surfactant systems. *Macromolecules*, *29* (9), 3188–3197.

Chronakis, I. S., & Alexandridis, P. (2001). Rheological properties of oppositely charged polyelectrolyte–surfactant mixtures: Effect of polymer molecular weight and surfactant architecture. *Marcomolecules*, *34* (14), 5005–5018.

Colby, R. H., Plucktaveesak, N., & Bromberg, L. (2001). Critical incorporation concentration of surfactants added to micellar solutions of hydrophobically modified polyelectrolytes of the same charge. *Langmuir*, *17* (10), 2937–2941.

Connors, K. A. (1997). The stability of cyclodextrin complexes in solution. *Chemical Review*, *97*, 1325–1357.

Eisenhart, E. K., & Johnson, E. A. (1992). *Method for improving thickeners for aqueous systems*. US Patent 5137571, Rhom and Haas Company, United States.

Funasaki, N., Yodo, H., Hada, S., & Neya, S. (1992). Stoichiometries and equilibrium constants of cyclodextrin-surfactant complexations. *Bulletin of the Chemical Society of Japan*, *65* (5), 1323–1330.

Glass, J. E. (1989). *Polymers in aqueous media, advances in chemistry*, Washington, DC: American Chemical Society.

Glass, J. E. (1996). *Hydrophilic polymers; performance with environmental acceptability, advances in chemistry*, Washington, DC: American Chemical Society.

Green, M. S., & Tobolsky, A. V. (1946). A new approach to the theory of relaxing polymeric media. *Journal of Chemical Physics*, *14*, 80–89.

Griffiths, P. C., Fallis, I. A., Teerapornchaisit, P., & Grillo, I. (2001). Hydrophobically modified gelatin and its interaction in aqueous solution with sodium dodecyl sulfate. *Langmuir*, *17* (9), 2594–2601.

Hoff, E., Nyström, B., & Lindman, B. (2001). Polymer–surfactant interactions in dilute mixtures of a nonionic cellulose derivative and an anionic surfactant. *Langmuir*, *17* (1), 28–34.

Immel, S., & Lichtenthaler, F. W. (1996). Per-*O*-methylated alpha- and beta-CD: Cyclodextrins with inverse hydrophobicity. *Starch/Stärke*, *48* (6), 225–232.

Islam, M. F., Jenkins, R. D., Bassett, D. L., Lau, W., & Ou-Yang, H. D. (2000). Single chain characterization of hydrophobically modified polyelectolytes using cyclodextrin/hydrophobe complexes. *Macromolecules*, *33* (7), 2480–2485.

Jiménez-Rigaldo, E., Selb, J., & Candau, F. (2000). Effects of surfactant on viscoelastic behavior of semidilute solutions of multisticker associating polycrylamides. *Langmuir*, *16* (23), 8611–8621.

Junquera, E., Tardajos, G., & Aicart, E. (1993). Effect of the presence of beta-cyclodextrin on the micellization process of sodium dodecyl sulfate or sodium perfluorooctanoate in water. *Langmuir*, *9* (5), 1213–1219.

Karlson, L., Joabsson, F., & Thuresson, K. (2000). Phase behavior and rheology in water and in model paint formulations thickened with HM-EHEC: Influence of chemical structure and the distribution of hydrophobic tails. *Carbohydrate Polymers*, *41*, 25–35.

Lau, W., & Shah, V. M. (1994). *Method for improving thickeners for aqueous systems*. US Patent 5376709, Rhom and Haas Company, United States.

Lindell, K., & Cabane, B. (1998). Structure of physical gels in the EHEC–SDS–water system. *Langmuir*, *14* (22), 6361–6370.

Loftsson, T., & Brewster, M. E. (1996). Pharmaceutical applications of cyclodextrins. 1. Drug solubilization and stabilization. *Journal of Pharmaceutical Science*, *85*, 1017–1025.

Miguel, M. D. G., Burrows, H. D., Formosinho, S. J., & Lindman, B. (2001). Fluorescence studies of polymer–surfactant association. *Journal of Molecular Structure*, *563–564*, 89–98.

Mwakibete, H., Bloor, D. M., & Wyn-Jones, E. (1994). Determination of the complexation constants between alkylpyridinium bromide and alpha- and beta-cyclodextrins using electromotive force methods. *Langmuir*, *10* (9), 3328–3331.

Mwakibete, H., Bloor, D. M., Wyn-Jones, E., & Holzwarth, J. F. (1995). Reliability of the experimental methods to determine equilibrium constants for surfactant/cyclodextrin inclusion complexes. *Langmuir*, *11* (1), 57–60.

Park, J. W., & Song, H. J. (1989). Association of anionic surfactants with beta-cyclodextrin. Fluorescence-probed studies on the 1:1 and 1:2 complexation. *Journal of Physical Chemistry*, *93* (17), 6454–6458.

Piculell, L., Thuresson, K., & Ericsson, O. (1995). Surfactant binding and micellisation in polymer solutions and gels: Binding isotherms and their consequences. *Faraday Discussions*, *101*, 307–318.

Piculell, L., Guillemet, F., Thuresson, K., Shubin, V., & Ericsson, O. (1996). Binding of surfactants to hydrophobically modified polymers. *Advances in Colloidal Interface Science*, *63*, 1–21.

Sandier, A., Brown, W., Mays, H., & Amiel, C. (2000). Interaction between an adamantane end-capped poly(ethylene oxide) and a beta-cyclodextrin polymer. *Langmuir*, *16* (4), 1634–1642.

Sasaki, K. J., Christian, S. D., & Tucker, E. E. (1989). Study of the stability of 1:1 complexes between aliphatic alcohols and beta-cyclodextrins in aqueous solution. *Fluid Phase Equilibria*, *49*, 281–289.

Schillen, K., Anghel, D. F., Miguel, M. D., & Lindman, B. (2000). Association of naphthalene-labeled poly(acrylic acid) and interaction with cationic surfactants. Fluorescence studies. *Langmuir*, *16* (26), 10528–10539.

Thuresson, K., Soderman, O., Hansson, P., & Wang, G. (1996). Binding of SDS to ethyl(hydroxyethyl)cellulose. Effect of hydrophobic modification of the polymer. *Journal of Physical Chemistry*, *100* (12), 4909–4918.

Thuresson, K., Karlson, L., & Lindman, B. (1999). Clouding of a cationic hydrophobically associating comb polymer. In Press.

Zhang, H., Hogen-Esch, T. E., Boschet, F., & Margaillan, A. (1998). Complex formation of beta-cyclodextrin- and perfluorocarbon-modified water-soluble polymers. *Langmuir*, *14* (18), 4972–4977.