Hydration of ethyl hydroxyethyl cellulose

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The hydration of ethyl hydroxyethyl cellulose (EHEC) has been investigated, utilizing three different methods: proton nuclear magnetic resonance, differential scanning calorimetry and water self-diffusion measurements. The results differ somewhat, depending on the method used, but lie around 2 g of bound water per g EHEC, which corresponds to about 30 water molecules per monomer unit. This is considerably higher than the more hydrophobic methyl cellulose and the more hydrophilic cellulose sulphate. The importance of ethylene oxide groups for water binding to EHEC is also reflected in differences in hydration between EHEC samples with different amounts of ethylene oxide groups. Mechanisms behind the observed hydration numbers are discussed and it is suggested that there is an important influence of water interaction with the polymer backbone. This is favoured by an increasing repulsion between the polymers when ethylene oxide groups are introduced.

(Keywords: ethyl hydroxyethyl cellulose; hydration; nonfreezable water; proton nuclear magnetic resonance; differential scanning calorimetry; water self-diffusion)

INTRODUCTION

Ethyl hydroxyethyl cellulose[1-3] (EHEC) is a water-soluble, nonionic cellulose ether, which is synthesized from cellulose by substitution with ethyl and ethylene oxide (EO) groups. The polymer is often characterized by the following two values: the degree of substitution (*DS*), which denotes the average number of substituted hydroxyl groups per monomer unit, and the molar substitution (*MS*), which denotes the average number of substituents per monomer unit. In the case of EO groups, MS_{EO} is always higher than DS_{EO}, due to the ability of EO to form oligo ethylene oxide chains.

EHEC is a multi-functional compound and, depending upon the application, different properties of the cellulose ether are utilized. It acts as a thickener and dispersing agent when added to paint. In cement-based mortar, the water retention and the workability as well as the adhesion of the mortar improve on addition of EHEC. The water-retentive effect is especially important, and it would be of great value to study how this effect is influenced by changes in the polymer structure. We have therefore investigated the correlation between the hydration (i.e. the amount of bound water as given by different experimental methods) and the MS_{EO}-value of the EHEC molecule. A brief comparison between the hydration of different cellulose ethers has also been made.

Recent work on well-defined systems has demonstrated a direct connection between hydration and water retention. The swelling and water uptake of, *inter alia*, lamellar liquid crystals (composed of water and surfactant) is caused by repulsive interbilayer interactions[4]. These are strong for ionic surfactant systems due to long-range electrostatic effects, but may also be sizeable for nonionic systems[5]. In the latter cases, the role of head–group–water interactions is generally underlined, hence the term 'hydration force'. The experimental characterization and theoretical rationalization of hydration forces are topics of intense current research[6].

The solvation of a macromolecule is a dominating factor determining the macroscopic properties of isotropic solutions and disperse systems. Much effort is thus devoted to quantifying macromolecular solvation, and in particular hydration[7,8], but there are important conceptual difficulties. Generally hydration is described in terms of a hydration number, which is a simplification; this, however, is reasonable if one wants to describe changes in hydration with structural parameters in a narrow group of systems.

Hydration numbers have been reported for many polymers, proteins and other macromolecules[8-20]. Two of the most common methods employed for estimation of such numbers are proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopy and differential scanning calorimetry (d.s.c.). Such measurements are performed on frozen water solutions or gels, and provide information on the amount of nonfreezable water. The relationship between this amount and the amount of bound water in the system considered has been examined recently[11,12,17], and it is a matter of controversy as to whether all nonfreezable water can be regarded as bound water. According to Hoeve[11], there are two types of nonfreezable water: water strongly interacting with a macromolecule and water which is entrapped in small cavities and channels formed by the immobilized solute. In addition to these two methods, hydration numbers can also be obtained from the self-

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diffusion coefficient of water[10,14]. In the present work, the hydration of EHEC has been determined utilizing all three of these methods. This allows an initial characterization of EHEC hydration as well as comparison between the three methods. The hydration of hydroxy ethyl cellulose (HEC) and methyl hydroxy ethyl cellulose (MHEC) has also been determined utilizing the d.s.c. and water self-diffusion methods.

MATERIALS

EHEC powders (trade name Bermocoll E) were obtained from Berol Kemi AB, Stenungsund, Sweden, which also provided the data in *Table 1*. The *DS* and *MS* values are based on gas–liquid chromatography analysis after HBr cleavage. The molecular weight per monomer unit, *M*, in the different polymer chains was calculated according to the formula

$$M = 162.1 + 28.0\,DS_{\text{Ethyl}} + 44.1\,MS_{\text{EO}} \qquad (1)$$

where the first term is the molecular weight of unreacted anhydroglucose. Samples A and B had been treated with glyoxal, which results in crosslinking of the polymers[21]. This considerably simplifies the dispersion of EHEC in water. Under alkaline conditions the crosslinks are hydrolysed and the system is transferred from a suspension of solid particles to a solution or gel. HEC powder (Natrosol 250 HR) was obtained from Hercules Incorporated, USA, and MHEC powder (Tylose MHB 30 000 y) was obtained from Hoechst AG, West Germany. Agarose powder (Electran, Agarose 15) was obtained from BDH Chemicals, Poole, England. D_2O for the water self-diffusion measurements was obtained from Norsk Hydro A/S, Oslo, Norway, and was of 99.8 atom% D isotopic purity. All chemicals were used without further purification. All concentrations are given in weight per cent.

EXPERIMENTAL

^1H n.m.r. spectroscopy

The procedure is based on the method described by Kuntz *et al.*[9]. EHEC and agarose solutions/gels were prepared directly in n.m.r. tubes. Agarose gels were used as a reference, assuming 0.59 g nonfreezable water per g agarose[10]. In order to achieve complete homogeneity, the gels were kept overnight at room temperature. The samples were then frozen and stored in a freezer.

N.m.r. spectra were recorded on a JEOL MH-100 n.m.r. spectrometer operating in the continuous wave mode at 100 MHz. The instrument was equipped with a liquid N_2 cooling system. Temperatures were measured with a Pt resistance thermometer placed in an n.m.r. tube filled with ethanol. The accuracy of the temperature measurements was estimated to be ± 1 K.

All quantitative ^1H n.m.r. measurements of nonfreezable water were performed at 263 K. The frozen samples were equilibrated for 10 min before spectra were recorded. No spinning of the n.m.r. tube was performed. The areas of the absorption signals were determined by cutting and weighing.

Table 1 Data on the samples investigated. The cloud point refers to a 1% solution in water

Sample	Mol. wt.	DS_{Ethyl}	MS_{EO}	Mol. wt./ monomer unit	Cloud point (K)
EHEC A	250 000	1.07	1.55	260	330
EHEC B	250 000	0.84	1.98	273	340
EHEC C	200 000	1.01	1.42	253	331
EHEC D	200 000	1.12	2.24	292	336
HEC	250 000	–	2.37	267	–
MHEC	250 000	–	*	–	334

* Not analysed

Differential scanning calorimetry

A Perkin–Elmer DSC-2 differential scanning calorimeter equipped with a cooling system and an electronic integrator was used in the calorimetric study. The instrument was kindly put at our disposal by the Thermochemistry Division, Chemical Center, Lund. The following experimental procedure agrees roughly with that described in ref. 18.

1–4 mg of the solutions/gels were sealed in aluminium pans. These were cooled at a rate of 0.62 K/min, and kept below the freezing point of water (at 253–258 K) for 10 min. No difference was observed in the result if the samples were cooled to 200 K instead. The pans were then heated to 277 K at a rate of 1.25 K/min. Only one transition peak, due to the free (bulk) water, was observed. The amount of freezable water was estimated by measuring the peak areas and comparing them with the corresponding peaks for neat water. Correction was made for the temperature dependence of ΔH in the range 253–273 K, assuming that the change in ΔC_p is negligible in the range studied. For the determination of the total water content, the lids of the aluminium pans were perforated and the samples evaporated at 378 K. The amount of nonfreezable water was taken as the difference between the total amount of water and the amount of freezable water.

Water self-diffusion

EHEC and HEC samples were prepared directly in n.m.r. tubes. EHEC samples A and B and the HEC samples were allowed to stand at room temperature overnight to obtain complete homogeneity. In contrast, EHEC samples C and D, which had not been treated with glyoxal, had to be kept at 323 K for 5 days before they were completely homogeneous.

The measurements were performed on a Bruker 322S pulsed NMR spectrometer operating at 13.8 MHz for the ^2H nucleus. A pulsed magnetic field gradient unit was connected to the spectrometer, and the pulsed field gradient technique developed by Stejskal and Tanner[22] was applied. The amplitude of the obtained spin echo, *E*, was fitted to the following equation:

$$E = E_0 \exp(-(\gamma g \delta)^2 D(\Delta - \delta/3)) \qquad (2)$$

where *D* is the self-diffusion coefficient of water in the system studied. Refs. 10 and 14 may be consulted for a detailed description of the method and explanation of the other symbols. The measurements were made relative to neat heavy water using the same spectrometer settings, to avoid calibration of the field gradient unit. The temperature measurements were made using a copper–

constantan thermocouple placed in an n.m.r. tube filled with glycerol. The accuracy in the temperature measurements was estimated to be ± 0.5 K.

RESULTS

^1H n.m.r. spectroscopy

Representative spectra of nonfreezable water in frozen EHEC and agarose solutions/gels are presented as an insert in *Figure 1a*. The Figure shows that a considerably larger absorption peak is obtained for EHEC when the two spectra are recorded at the same spectrometer settings. *Figure 1a* also shows the relative signal area, A/A_{ref}, as a function of concentration for EHEC samples A and B at 263 K. A_{ref} is the signal area obtained from an agarose gel (6.6%). The signal area for EHEC (sample B, 6.9%) as a function of temperature is shown in *Figure 1b*.

Differential scanning calorimetry

The amount of nonfreezable water has been calculated from the freezing as well as the melting enthalpy of water

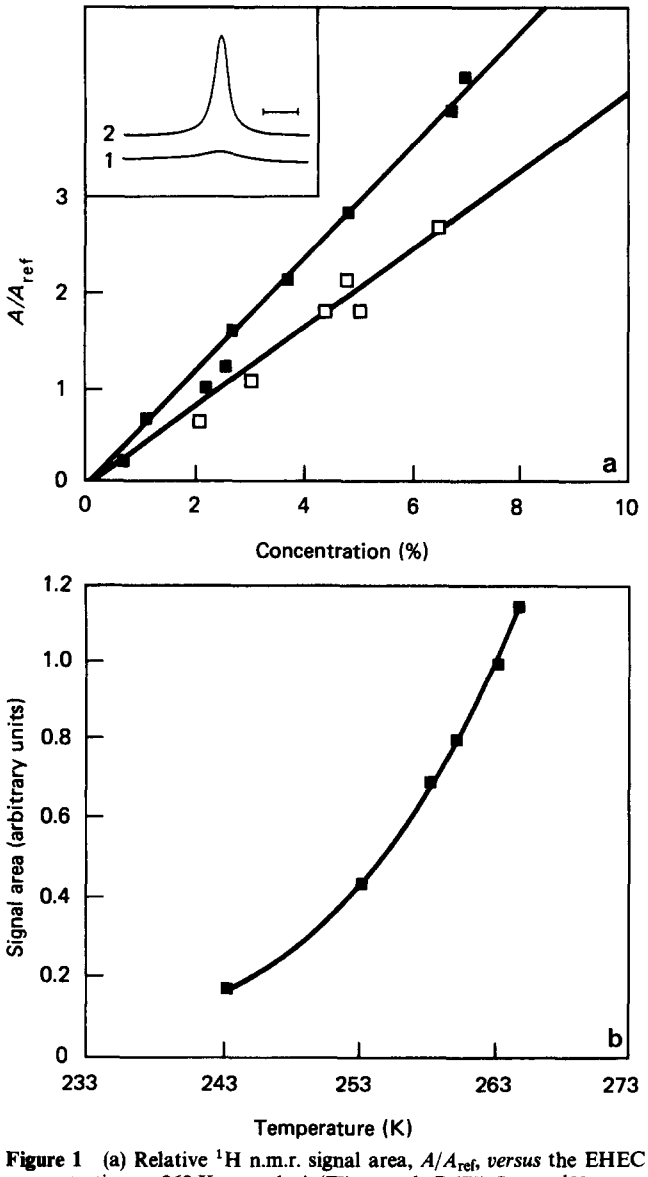

Figure 1 (a) Relative ^1H n.m.r. signal area, A/A_{ref}, *versus* the EHEC concentration at 263 K: sample A (□); sample B (■). Insert. ^1H n.m.r. spectra of nonfreezable water at 263 K (the scale bar represents 200 Hz): agarose 6.6% (1); EHEC sample B 6.9% (2). (b) ^1H n.m.r. signal area *versus* temperature: EHEC sample B 6.9%

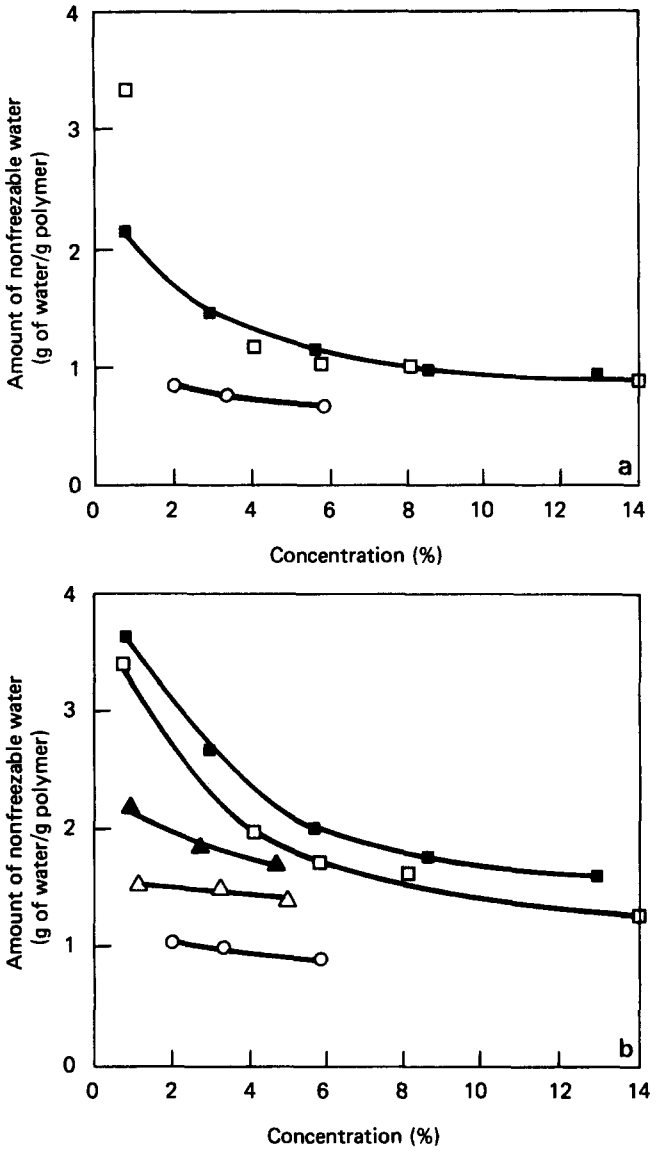

Figure 2 (a) Amount of nonfreezable water (in g of water per g of polymer) from d.s.c. studies *versus* the polymer concentration (calculated from the freezing experiment): EHEC sample A (□); EHEC sample B (■); agarose (○). (b) Amount of nonfreezable water (in g of water per g of polymer) from d.s.c. studies *versus* the polymer concentration (calculated from the melting experiment): EHEC sample A (□); EHEC sample B (■); MHEC (▲); HEC (△); agarose (○)

in the EHEC samples (A and B), and is presented as a function of concentration in *Figures 2a* and *2b*, respectively. The amount of nonfreezable water in HEC, MHEC and agarose samples is also presented.

The result for agarose obtained from the melting experiment is approximately 1 g of nonfreezable water per g agarose. As a check of the method, this could be compared with 0.95 g per g agarose[23], also obtained by d.s.c., but at a higher agarose content (water sorbed on a dry agarose sample directly in the aluminium pan).

Water self-diffusion

The primary result is the relative self-diffusion coefficient, D_{obs}/D_{D_2O}. D_{obs} denotes the self-diffusion coefficient in the sample and D_{D_2O} denotes the self-diffusion coefficient of neat heavy water at the same temperature. EHEC samples A and B were studied at 298 and 323 K, while samples C and D were studied at 278 and 323 K. HEC was studied at 298 K only. D_{obs}/D_{D_2O} as a

function of EHEC concentration at 323 K (samples C and D) is presented in *Figure 3a*.

DISCUSSION

The concept of a single hydration number describing EHEC or any other macromolecule is a simplification and it is not surprising that different experimental methods may provide somewhat different hydration numbers. Thus, it is not straightforward to make a distinction between free and polymer-bound water molecules. As can be seen from *Figure 1a*, there is a linear relationship between the signal area, measured by ^{1}H n.m.r., and the EHEC concentration. This observation is consistent with (and strongly indicates) a constant hydration over the investigated concentration range. It is suggested that the contribution from water entrapped between polymer molecules is relatively insignificant. The amounts of nonfreezable water calculated from the slopes are 1.6 and 2.2 g of water per g EHEC for samples A and B, respectively. Thus, an increase in the MS_{EO} value from 1.6 to 2.0 results in an increased amount of nonfreezable water by 40%. In contrast to agarose gels (ref. 12 and verified in the present study), the ^{1}H absorption signal from EHEC solutions/gels shows a strong temperature dependence (*Figure 1b*). If the temperature is decreased from 263 to 253 K, the signal area is reduced by 55%. Below 233 K no signal could be detected. This strong temperature sensitivity is, firstly, a considerable methodological limitation and, secondly, the cause of a reduced precision because of the temperature instability in the n.m.r. probe. The temperature dependence of the ^{1}H n.m.r. signal from frozen aqueous samples has been discussed by Derbyshire[12].

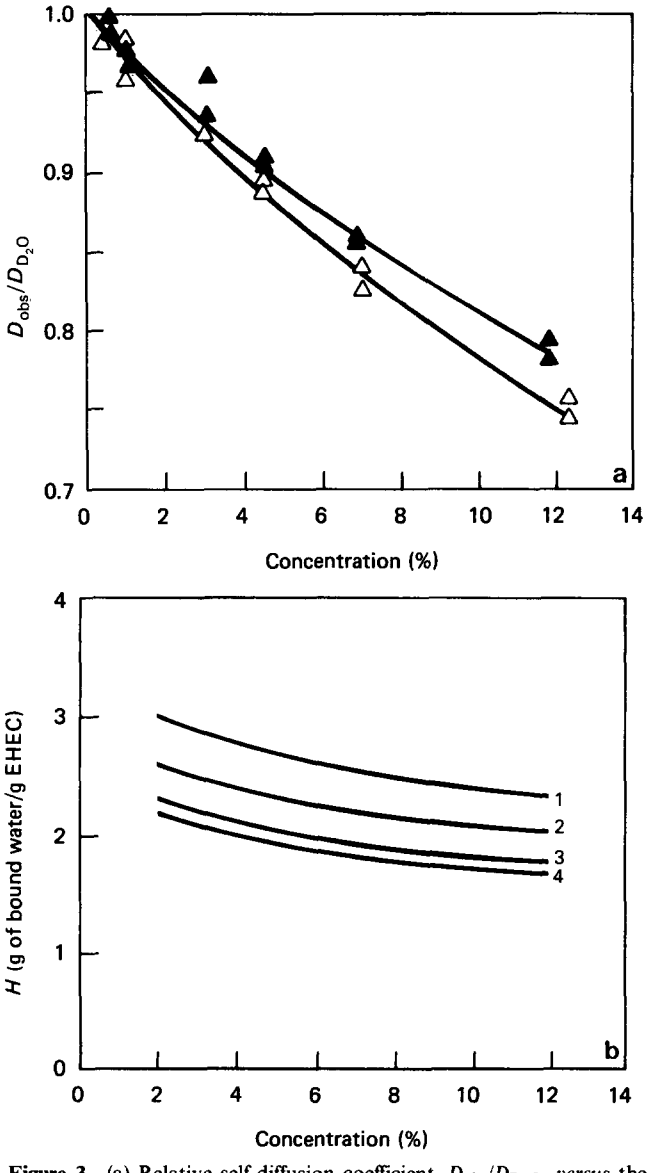

Figure 3 (a) Relative self-diffusion coefficient, D_{obs}/D_{D_2O}, *versus* the concentration at 323 K: EHEC sample C (▲); EHEC sample D (△). (b) Hydration, H (in g of bound water per g of EHEC), obtained from the water self-diffusion measurements *versus* the concentration: EHEC samples C and D at 278 K (curve 1); EHEC samples A and B and HEC at 298 K (curve 2); EHEC sample D at 323 K (curve 3); EHEC sample C at 323 K (curve 4)

The hydration numbers obtained from the d.s.c. experiment show a concentration dependence different from that in the ^{1}H n.m.r. experiment (*Figures 2a* and *2b*). Instead of being constant, the hydration number decreases somewhat as the EHEC concentration is increased. This could be a result of either a polymer–polymer interaction, which gives rise to fewer hydration sites, or displacement of entrapped water. Because of a higher sensitivity in the d.s.c. experiment, it is likely that the result obtained by this method gives a better description of the concentration behaviour at low concentration. The hydration number calculated from the freezing of water in the samples is lower than the hydration number calculated from the melting. If one considers that the freezing occurred after a supercooling of 15–20 K, this could be due to the progressive freezing of the bound water. This change in the hydration number with temperature is, at least in a qualitative way, in agreement with the temperature dependence observed in the ^{1}H n.m.r. experiment. From the melting experiments, it can be seen that there is a significant difference between samples A and B, but not as large as in the ^{1}H n.m.r. experiment. Again, agarose showed a considerably lower degree of hydration than EHEC. The hydration of HEC and MHEC was found to be lower than that of EHEC. However, the hydration numbers of the different cellulose ethers seem to converge at high concentrations. According to this experiment the amount of nonfreezable water per g agarose is about 1 g, compared with 0.59 g obtained by n.m.r.[10]. Similar discrepancies between the two methods have been recently reported for protein solutions[20].

Hatakeyama *et al.* have examined cellulose sulphate ($DS_{sulphate} \simeq 2.3$) by the d.s.c. technique[19]. They obtain a hydration of 0.38 g of water per monomer unit, i.e. five times less than obtained for EHEC in the present investigation.

The observed self-diffusion coefficient of water in an EHEC solution or gel is lower than that of neat heavy water. According to the two-site model, applied to interpret the experimental data, D_{obs} is a population-weighted average,

$$D_{obs} = P_f D_f + P_b D_b \quad (3)$$

Here P_f and P_b are the fractions of free and bound water, respectively. D_f and D_b are the self-diffusion coefficients of free and bound water, respectively. Because of the low polymer concentrations, the obstruction effect is

considered to be insignificant[24]. Assuming that D_f equals D_{D_2O}, equation (3) gives

$$\frac{D_{obs}}{D_{D_2O}} = (1 - P_b) + P_b \frac{D_b}{D_{D_2O}} \simeq 1 - P_b \quad (4)$$

the latter because $D_b \ll D_{D_2O}$. In order to obtain a hydration number, H, in g of bound water per g EHEC, the following equation was employed:

$$H = \frac{(1 - D_{obs}/D_{D_2O})(1 - C/100)}{C/100} \quad (5)$$

Here, C is the concentration of EHEC in %. Errors in the diffusion ratio, which would cause large errors in H, were minimized by the fitting of D_{obs}/D_{D_2O} *versus* concentration to an exponential function (*Figure 3a*). *Figure 3b* shows H as a function of concentration at three different temperatures. From this Figure it can be seen that the hydration number lies between 2 and 3 g of water per g EHEC depending on concentration and temperature. When the temperature of a water solution of EHEC is raised above the cloud point, the solubility of the polymer decreases, and a phase separation will occur. In the present study, the hydration value decreases when the temperature is raised (samples C and D). This suggests that the clouding phenomenon is caused by the dehydration of the polymer. Samples C and D also show a small difference in hydration, but only at 323 K. At the two lower temperatures, no significant difference between any of the samples can be observed. As in the d.s.c. experiment a decrease in hydration with increasing polymer concentration is found.

Table 2 presents the results for all polymers investigated. Here, the hydration is given as the number, N, of bound water molecules per monomer unit as calculated from the equation

$$N = \frac{HM}{M_{aq}} \quad (6)$$

where M is obtained from equation (1) and M_{aq} is the molecular weight of water.

CONCLUSIONS

In this study it is found that the total substitution value has a significant influence on the hydration, and this is most accurately and readily determined by the d.s.c. technique. According to *Table 2*, the value of N increases when the number of substituents is increased. There are two mechanisms which are likely to contribute to this effect. Firstly, the hydrophilic groups are more strongly hydrated than the polymer backbone and, therefore, increasing the fraction of EO increases the hydration number. The importance of residual hydroxyl groups and ether linkages is underlined by a comparison with methyl cellulose, which is reported to have 0.3 g of nonfreezable water per g polymer[11]; this corresponds to about 3.2 water molecules per monomer unit. The second mechanism is that the EO chains, either terminated by ethyl or hydroxyl groups, repel each other because of a favourable EO–water interaction. Thus, the possibility of attractive interaction between polymer backbones is reduced. The repulsion between the EO groups then contributes to a less rigid structure of the polymer and, because of an irregular distribution of the substituents, water may interact with the polymer to a larger extent[25]. The latter effect is indicated by the rather large effect caused by small changes in the MS_{EO} value. It has been shown that the hydration of EO groups is not very dependent on the systems where they appear[14]. This result has been used for a calculation of the fractions of bound water interacting with the EO groups and with the polymer backbone, respectively. It was found that 70–80% of the bound water in the EHEC–water system interacts with the polymer backbone.

The observed temperature and concentration dependences of the hydration of EHEC are as expected. A decreased hydration and a more unfavourable water–EO

Table 2 Comparison between hydration numbers obtained by three different methods and at three polymer concentrations

Method	Sample	DS_{Ethyl}	MS_{EO}	T (K)	N (moles water/mole monomer) 4%	6%	12%
Water self-diffusion (D_2O)	EHEC A	1.1	1.6	298	31	29	26
				323	28	26	23
	EHEC B	0.8	2.0	298	35	33	29
				323	34	32	28
	EHEC C	1.0	1.4	278	35	34	29
				323	26	25	22
	EHEC D	1.1	2.2	278	42	40	34
				323	32	31	27
	HEC	–	2.4	298	33	31	27
	Agarose[a]	–	–	298	17	16	15
^{1}H-n.m.r.[b]	EHEC A	1.1	1.6	263	23		
	EHEC B	0.8	2.0	263	33		
	Agarose	–	–	263	5		
D.s.c.	EHEC A	1.1	1.6	~256	19	16	13
				273	29	25	20
	EHEC B	0.8	2.0	~256	20	17	14
				273	36	30	25
	HEC	–	2.4	273	22	20	
	Agarose	–	–	~256	7	6	
				273	9	8	

[a] Calculated from ref. 10, assuming the measurement was made at room temperature
[b] No concentration dependence

interaction with increasing temperature has previously been found for oligo-EO surfactants[14]. Furthermore, since a phase separation occurs at higher temperatures, a weakened attraction between EHEC and water with increasing temperature is expected. Because of the increasing interaction between different EHEC molecules when the concentration is raised, one also expects the hydration to be decreased when the concentration is raised.

Finally, an important question, which can only be touched on here, concerns the connection in terms of a molecular mechanism between hydration and water retention. When EHEC is used as a water retention agent in cement-based mortar, the desired effect is obtained even when the EHEC content is in the order of 100 times less than in the systems investigated in this study. On the other hand, as argued in the introduction, one expects a direct connection between hydration and water retention. Thus, other factors remaining unchanged, one expects water retention to increase with hydration due to a swelling effect associated with the hydration forces.

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