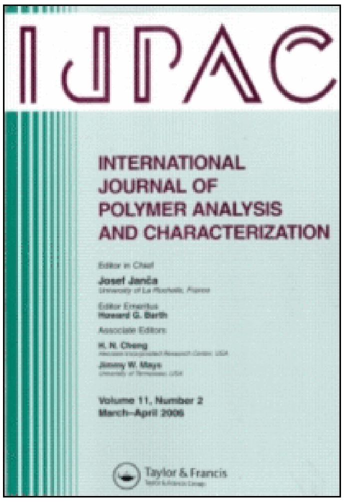

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Solution Behavior of Hydrophobically Associating Cellulosic Derivatives

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Dilute and semidilute solution properties of hydrophobically modified polysaccharides derived from neutral (hydroxyethylcellulose) and ionic (carboxymethylcellulose) cellulosic ethers were studied by means of low-shear viscometry, controlled-stress rheometry, static laser light scattering, and size exclusion chromatography. The differences between the solution properties of the hydrophobic polysaccharides and their parent polymers were interpreted in terms of both intramolecular (in the dilute concentration domain) and intermolecular (above the polymer coil overlap concentration C*) association through the grafted hydrophobic side chains.

KEY WORDS Hydrophobic cellulose ethers, viscosity, laser light scattering, size exclusion chromatography

INTRODUCTION

In recent years there has been increasing interest in hydrophobically modified polymers as these amphiphatic polymers represent a new class of products of considerable advantage for viscosifying aqueous solutions. The peculiar rheological behavior of such polymers is the consequence of hydrophobic associations that occur between the hydrophobic groups incorporated into the precursor molecule through appropriate modification, for example, chemical grafting or copolymerization. Such associations minimize water-hydrophobe contacts and establish the structural conformation, and influence macroscopic properties, mainly rheology [1].

Intramolecular hydrophobic interactions principally prevail in dilute solutions. In more concentrated solutions, that is above the critical concentration for chain overlapping, the establishment of intermolecular associations gives rise to a three-dimensional network with physical gel-like properties [2]. This results in solutions presenting strong thixotropic characteristics which depend on intrinsic parameters such as the percentage, length and/or nature of hydrophobic groups, the flexibility of the main chain, as well as extrinsic parameters such as temperature and/or solvent conditions [3], including pH and salinity in the case of hydrophobic ionic polymers.

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Literature dealing with the properties of hydrophobic polymers mainly considers different classes of polymers, that is, nonionic and ionic copolymers (graft or block-type) of synthetic origin [4–9]. By comparison hydrophobically modified polysaccharide derivatives have received less attention [3, 10–14]. As compared to synthetic polymers, natural biopolymers appear to be more attractive in view of the current trend towards renewable ressources and minimizing environmental effects. In this regard, cellulose is a good candidate and our research has focused on the solution characteristics of both ionic and nonionic hydrophobically modified cellulose derivatives.

Carboxymethylcellulose (CMC) has been chosen as the ionic polymer precursor, whereas hydroxyethylcellulose (HEC) was the nonionic parent polymer. Both precursors were modified through chemical grafting of C_{16}-aliphatic side chains. Low-shear viscometry, controlled-stress rheometry, low-angle laser light scattering (LALLS), and on-line size exclusion chromatography/multiangle laser light scattering (SEC/MALLS) were used for the characterization of precursors and hydrophobically modified derivatives (HMCMC and HMHEC) in dilute and semidilute concentration.

EXPERIMENTAL SECTION

Materials and Solutions

HEC and CMC precursors were supplied by Aqualon Ltd (Wilmington, Delaware) with a molar substitution MS of 3.6 moles hydroxyethyl groups per anhydroglucose unit (HEC) and a degree of substitution DS of 1.0 carboxymethyl group per anhydroglucose unit (CMC) respectively. HMHEC from Aqualon was prepared according to the method reported by Landoll [15]. It contains 0.6% w/w of chemically grafted C_{16}-alkyl side chain (cetyl group).

HMCMC samples were prepared in our laboratory. Substitution of carboxyl groups of CMC precursors of two different molecular weights was achieved by treatment with hexadecylamine (HDA) in the presence of the water-soluble carbodiimide, *N*-(dimethylaminopropyl)-N′-ethyl carbodiimide (EDC), at room temperature during 12 h [16–17]. Different extents of grafting have been obtained by changing the CMC/HDA ratio. However, the exact amount of hydrophobe subtitution was not known precisely. Therefore, the extent of modification of CMC is given in terms of theoretical values.

After preparation, the modified CMC was twice-precipitated in ethyl alcohol, then extensively dialyzed against Milli-Q (Millipore) water, and finally freeze-dried to give a clean white powder. Dry samples were obtained by heating the polymer powders at 110°C overnight. The moisture percent, which was close to 10%, decreased with increased hydrophobicity. For measurements in dilute concentration, stock solutions of 1g/L (HEC and HMHEC) and 2g/L (CMC and HMCMC) were prepared by dissolving the required amount of polymer powder in pure water, then stored at 4°C for one day and finally filtered through Millipore filters in the following pore-size sequence: 8, 3, 1.2, 0.65, and 0.45 μm. Known amounts of concentrated NaCl solutions were added to the previously prepared aqueous polymer solutions to give 0.1M solutions. During the filtration step, no loss of HEC, CMC and HMCMC was detected, whereas about 50% of HMHEC was retained on the filters. These results indicate that the associative tendency is higher for the neutral polymer (HMHEC) than for the ionic polymer (HMCMC), other things being equal (extent of hydrophobe modification, length of side chain, etc.).

Measurement techniques

Low-angle laser light scattering A Chromatix Model *KMX*-6 low-angle laser photometer was used for classical light scattering measurements and data were collected at a forward angle of 6–7° and a 0.2-mm diameter aperture. All solutions were filtered directly into the cell through 0.45-and/or 0.22-µm Millex filters. To facilitate identification of anomalous scattering due to dust and/or other large particules, the solutions were usually slowly flowed through the measuring cell. The weight-average molecular weight M_w and the second virial coefficient A_2 were calculated from the following relationship:

$$Kc/\Delta R_\theta = 1/M_w + 2A_2\, c + \ldots \tag{1}$$

where ΔR_θ is the excess Rayleigh factor, K is the optical constant which includes the refractive index increment dn/dc. For both HEC and HMHEC samples, dn/dc = 0.159 mL/g in 0.1M NaCl, whereas dn/dc = 0.147 mL/g for CMC and HMCMC in 0.1M NaCl.

On-line size exclusion chromatography/multiangle laser light scattering On-line absolute determination of both the molecular weight and the radius of gyration distributions (*MWD* and *RGD*) of eluting polymers was performed using a multiangle laser light scattering photometer (Dawn DSP-F, Wyatt Technology, Santa Barbara, California) and size exclusion chromatography. All the measurements were performed in filtered 0.1M $LiNO_3$ solution using two serially connected TSK PW4000 and PW6000 columns from Toyo Soda (4.10^4 to 8.10^6 g/mol). Data collection from the Dawn DSP-F and the DRI detector was controlled using Wyatt Technology Astra program (V 3.0)and the results were analyzed using the Easi (V 7.0) software package.

Rheological measurements The viscosity of dilute solutions was measured with a low-shear 30 Contraves apparatus (Sc Zurich Switzerland), at a shear rate from 10^{-2} to 10^2 s^{-1}.

The response of polymer systems to oscillatory shear was measured using a Carrimed CSL100 controlled-stress rheometer (Carri-Med Ltd, Dorking, Surrey, England). The elastic G′ and loss G″ moduli, the loss angle ($tg\delta = G''/G'$), and the dynamic viscosity η^* were measured over the frequency range 0.01-10 Hz at a fixed amplitude of 10^{-3} radian (strain = 2.5%) corresponding to the linear strain region for all the investigated solutions.

RESULTS AND DISCUSSIONS

Light scattering data in dilute solution

Typical plots of $Kc/\Delta R_\theta$ vs. concentration are shown in Figure 1 for HEC and HMHEC and in Figure 2 for CMC and HMCMC. The light scattering data (LALLS and SEC/MALLS) for both precursors and hydrophobically modified derivatives are reported in Table I.

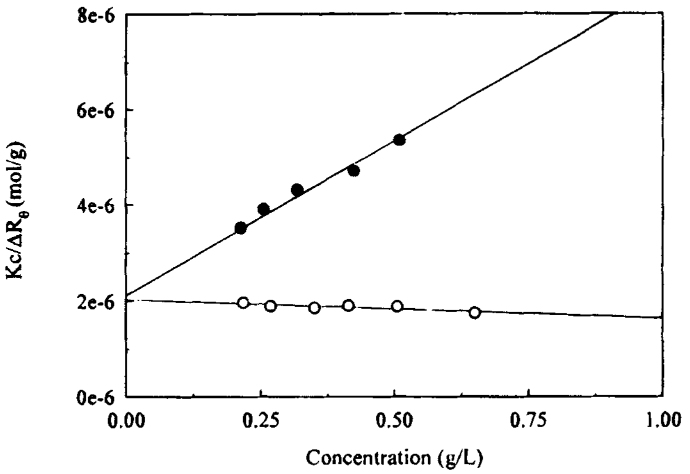

FIGURE 1 Reciprocal reduced scattered intensity at low angle (θ ~6°) against polymer concentration for HEC (●) and HMHEC (○) solutions in 0.1M NaCl at 25°C.

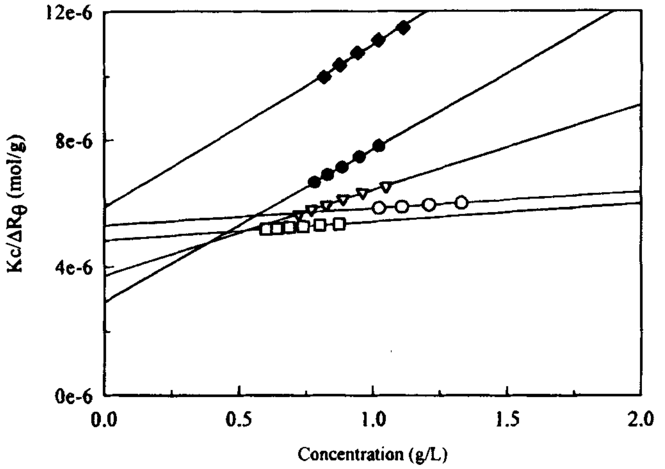

FIGURE 2 Reciprocal reduced scattered intensity at low angle (θ~6°) against polymer concentration for CMC (●), and HMCMC (▽ 0.5mol%, □ 1.0mol%, ○ 1.5mol%), and activated CMC (EDC carbodiimide) without hydrophobic reagent (♦), solutions in 0.1M NaCl at 25°C.

For the two sets of polymers, the M_w values determined from LALLS are in good agreement with those found by on-line SEC/MALLS. The second virial coefficients A_2 are larger than $2 \cdot 10^{-3}$ for both precursors in the same salt conditions. This indicates a rather extended conformation and agrees with the semi-flexible molecular backbone of cellulose derivatives, the persistence length of q of which is larger (~80Å) than that of vinyl-type polymers (~8Å) [18–20]. However, a strong decrease in A_2 is observed for the modified polymers, particularly noticeable for the neutral derivative HMHEC. This is clearly indicative of a poorer solvent strength with increasing hydrophobic character of the polymer chain. The slightly negative A_2 value observed for HMHEC indicates that near Θ-sol-

TABLE I

Laser light scattering data.

SAMPLES		LALLS		ON-LINE SEC/MALLS	
	% alkyl	M_w(g/mol)	A_2(mol·ml·g^{-2})	M^w (g/mol)	Rg (nm)
HEC	—	480,000	$2.2 \cdot 10^{-3}$	470,000	60
HMHEC	0.6 w.%	480,000	$-3.3 \cdot 10^{-5}$	450,000	45
CMC	—	344,000	$2.4 \cdot 10^{-3}$	334,000	85
HMCMC	0.5 mol%	269,000	$1.3 \cdot 10^{-3}$	278,000	54
	1.0 mol%	207,000	$2.9 \cdot 10^{-4}$	200,000	42
	1.5 mol%	188,000	$2.6 \cdot 10^{-4}$	185,000	40
CMC/EDC	without HDA	170,000	$2.5 \cdot 10^{-3}$	—	—

vent conditions prevail. The larger A_2 values measured for HMCMC derivatives reflect better solvent quality and are related to the ionic character of the polymer molecule. The sharp decrease in A_2 is accompanied by a decrease in the coil dimension of HMHEC, as reflected by the measured radii of gyration which are found to be much smaller than for the parent polymer. Since this change in the dimension of the modified polymers occurs at nearly constant M_w, the contraction of the HMHEC molecule can be attributed to intramolecular association between cetyl side chains.

These results are fully confirmed by the SEC/MALLS data from which both M_w and R_g at each retention volume can be extracted from the intercept and the slope near the origin of the Zimm and/or Debye plots. Figure 3 shows the dependence of the radius of gyration R_g on the molecular weight M_w ($R_g \sim M_w^x$) for HMHEC and its parent polymer. It is obvious that R_g of HMHEC scales with M_w with a slope much smaller ($x \sim 0.3$) than that measured for the precursor ($x \sim 0.6$), therefore indicating a more compact coil conformation.

A similar tendency is observed with respect to the change of both A_2 and the radius of gyration R_g (Figure 4) of hydrophobically modified CMC derivatives. However, the coil dimension change and the interaction parameter are accompanied by a continous decrease of molecular weight with increasing extent of modification. Consequently, by considering only the light scattering data, it was difficult to decide if the change in R_g was the consequence of the M_w decrease only or due to a combination of two factors, that is M_w degradation and coil contraction. As shown by data reported in the last line of Table I, it is clear that the change in M_w occurs during the carbodiimide activation step and is not the consequence of the hydrophobic grafting. It is interesting to note that A_2 of the CMC, which has been activated (CMC/EDC), has the same value as that of the precursor and is definitively larger than that of the hydrophobically modified HMCMC of similar M_w. This observation reflects the role of hydrophobic modification on the polymer/solvent interactions and suggests that the modified HMCMC should adopt more compact conformations than those of the precursors CMC and/or activated CMC/EDC of identical M_w.

Dilute solution viscosity

In Table II are the values of intrinsic viscosities $[\eta]$ and the Huggins constants k' which were determined by plotting the low-shear reduced viscosity changes against polymer concentration for dilute solutions of precursors and hydrophobically modified polysaccharides in 0.1M NaCl as illustrated in Figure 5. By comparison with their parent poly-

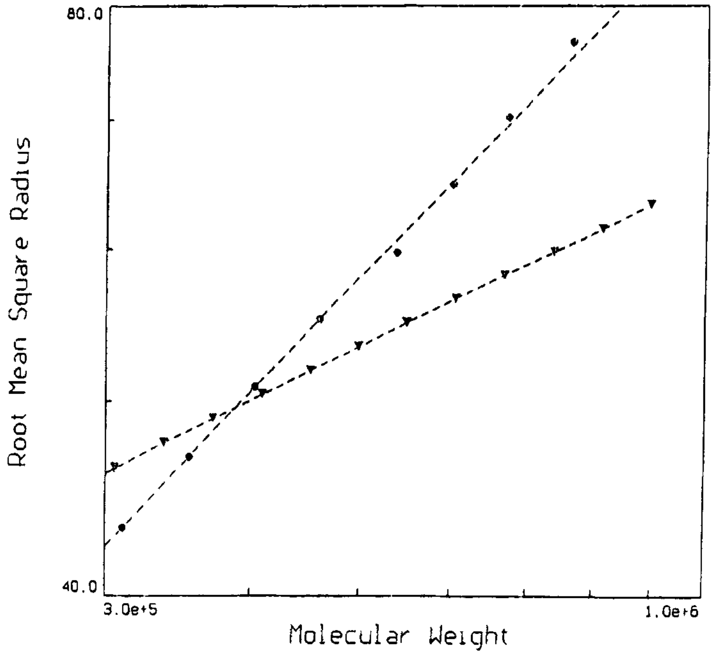

FIGURE 3 Molecular weight dependence of the radius of gyration determined from on-line SEC/MALLS experiments: HEC (●) and HMHEC (▼) solutions in 0.1M NaCl at 25°C.

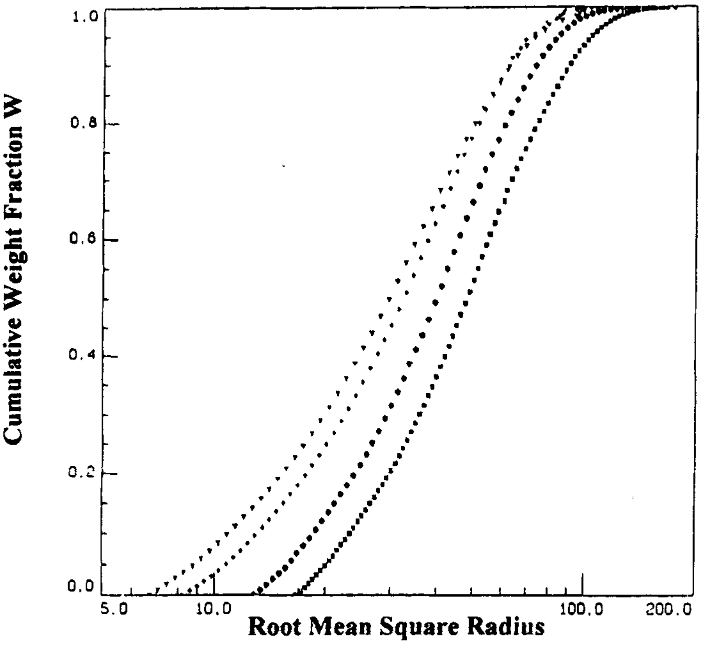

FIGURE 4 R_g cumulative distribution of CMC (■) and HMCMC (● 0.5 mol%, ♦ 1.0 mol%, ◀ 1.5 mol%)

TABLE II

Viscosity data of Precursors and modified polysaccharides

SAMPLES	HEC	HMHEC	CMC	HMCMC		
Alkyl%	—	0.6 weight. %	—	0.5 mol%	1.0 mol%	1.5 mol%
[η] (mL/g)	580	415	523	453	263	215
k′	0.4	2.2	0.3	0.9	2.7	4.7

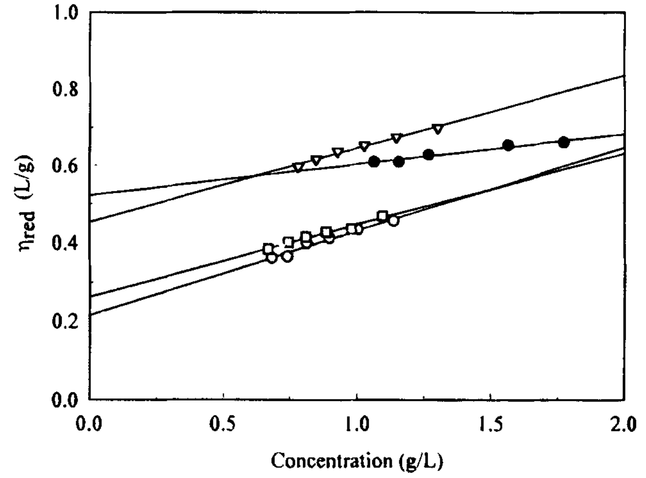

FIGURE 5 Reduced viscosity vs. concentration of CMC (●) and HMCMC (∇ 0.5 mol%, □ 1.0mol%, ○ 1.5mol%) solutions in 0.1M NaCl at 25°C.

mers, both modified polysaccharides show viscosity behavior giving evidence of the existence of intramolecular interactions responsible for the decrease in [η with increased hydrophobic modification. The Huggins constants, which characterize the effect of polymer-polymer interactions on the viscosity, assume values much larger than those predicted for free ($k \sim 0.4$) and nondraining coils ($k \sim 0.76$ [21], indicating a higher tendency for intermolecular attractions. Such viscosity behavior totally agrees with the light scattering data in the case of HMHEC.

In the peculiar case of modified CMC, the observed viscosity decrease is only partly caused by the molecular weight degradation evidenced from light scattering measurements and results from the unexpected action of the dehydrating agent (EDC) used for activating the carboxylic groups. This can be demonstrated by data in Figure 6. In this figure, we have reported the experimentally determined intrinsic viscosities and M_w for CMC, CMC/EDC, and modified CMC together with the log-log plot of [η] vs. M_w (solid line) established by Wirick [22] for CMC of DS~1 in the same salt and temperature conditions as those used here. It is clear that our experimental data that both CMC and CMC/EDC obey the Mark-Houwink relationship established by Wirick [22]. On the contrary, modified CMC samples deviate from that relationship and show smaller values of [η] for a given M_w than the unmodified CMC. It is reasonable to speculate that the deviation from the Mark-Houwink plot for CMC reflects the contribution of hydrophobic substitution to intrinsic viscosity. These results clearly indicate that modified CMC assumes

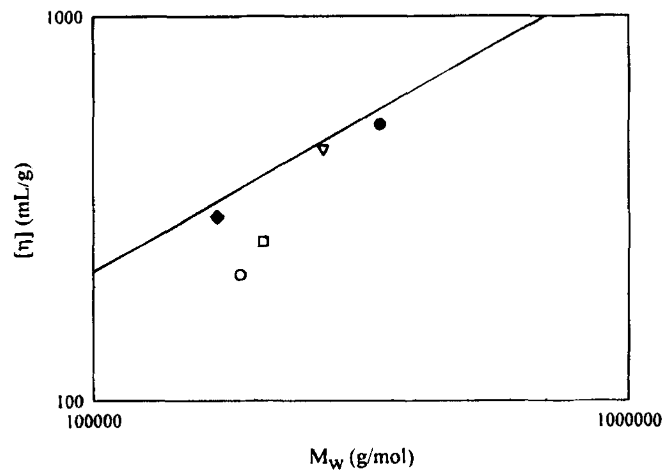

FIGURE 6 Intrinsic viscosity vs. concentration of CMC (●), HMCMC (∇ 0.5mol%, □ 1.0mol%, ○ 1.5mol%), and activated CMC (EDC carbodiimide) without hydrophobic reagent (♦). The solid line was calculated from the Mark-Houwink relationship established by Wirick [22].

a more compact conformation than the parent CMC of identical molecular weight in accordance with the above reported A_2 behavior.

Salinity dependence

The data in Table III illustrate the effect of salinity on the viscosity behavior of HEC and HMHEC. As expected, addition of salt has no effect on the viscosity behavior of the HEC precursor. Upon addition of salt, however, a decrease of the intrinsic viscosity together with an increase in k′ is observed for HMHEC as shown in Figure 7. This behavior indicates that the addition of salt enhances the hydrophobicity and therefore the intramolecular interactions responsible for a more compact conformation than in pure water, as shown for synthetic associative polyacrylates [23].

Semidilute solution

Figure 8 shows the effect of varying salinity and temperature on the resulting apparent viscosity of semidilute HEC and HMHEC solutions. The temperature dependence of viscosity is unaffected by salinity in the case of HEC. For modified HMHEC, the establishment of hydrophobic associations, predominantly intermolecular in this concentration range above the critical c*, leads to improved rheological properties as indicated by the lower temperature dependency of viscosity at higher salinity. As illustrated in Figure 9, the temperature dependence of the loss angle δ (at $\omega = 1$Hz) for 0.1 M NaCl HMHEC in the semidilute concentration range shows that tgδ linearly increases with temperature regardless of the polymer concentration but with a slope which becomes smaller as the polymer concentration increases. Finally for the highest concentration studied (15g/L) a solid-like behavior predominates over a more extended temperature range as indicated by the smaller value of *tgδ*.

TABLE III
Effect of salinity on viscosity behavior of HEC and HMHEC in dilusolution

SAMPLES	HEC		HMHEC		
	water	0.1M NaCl	water	0.1M NaCl	1.0M NaCl
[v], mL/g	580	580	515	415	350
k′	0.4	0.4	0.7	2.2	4.3

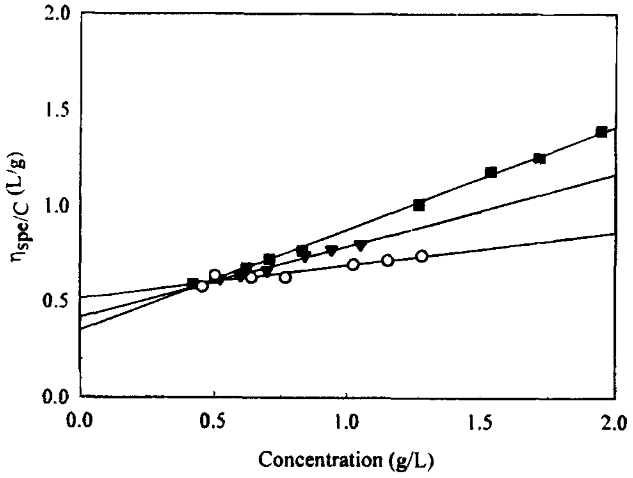

FIGURE 7 Effect of salinity on the concentration dependence of the reduced viscosity of HMHEC (○ water, ▼ 0.1M NaCl, ■ 1M NaCl) at 25°C.

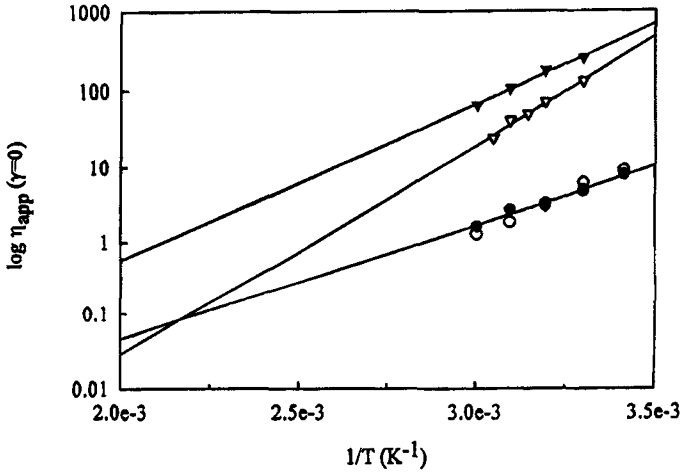

FIGURE 8 NaCl concentration and temperature influence on rheological properties of HEC and HMHEC in semidilute domain of concentration. ○ HEC 0.1M NaCl, ● HEC 1M NaCl, ∇ HMHEC 0.1M NaCl, ▼ HMHEC 1M NaCl

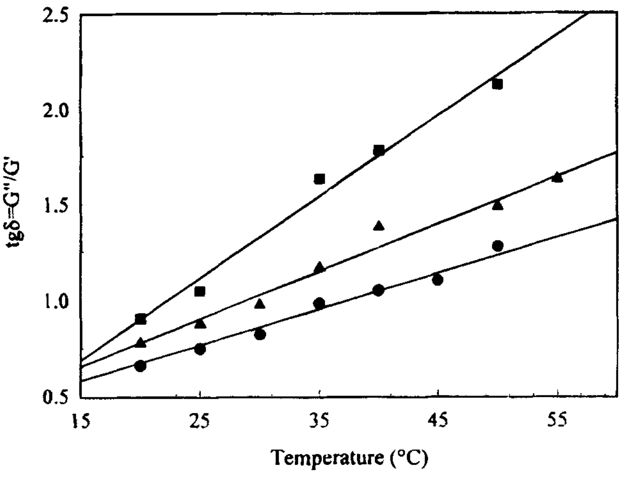

FIGURE 9 Effect of temperature and concentration on the viscoelastic properties of HMHEC (● 15g/L, ▲10g/L & ■ 5g/L) in 0.1M NaCl at 25°C.

The temperature dependence of the apparent viscosity for HMHEC and its precursor at the same salt concentration in Figure 10 shows a similar trend. For both polysaccharides, a significant reduction in low-shear viscosity is observed upon increasing temperature. Nevertheless, the viscosity of the modified HMHEC at 60°C remains larger than that of its precursor indicating that the modified polysaccharide partly retains its structural organization at this temperature. Further work is in progress concerning the effect of temperature on the rheological properties of hydrophobically modified polysaccharides considering its importance for industrial applications.

CONCLUSION

Our objective was to compare two hydrophobically modified cellulose derivatives which differed by their ionic character only. For this purpose we prepared amido-caboxylic derivatives of CMC. Starting with a CMC precursor with a degree of substitution *DS* = 1, the relative proportion of alkyl side chains was varied for obtaining ionic HMCMC with different hydrophobic content. Substitution of carboxylic groups was achieved by treatment with a long-chain aliphatic amine (hexadecylamine) by previously activating the carboxylic groups with a soluble carbodiimide.

A comparison between the solution properties of the hydrophobic ionic polysaccharide (HMCMC) and its parent polymer was disappointing because molecular weight degradation occurred as a result of the coupling reaction. Moreover, due to the poor water solubility of hexadecylamine we found from micro-Kjeldhal analysis, the real extent of modification was only 10% of the theoretical expected one.

More complete results are now obtained by performing the chemical modification in an organic medium wherein both precursor and the C_{16}-amine are soluble. Under these conditions the modification was quantitative. We are presently exploring the effect of pH and salinity on the rheological properties of ionic HMCMC sample obtained by this procedure, results, of which will be reported in a subsequent paper.

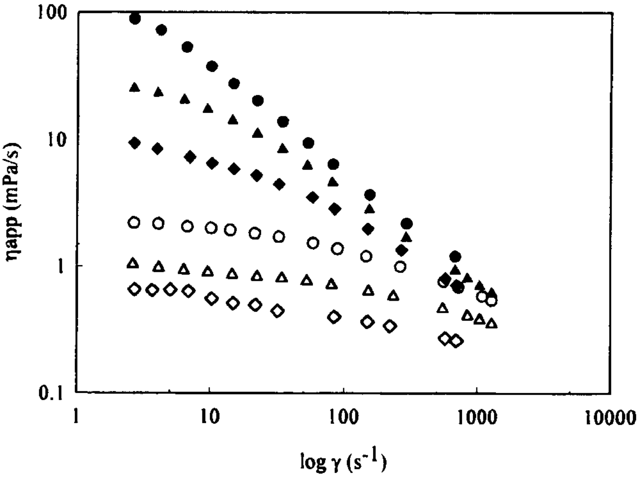

FIGURE 10 Temperature dependence on shear thinning behavior of 15 g/L solutions of HEC at ○ 20°C, Δ 40°C, ◇60°C and HMHEC at ● 20°C, ▲ 40°C, and ◆ 60°C in 0.1M NaCl.

Acknowledgments

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References

1. K. G. Shaw and D. P. Leipold, *J. Coat. Technol.*, **57**, 63 (1985).
2. C. A. Sau and L. M. Landoll, In *Polymers in Aqueous Media: Performance Through Association*, J. E. Glass, Ed.; ACS Advances in Chemistry Series 223; American Chemical Society: Washington, DC, 1989.
3. R. A. Gelman and H. G. Barth, In *Water-Soluble Polymers Beauty with Performance*; J. E. Glass Ed.; ACS Advances in Chemistry Series 213, American Chemical Society: Washington, DC, 1986.
4. S. A. Ezzel, J. C. Middleton, and C. L. MacCormick, *Polym. Prep., Am. Chem. Soc.*, **32** (1), 573 (1991).
5. A. Hill, F. Candau, and J. Selb, *Progr. Colloid Polym. Sci.*, **84**, 61 (1991).
6. D. N. Schulz and J. Bock, *J. Macromol. Sci., Chem.*, **A28**, 1235 (1991).
7. S. Biggs, J. Selb, and F. Candau, *Polymer*, **34**, 580 (1993).
8. C. L. MacCormick and K. P. Blakmom, *Macromolecules*, **19**, 1512 (1986).
9. K. T. Wang, I. Illiopoulos, and R. Audebert, *Polym. Bull.*, **20**, 557 (1988).
10. L. M. Landoll, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 443 (1982).
11. R. Tanaka, *Carbohydr. Polym.*, **12**, 443 (1990).
12. R. Sivadasan and P. Somasundaran, *Colloids Surf.*, **49**, (1990).
13. A. J. Dualeh and C. A. Steiner, *Macromolecules*, **23**, 251 (1990).
14. M. T. King and V. G. Constien, *Am. Chem. Soc. Div. Polym. Mater. Sci. Eng. Prepr.*, **55**, 869 (1986).
15. L. M. Landoll, U. S. Patent 4 228 277 (1980).
16. M. Yalpani, *Tetrahedron, 31*, 2957 (1985).
17. M. I. Papisov, A. V. Marsimenko, and V. P. Torchilin, *Enzyme Microb. Technol.*, **7**, 11 (1985).
18. M. Tricot, *Macromolecules*, **17**, 1698 (1984).
19. K. Kaminde and M. Saito, *Makromol. Chem., Rapid Commun.*, **4**, 83 (1983)
20. W. Brown, D. Henley, and J. Ohmon, *Makromol. Chem.*, **64**, 49 (1963).
21. K. F. Freed and S. F. Edward, *J. Chem. Phys.*, **62**, 4032 (1975).
22. M. G. Wirick, *J. Polym. Sci.*, A-1, **6**, 1965 (1968).
23. B. Magny, I. Illiopoulos, and R. Audebert, *Polym. Commun.*, **32**, 456 (1991).