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Notes

Concentration Dependence of Aqueous Solution Viscosities of Amphiphilic Polymers

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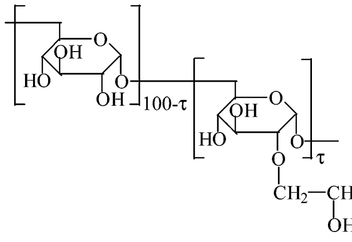
Introduction

Since the pioneering work of Landoll,[1] polymeric surfactants prepared by hydrophobic modification of polysaccharides have been widely studied. Their solution properties have been extensively detailed through the concept of associative behavior. Nevertheless, it is still a great challenge to be able to estimate the solution viscosity by simple relations for that kind of "associative polymer".

In the present work, hydrophobic derivatives of dextran (a neutral, bacterial polysaccharide) have been prepared according to a previously depicted procedure.[2] The dextran precursor has a number-average molecular weight equal to 26 000 g/mol and a polydispersity index of 1.6. It was purchased from Pharmacia (Uppsala, Sweden). Hydrocarbon tails (containing 6 or 10 carbon atoms) have been chemically attached on the glucose rings. The modified polysaccharides are named DexC6$_\tau$ and DexC10$_\tau$, where τ is the percentage of modified glucose units in the chains (Scheme 1). The values of τ have been determined by ^{1}H NMR in deuterated dimethyl sulfoxide. The variation of solution viscosity as a function of polymer concentration has been studied by capillary viscometry.

Scheme 1[a]



[a] Note that this scheme does not imply that the same hydroxyl group is substituted within all the glucopyranose units. The detailed study of the position modified by the aliphatic epoxide has not been performed yet. For the different polymers, $n = 5$ or 9 (see text).

Experimental Section

Viscometric measurements with aqueous solutions were carried out using an Ostwald-type capillary viscometer (0.46 mm diameter). The temperature was regulated by a circulating bath. Prior to measurements, the aqueous solutions were filtered through 0.2 μm filters. Polymer concentration was checked by weighting dry extracts obtained after letting the solutions 24 h in an oven at 110 °C. The found values were always about 90% of the calculated ones. No kinetic corrections were performed since we verified that the flow time was proportional to the cinematic viscosity.[3]

Table 1. Viscometric Results with Amphiphilic Dextrans in Water at 298 K

polymer	$[\eta]$ (mL/g)	k_H	C^{ass} (g/L)
dextran	20.0	0.55	60[a]
dexC6$_{12}$	16.8	1.13	55
dexC6$_{21}$	9.2	2.73	54
dexC6$_{38}$	8.0	3.65	50
dexC10$_{11}$	8.1	6.98	38

[a] For the unmodified polysaccharide, this value is that of the overlap concentration, C^*.

Results and Discussion

In the dilute domain, the viscosity follows the Huggins relation[4] (eq 1) which allows to determine the intrinsic viscosity, $[\eta]$ (in L/g), and the Huggins coefficient, k_H (Table 1). The latter reflects the interactions between the repeating units of the macromolecules.

$$\eta_{red} = \frac{\eta_{sp}}{C} = \frac{\eta - \eta_s}{\eta_s C} = [\eta] + k_H[\eta]^2 C \qquad (1)$$

In eq 1, η and η_s are the viscosity (Pa s) of the polymer solution and that of the pure solvent, respectively, and C is the polymer concentration (g/L).

Above a given concentration (C^{ass}, Table 1), the linear variation of η_{red} with C is no longer followed, and the viscosity increase with polymer concentration becomes much sharper. This is usual evidence of intermolecular associations setting in the solution.[5−8] Although this is a well-known phenomenon, there are no papers providing an equation able to describe the variation of the viscosity over the whole concentration range (below and above C^{ass}).

An equation has been proposed by Matsuoka and Cowman[9−11] (eq 2) and was shown to depict conveniently the viscosity of polymer solutions in good solvents. This equation was shown to be valid for solutions of rigid polymers.[12]

$$\eta_{sp} = C[\eta](1 + k_1 C[\eta] + k_2(C[\eta])^2 + k_3(C[\eta])^3 + ...) \qquad (2)$$

In eq 2, k_1, $k_2 = (k_1)^2/2!$, $k_3 = (k_1)^3/3!$, ... are experimental coefficients, and among them, k_1 is the Huggins constant which is expected to be close to 0.4 for polymers in good solvents. As for polysaccharides in aqueous solutions,

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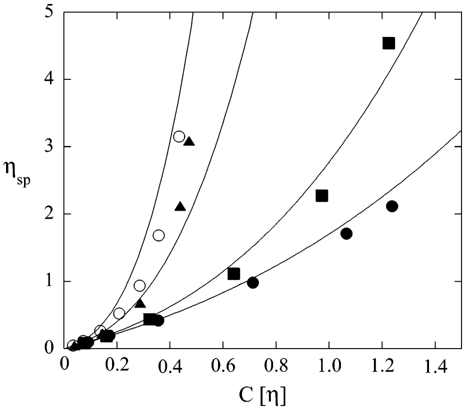

Figure 1. Specific viscosity of aqueous solutions of amphphilic dextrans as a function of polymer concentration at 298 K: unmodified dextran (●), $DexC6_{12}$ (■), $DexC6_{38}$ (◆), and $DexC10_{11}$ (○). The lines represent the calculated curves using the Matsuoka−Cowman equation (see text).

eq 2 was shown to depict conveniently the viscosity of aqueous solutions of hyaluronan[11] and chitosan[13] (with $k_1 = 0.4$).

We propose to extend eq 2 to amphiphilic polymers using the values of k_H ($=k_1$) determined previously from the results of the dilute domain (between 0.5 and 7, Table 1). The calculated curves fit the experimental in a fairly good way (Figure 1). The general tendency is conveniently depicted by the calculated curves which are close to the experimental points. To our knowledge, this is the first example of application of this equation to associative polymers whose k_H values are much higher than unity.

Since the range of overlap parameter covered by this work was limited to $C[\eta] \leq 1$, it seemed necessary to check the validity of the "Matsuoka−Cowman equation" with other results. To that goal, we used the values published recently by Desbrieres about amphiphilic derivatives of chitosan[8,13] and those previously given by Volpert et al. for amphiphilic copolymers of acrylamide.[7] The calculated curves were obtained using the k_H values (up to 5) given in the two papers (Figure 2). The experimental results are described in a fairly good way up to $\eta_{sp} = 10$ and $C[\eta] = 4$ with three constants k_1, k_2, and k_3 calculated with the experimental k_H.

For higher polymer concentrations the calculated values generally overestimate the experimental ones. This could be related to the well-documented fact that the viscosity of aqueous solutions of associative polymers is significantly dependent on the shear rate. This dependence is much more pronounced than that corresponding to the hydrophilic homologues.[7,13] For instance, with our experimental device, the shear rate at the wall, $\dot{\gamma}_w$, can be estimated between 300 and 3000 s^{-1} for our experiments.[3] Whereas, for aqueous solutions of highly soluble polymers, the shear rate effect could be negligible in that range, solutions of amphiphilic polymers exhibit a significant shear-thinning behavior.[7,13] Obviously, no shear rate effect is included in eq 2 so that it should be expected to predict the viscosity at $\dot{\gamma} = 0$ which could exceed significantly the experimental one.

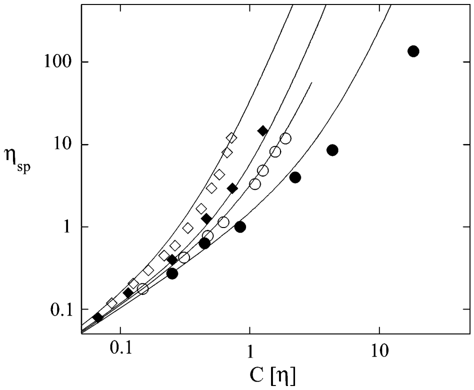

Figure 2. Specific viscosity of aqueous solutions of amphphilic polymers as a function of polymer concentration at 298 K. Results of Desbrieres for amphiphilic derivatives of chitosan[13] ($ChitC3_{100}$, ●; $ChitC12_5$, ◆; solvent = AcOH 0.3 M/AcONa 0.05 M). Results of Volpert et al. for amphiphilic copolymers of acrylamide[7] (containing 1% dihexylacrylamide and differing in the blockiness, solvent = pure water, open symbols). The lines represent the calculated curves using the Matsuoka−Cowman equation (see text).

As a conclusion, we have demonstrated that a unique equation is able to describe the zero-shear viscosity behavior of solutions of highly hydrophilic polymers as well as amphiphilic ones, using the Huggins constant determined in the dilute domain. The latter is enough to take into account the associative behavior up to $C[\eta] \approx 4$ through the Matsuoka−Cowman equation.

References and Notes

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