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Viscosity of aqueous solutions of polysaccharides and hydrophobically modified polysaccharides: Application of Fedors equation

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Abstract

Amphiphilic polysaccharides have been obtained by hydrophobic modification of a neutral bacterial polysaccharide, dextran. Various amounts and types of aliphatic hydrocarbon groups have been attached to dextran.

The solution behaviour of unmodified dextran samples and amphiphilic dextran derivatives is characterized by viscometric measurements. The overall viscosity behaviour of unmodified polysaccharides is described up to $C \times [\eta] = 3$, using the equation of Fedors [Fedors RF. Polymer 1979;20:225] which involves only a concentration parameter. The latter is shown to depend on the hydrodynamic volume of the macromolecules in solution.

The equation of Fedors is shown to conveniently estimate the viscosity behaviour of amphiphilic dextran derivatives up to $C \times [\eta] = 1$. The interdependence between Fedors parameter and other viscometric characteristics (intrinsic viscosity, Huggins coefficient) is evidenced. These results are extended to the data of other authors.

Keywords: Dextran; Viscosity; Amphiphilic polymers; Fedors equation

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1. Introduction

Since the pioneering work of Landoll [1], polymeric surfactants prepared by hydrophobic modification of polysaccharides have been widely studied. These polymers exhibit emulsifying properties that can be adjusted by controlling the hydrophobic modification. Moreover, the polysaccharide backbone can provide biocompatibility, biodegradability and other specific properties. Another important property of that kind of polymers is their associative behaviour in aqueous solutions [2–8]. The hydrophobic groups grafted onto the polysaccharide backbone tend to aggregate together in order to limit their contact with the solvent [9]. For high enough polymer concentrations, hydrophobic groups from distinct macromolecules are involved in the aggregates, leading to the formation of a physical gel. With specifically designed polymers, viscoelastic gels are formed with relatively low polymer concentrations (10–20 g/L) [7]. Despite

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the number of papers dealing with such polymers, it is still difficult to find equations that account for the viscosity of the aqueous solutions in a large range of concentration. Moreover, there are no general equations able to depict correctly the viscosity behaviour of associative polymers both in the dilute and semi-dilute regimes.

In the dilute domain, the well-known Huggins equation [10] (Eq. (1)) is generally followed by all polymers, provided that they are not polyelectrolytes (except if an electrolyte is added in order to screen electrostatic repulsions).

$$\eta_{\mathrm{red}} = \frac{\eta_{\mathrm{sp}}}{C} = \frac{\eta - \eta_{\mathrm{s}}}{\eta_{\mathrm{s}} C} = [\eta] + k_{\mathrm{H}}[\eta]^2 C \tag{1}$$

In Eq. (1), η and η_{s} are the viscosity of the polymer solution and of the pure solvent (Pa s), respectively, η_{red} is the reduced viscosity of the solution (L/g), C is the polymer concentration (g/L), $[\eta]$ is the intrinsic viscosity of the polymer (L/g) and k_{H} is the Huggins constant. The latter is an indication of polymer–solvent affinity.

In the case of amphiphilic polymers, the meaning of the intrinsic viscosity can sometimes be doubtful since macromolecules can form aggregates even in the dilute domain [2–4]. As a result, it can be difficult to relate $[\eta]$ to the characteristics of isolated macromolecules. The upper limit of the applicability of Eq. (1) is the concentration above which the interactions between the isolated objects (single macromolecules or aggregates) start to become significant. This concentration, which will be noted C^{ass}, can be detected easily by the Huggins plot (i.e. η_{red} vs. C) since a sharp break occurs in the linear variation observed in the dilute domain.

For dilute and moderately concentrated polymer solutions, Fedors proposed Eq. (2), initially derived for latex suspensions [11–13].

$$\frac{1}{2(\eta_{\mathrm{rf}}^{1/2} - 1)} = \frac{1}{C[\eta]} - \frac{1}{C_{\max}[\eta]} \tag{2}$$

In Eq. (2), $\eta_{\mathrm{r}} = \eta/\eta_{\mathrm{s}}$ is the relative viscosity of the solution and $C_{\max}$ is a concentration parameter. The equation of Fedors has the peculiarity of involving only a concentration parameter apart from intrinsic viscosity. Later, Eq. (2) was applied to various polymer–solvent systems [14–16] and even to polyelectrolyte solutions [17–19]. Recently, Eq. (2) was applied to aqueous solutions of amphiphilic polymers and compared with other equations but the study was limited to the dilute domain [20].

The purpose of the present work was to depict the viscosity behaviour of solutions of polysaccharides and amphiphilic polysaccharides in the dilute and semi-dilute regimes using of Fedors equation. Moreover, we wanted to relate $C_{\max}$ to other usual viscometric parameters.

2. Experimental

2.1. Materials

The amphiphilic derivatives of dextran were prepared from dextran fractions obtained from Pharmacia (Uppsala, Sweden) with the commercial names T10©, T40© and T500©. The average molar masses of these fractions were determined by size exclusion chromatography coupled to multi-angle laser light scattering analysis, SEC-MALLS (Table 1). The eluent used was 0.1 M $NaNO_3$. The found values of $\overline{M}_{\mathrm{w}}$ are close to those given by the manufacturer. The other chemicals were from Aldrich (St Quentin Fallavier, France) and were used as received.

2.2. Polymer synthesis and characterization

The modification of dextran was performed following a procedure already described in a previous paper [21]. The T40© sample was used. Briefly, 1 g of dextran is dissolved in 20 mL dimethylsulfoxide (DMSO) at 40 °C. Then, 5 mL of a 1 M aqueous solution tetrabutyl ammonium hydroxide is added followed by the required amount of aliphatic epoxide (epoxyoctane or epoxydodecane in that study). The reaction is allowed to proceed at room temperature during several days according to the expected degree of substitution. The reaction medium was

Table 1
Number-average and weight-average molecular weights with polydispersity index of dextran samples as determined by SEC-MALLS

Dextran sample	$\overline{M}_{\mathrm{n}}$ (g/mol)	$\overline{M}_{\mathrm{w}}$ (g/mol)	I_{p}	$\overline{M}_{\mathrm{w}}$ (g/mol) manufacturer's data
T10©	10,500	12,000	1.1	10,000
T40©	26,000	39,000	1.6	40,000
T500©	281,000	520,000	1.8	500,000

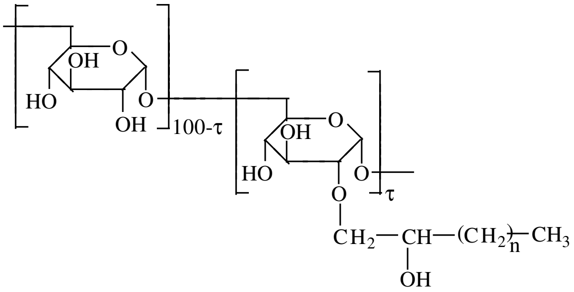
dialysed against a water/ethanol mixture (50/50 v/v) and finally pure water. The polymer was recovered by freeze-drying the resulting aqueous solution.

2.3. Viscometry

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 [22].

3. Results and discussion

The hydrophobic modification of dextran was performed in dimethylsulfoxide (DMSO) in the presence of tetrabutylammonium hydroxide (TBAOH) as previously described [21]. Two aliphatic epoxides were used, epoxyoctane and epoxydodecane, allowing the attachment of C6 and C10 hydrocarbon chains onto the polysaccharide backbone. The degree of substitution, τ, is the fraction of sugar units carrying a hydrocarbon group (Scheme 1). The modified dextran samples will be named DexC6$_\tau$ and DexC10$_\tau$, with τ expressed in %.



Scheme 1. This representation is only schematic and does not imply that the same hydroxyl group is substituted within all the sugar units.

3.1. Viscometric behaviour of unmodified dextran samples

The viscometric behaviour of the three unmodified dextran samples (Table 1) was first characterized. Applying Eq. (1) to the results of the dilute domain ($C < C^*$), the intrinsic viscosity and the Huggins coefficient were determined for the three dextran samples (Table 2). The upper limit of the dilute concentration range (C^* in g/L) was identified to the concentration at which the slope of the linear variation changes (in a plot of η_{red} vs. C). The found values of $[\eta]$ are consistent with previously published Mark–Houwink–Sakurada relations for dextran [23]. From our experiments (Fig. 1), the overlap concentration, C^*, appears to be related to $[\eta]$ by the following equation:

$$C^* = \frac{1.2}{[\eta]} \tag{3}$$

For unmodified dextrans, the overlap concentration is related directly to the hydrodynamic volume of the macromolecules according to the widely accepted theory.

We applied Eq. (2) to the viscometric results obtained with native dextran samples over the whole concentration range, i.e. below and above C^* (Fig. 2 and inset). Within that concentration range, we observed a linear variation of $\frac{1}{2(\eta_{\mathrm{rf}}^{1/2}-1)}$ with $\frac{1}{C[\eta]}$ (inset of Fig. 2), which clearly indicates the valid-

Table 2
Viscometric results with hydrophilic polymer solutions (for symbols see text)

Polymer	T (°C)	Solvent	$[\eta]$ (mL/g), Eq. (1)	k_{H}, Eq. (1)	C^* (g/L)	$[\eta]$ (mL/g), Eq. (2)	$C^{\max}$ (g/L), Eq. (2)	$C^{\max} \times [\eta]$
T10©	25	Water	11.8	0.55	101	11.8	760	9.0
T40©	25	Water	20.0	0.55	60	20.3	309	6.3
	45	Water	16.5	0.60	65	16.9	353	6.0
	65	Water	15.3	0.67	80	16.7	461	7.7
T500©	25	Water	51.6	0.58	30	52.4	140	7.3
PGA[a]	25	5% NaCl	376[a]	0.63[a]	3.9[a]	–	16.7	6.3
PAM[b]	25	Water	530[b]	0.40[b]	4.3[b]	502	18.8	9.4

The data of propylene glycol alginate (PGA) and poly(acrylamide) (PAM) samples are given for comparison.

[a] Data of Sinquin et al. [8,30].

[b] Data of Volpert et al. [24].

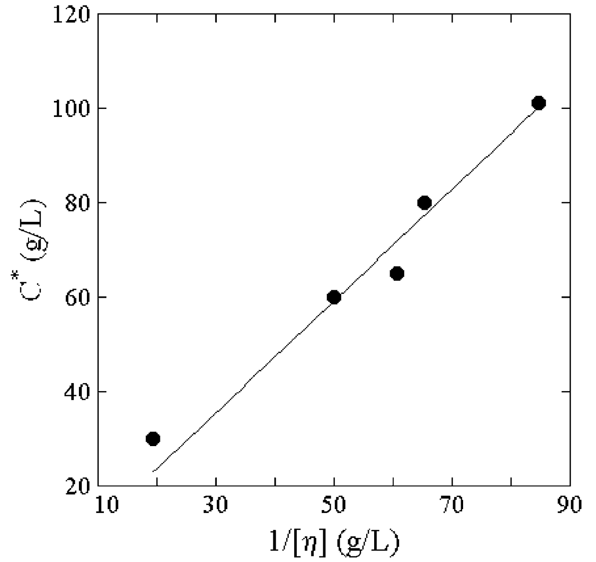


Fig. 1. Overlap concentrations of dextran samples (T10©, T40© and T500©) as a function of the inverse of their intrinsic viscosities, in water at various temperatures (25, 45 and 65 °C, see Table 2). The line corresponds to Eq. (3).

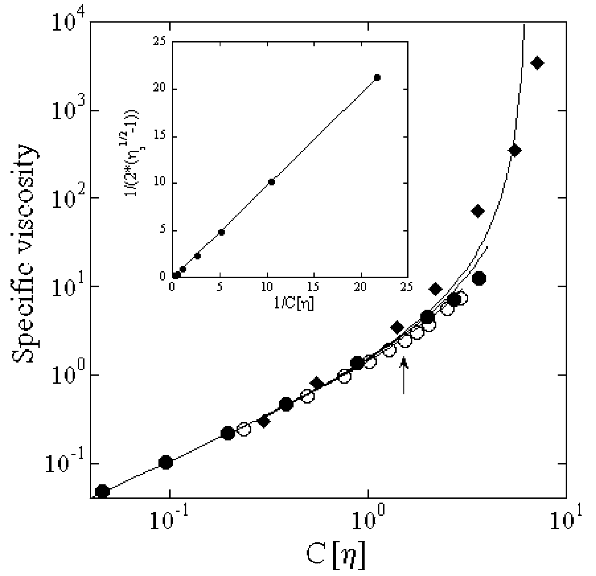


Fig. 2. Viscometric results obtained with unmodified dextran in water (T500©, ●), propylene glycol alginate in 5% NaCl (data of Sinquin et al. [8,30], ◆) and poly(acrylamide) in water (data of Volpert et al. [24], ○) at 25 °C. The lines represent curve fitting by Eq. (2). The arrow indicates the position of C^* for T500© sample. Inset: usual linear Fedors plot for T500© sample.

ity of Fedors equation in that domain. Moreover, the found values of $[\eta]$ are consistent with those derived from Huggins equation in the dilute domain. The linearization of Eq. (2) allows the determination of the concentration parameter, $C_{\max}$, for the various considered polymers. This concentration parameter, $C_{\max}$, increases proportionally to C^* and we observe the approximate relation: $C_{\max} \approx 5 \times C^*$. The results of Sinquin et al. [8] with propylene glycol alginate (PGA) as well as those of Volpert et al. [24] with aqueous solution of poly(acrylamide) (PAM, $\overline{M}_w = 2.5 \times 10^6$ g/mol) are similar to ours (Table 2). In the initial derivation of Fedors [13], $C_{\max}$ is analogous to ϕ_m, the maximum volume fraction to which solid spheres can pack in a suspension. At $C = C_{\max}$, the viscosity of the solution would be infinite. The overlap concentration, C^*, is directly related to the hydrodynamic volume of macromolecules assumed to occupy a spherical volume on average. Above C^*, the solution viscosity increases rapidly with concentration. So the link between the empirical parameter $C_{\max}$ and the experimental C^* seems justified, but there is no reason for a universal proportionality constant between the two. Considering the results of Ioan et al. [14] with solutions of poly(butyl methacrylate) in methyl ethyl ketone, we can deduce $C_{\max} \approx 20 \times C^*$. The same trend appears in the viscometric results of Papanagopoulos et al. [25] about solutions of poly(styrene) and poly(methyl methacrylate) in ethyl acetate. Applying Fedors equation to their results leads to the following relation: $C_{\max} \approx 6 \times C^*$. These series of results are consistent with the previous discussion and demonstrate that the empirical parameter $C_{\max}$ contained in the Fedors equation is dependent on the upper limit of the dilute regime and consequently on the hydrodynamic volume of the macromolecules for non-associative polymers.

As for the range of concentration covered by Eq. (2), it is clear that its validity is limited to $C < C_{\max}$. In fact, up to $C \times [\eta] = 3$, the experimental curves are conveniently depicted (Fig. 2) even if the limit of $C_{\max}$ would correspond to $C \times [\eta] \approx 6$. Interestingly, rheological studies of dextran solutions have shown that for $C \times [\eta] > 4$, the viscosity increases with polymer concentration following a power-law with an exponent of about 4 while for $C \times [\eta] \leqslant 4$, the exponent is only 1.5 [26–28]. As a result, we can conclude that Fedors equation is valid within the semi-dilute unentangled regime. In this domain, the assumption that polymer solution behaves like a suspension of spheres, as long as the viscosity is concerned, is correct. Nevertheless, when the entangled regime is reached, this simple picture is no longer correct. The establishment of entanglements depends on the polymer–solvent system considered. As a result, the proportionality constant between C^* and C_{max} should be system specific even if, for the various examples considered here, a value around 6 seems to be a good approximation.

3.2. Viscometric behaviour of amphiphilic dextran derivatives

The same kind of viscometric experiments was carried out for hydrophobically modified polysaccharides. These polymers were prepared by chemical modification of the T40© dextran sample (see Section 2). In a similar way, it is possible to determine the intrinsic viscosity ($[\eta]$ in mL/g), the Huggins coefficient (k_H) and the upper limit of the dilute concentration range (C^{ass} in g/L) for each polymer (Table 3). In the case of such polymers, k_H could be much higher than unity because of the increase of polymer–polymer interactions [4]. When the amount of grafted hydrocarbon groups is increased up to 38% in the DexC6 series, the k_H value also increases indicating the lowering of solvent quality. The same effect is observed when replacing C6 groups by C10 groups at a given degree of substitution. An increase of the ionic strength gives rise to a salting-out effect leading to a significant increase of k_H. With the dextran derivatives considered here, the variation of intrinsic viscosity is exactly the reverse as that of k_H.

The results were also analysed with Fedors formalism. As for unmodified polysaccharides, the intrinsic viscosity derived from Eq. (2) is close to that obtained with Eq. (1) in the dilute domain. The concentration parameter C_{max} appears to be related to the association concentration C^{ass} which is the upper limit of the dilute domain. For amphiphilic polysaccharides, we observe the relation $C_{max} \approx 2 \times C^{ass}$. Using the data of Sinquin et al. [8] as well as those of Volpert et al. [24], the same relation is found between C_{max} and C^{ass} (Fig. 3). Obviously no generalization is possible but the numerical relation found here could give a good approximation of C_{max} for solutions of amphiphilic polymers in water.

With amphiphilic polymers, Eq. (2) depicts conveniently the experimental points up to $C \times [\eta] \approx 2$ (Fig. 4). For higher concentrations, Eq. (2) greatly overestimates the viscosity of the solution. When using Eq. (2), the solution of amphiphilic polysaccharides is assimilated to a suspension of spheres. The associative behaviour is taken into account by the value of C_{max}, that is much lower than it would be for non-associative polymers with the same intrinsic viscosity. Since we established in the previous section that for non-associative polymers that C_{max} is proportional to $[\eta]^{-1}$ (i.e. to C^*), we can consider that, for associative polymers, $C_{max} \times [\eta]$ is a measure of the sticking effect coming from the hydrocarbon groups which leads to lower values of C_{max}. Consequently, the product $C_{max} \times [\eta]$

Table 3
Viscometric results with aqueous solutions of dextran derivatives at 25 °C (for symbols see text)

Polymer	Solvent	$[\eta]$ (mL/g), Eq. (1)	k_H, Eq. (1)	C^{ass} (g/L)	$[\eta]$ (mL/g), Eq. (2)
DexC6_{12}	Water	16.8	1.1	55	17.2
	0.1 M NaCl	10.9	4.2	35	12.2
DexC6_{21}	Water	9.2	2.7	54	9.7
DexC6_{38}	Water	8.0	3.7	50	8.6
DexC10_{11}	Water	8.1	7.0	38	9.5
PGA-C12-9[a]	0.05% NaCl	618[a]	0.5[a]	3.3[a]	–
	5% NaCl	268[a]	3.0[a]	3.5[a]	–
PGA-C14-9[a]	0.05% NaCl	583[a]	0.5[a]	2.6[a]	–
1DH1.9[b]	Water	330[b]	1.2[b]	2.6[b]	355
1DH3.2[b]	Water	175[b]	4.7[b]	1.8[b]	215

The modified dextrans were obtained from T40© dextran sample (Table 2). The data about hydrophobically modified propylene glycol alginate (PGA) and amphiphilic copolymers of acrylamide are given for comparison.

[a] Data of Sinquin et al. [8,30].

[b] Data of Volpert et al. [24]. The two copolymers were prepared by aqueous micellar copolymerization of acrylamide and *N*,*N*-dihexylacrylamide. Both copolymers contain 1 mol% of *N*,*N*-dihexylacrylamide and have a weight-average molecular weight close to 2×10^6 g/mol. The sequence distribution of *N*,*N*-dihexylacrylamide is different with longer sequences of hydrophobic monomer in 1DH3.2 as compared to 1DH1.9.

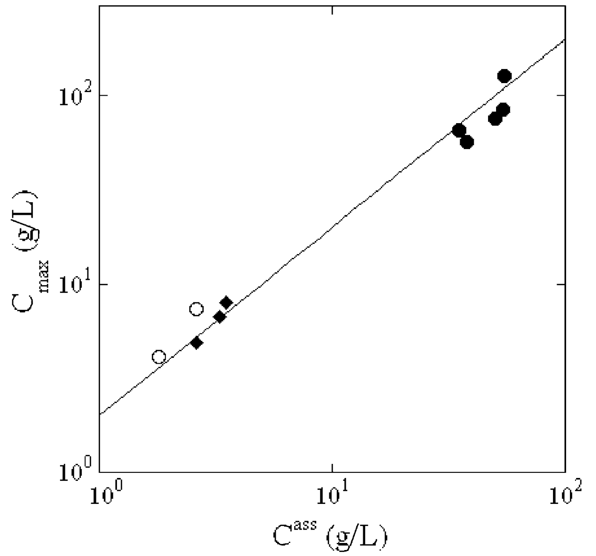


Fig. 3. Empirical parameter of Fedors equation, C_{max}, as a function of the upper limit of dilute domain, C^{ass}, determined by viscometric measurements. Hydrophobically modified dextrans in water (●), hydrophobically modified propylene glycol alginate in brine (data of Sinquin et al. [8,30], ◆) and amphiphilic copolymers of acrylamide in water (data of Volpert et al. [24], ○) at 25 °C. The line is the curve giving $C_{max} = 2 \times C^{ass}$.

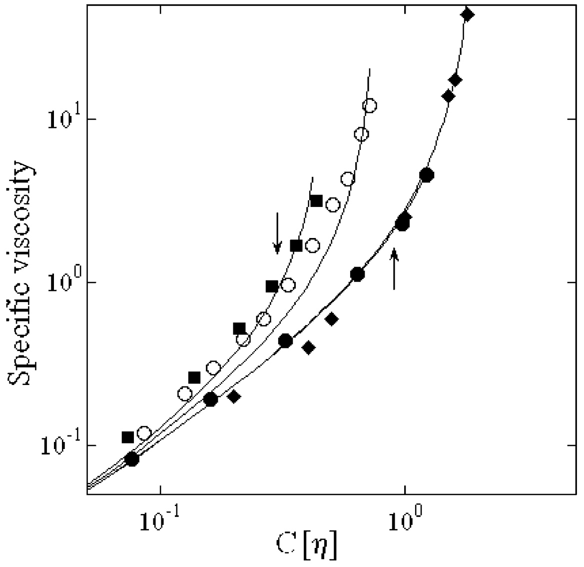


Fig. 4. Specific viscosity of aqueous solutions of amphiphilic polymers as a function of overlap parameter ($C[\eta]$) at 25 °C. DexC6_{12} (●) and DexC10_{11} (■) in water. Hydrophobically modified propylene glycol alginate PGA-C12-9 in 5% NaCl (data of Sinquin et al. [8,30]) (◆). Amphiphilic copolymer of acrylamide 1DH3.2 in water (data of Volpert et al. [24]) (○). Arrows indicate the position of C^{ass} for DexC6_{12} and DexC10_{11}. The lines represent curve fitting by Eq. (2).

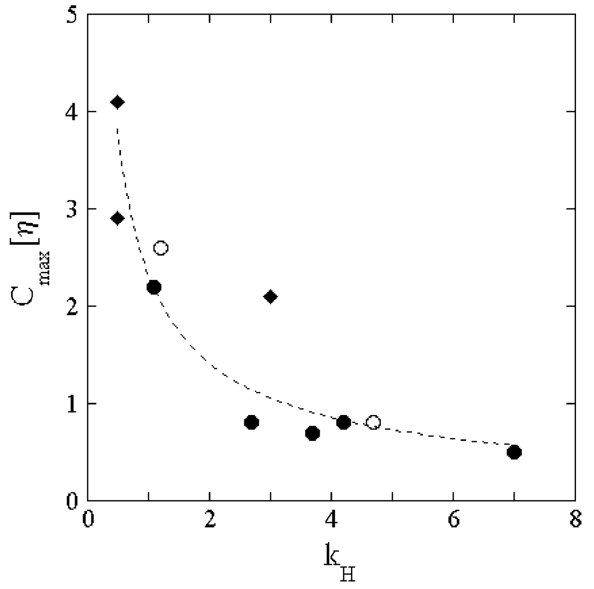


Fig. 5. Variation of the product $C_{max} \times [\eta]$ deduced from Fedors equation with the Huggins coefficient. Hydrophobically modified dextrans in water (●), hydrophobically modified propylene glycol alginate in brine (data of Sinquin et al. [8,30], ◆) and amphiphilic copolymers of acrylamide in water (data of Volpert et al. [24], ○) at 25 °C. Dotted line is a guide for the eyes.

should be a decreasing function of k_H. Indeed this trend is observed and the variation is similar for the three families of amphiphilic polymers considered here (Fig. 5).

Nevertheless, for concentrations exceeding significantly C^{ass}, large aggregates start to form in the solution and Eq. (2) is no longer followed since this representation of "sticking spheres" is not adequate.

In the case of our experiments which were carried out in a capillary viscometer, the shear rate is not precisely defined. Nevertheless, the data concerning hydrophobically modified PGA [8] and amphiphilic copolymers of acrylamide [24] have been obtained at low shear rate (0.06 s^{-1} and 10 s^{-1} respectively).

Although previous work has shown that Fedors equation could be applied to dilute solutions of amphiphilic polymers [20] as well as to moderately concentrated polymer solutions in oil [29], this is, to our knowledge, the first example of application of Fedors equation to a part of the semi-dilute domain for aqueous solutions of associative polymers, covering several decades of viscosity.

4. Conclusion

A family of neutral amphiphilic polysaccharides has been prepared using dextran. The solution behaviour of the unmodified and modified polysaccharides has been examined through the viscometric properties of their aqueous solutions.

The overall viscosity behaviour (dilute and first part of semi-dilute domain) is described using the equation proposed by Fedors which contains a concentration parameter. For both native and modified dextran samples, the equation of Fedors has been shown to give the same intrinsic viscosity value as the Huggins equation applied in the dilute domain. In the semi-dilute domain, Fedors equation gives correct value up to $C \times [\eta] = 3$ for native polysaccharides and 1 for hydrophobically modified dextrans. The interdependence between Fedors parameter and usual viscometric parameters (intrinsic viscosity and Huggins coefficient) has been precised for native and hydrophobically modified polysaccharides. The numerical relations found have been shown to hold for aqueous solutions of other amphiphilic polymers with distinct chemical structures.

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