Aqueous Solutions of Native and Hydrophobically Modified Polysaccharides: Temperature Effect

A. Durand* and E. Dellacherie

Laboratoire de Chimie Physique Macromoléculaire, UMR CNRS−INPL 7568, Groupe ENSIC, BP 20451, 54001 Nancy Cedex, France

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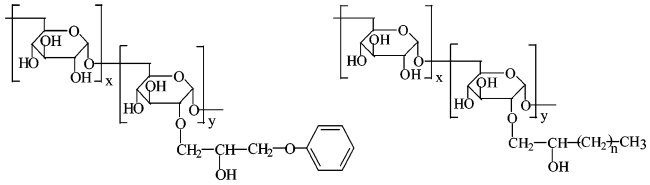
Amphiphilic polysaccharides, obtained by the attachment of various hydrocarbon groups onto dextran, are studied in aqueous solutions. The viscosity of their aqueous solutions is examined as a function of concentration and temperature in the range 25−65 °C. Varying polymer concentration, viscosity follows a polynomial development of Huggins equation in which the coefficients can be calculated from the Huggins constant determined in the dilute domain (Matsuoka−Cowman equation). For all polymers, the solution viscosity follows an Arrhenius-like variation with temperature. The activation energy of the aqueous solutions is determined as a function of polymer concentration and structural characteristics (nature and amount of grafted hydrocarbon groups). The variation of activation energy with polymer concentration is shown to be consistent with predictions based on the Matsuoka−Cowman equation combined with the equation of Andrade. This conclusion is extended to other polysaccharides using data from the literature.

Introduction

Polymeric surfactants derived from renewable resources have attracted increasing interest in the past 20 years. Polysaccharides are an important class of natural products used as raw materials for the preparation of amphiphilic macromolecules. Even if the bacterial production of amphiphilic polysaccharides has been known for more than 20 years,[1] the chemical modification of native polysaccharides remains a widely used method of synthesis. This method allows for control of the chemical characteristics of the polymers and, thus, their surface active properties. Since the pioneering work of Landoll dealing with cellulose ethers,[2] many polysaccharides have been hydrophobically modified. The applications of the obtained polymers extended to various fields like rheology modifiers,[3,4] emulsion stabilizers,[5−7] or polymeric surfactants for miniemulsion polymerization.[8]

There have been several studies about the variation of the viscosity of aqueous solutions of polysaccharides with temperature.[9−20] Nevertheless, no unified approach has been attempted and each study focused on one polysaccharide. As for amphiphilic polysaccharides, although their solution properties have been largely examined, the effect of temperature on the solution viscosity is much less considered.[15] Nevertheless, some of their applications require temperatures like 70−80 °C and their solution behavior can be significantly modified. The temperature sensitivity of cellulose ethers is well-known. In particular, the thermothickening behavior observed with some of them has been largely described.[21−24] Other inverse temperature behaviors have been briefly reported with derivatives of chitosan[25] or inulin[26] and even for xanthan gum.[27] Nevertheless, to the best of our knowledge, there is no detailed examination of the relation between the chemical structure of the polymers and the temperature sensitivity of their aqueous solutions.

Scheme 1. Chemical Structure of DexP_τ (Left) and DexCn_τ (Right, $n = 5$ or 9)[a]



[a] The substituent is represented on the more reactive position. No detailed study of the position of the modified hydroxyls has been performed up to now.

It is the aim of the present paper to examine the temperature sensitivity of the viscosity of aqueous solutions of amphiphilic polysaccharides derived from dextran, a neutral polysaccharide produced from sucrose by microorganisms. Dextran consists of α-D glucose units with a majority of α(1→6) glucosidic linkages between them. A few percent of α(1→3) glucosidic linkages provide side chains which appear to be short.[28] Hydrophobically modified dextran samples have been prepared following a synthetic procedure described elsewhere.[29−31] The percentage of modified glucose units is called the degree of modification and denoted τ: $\tau = 100 \times y/(x + y)$ (see Scheme 1). The polymers will be named DexP_τ, Dex$C6_\tau$ and Dex$C10_\tau$ according to the nature of the hydrocarbon groups attached: phenoxy (P), n-C_6H_{13}− (C6), or n-$C_{10}H_{21}$− (C10). The case of aqueous solutions of native dextran will be first considered. Then, the observed behaviors with chemically modified polysaccharides will be depicted quantitatively using semiempirical equations. Moreover, we will try to highlight the relation between the macroscopic behavior and the chemical structure of the polymeric surfactants.

Experimental Section

Materials. The native dextran was obtained from Pharmacia (Uppsala, Sweden). This dextran sample, T40, has been characterized by size exclusion chromatography: $\bar{M}_n = 26\,000$ g/mol, $\bar{M}_w = 40\,000$

* To whom correspondence should be addressed. Telephone: 33 (0)3 83 17 52 92. Fax: 33 (0)3 83 37 99 77. E-mail: alain.durand@ensic.inpl-nancy.fr.

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g/mol, and $I_p = 1.6$. The other chemicals were from Aldrich (St Quentin Fallavier, France) and were used as received. Milli-Q water was used for all the experiments.

Dextran Chemical Modification. Hydrophobic dextran derivatives were prepared by reacting dextran T40 with various epoxides: phenylglycidyl ether (P), 1,2-epoxyoctane (C6), and 1,2-epoxydodecane (C10). Details about the reaction procedure are given elsewhere.[29,30]

Briefly, 1 g of dextran is dissolved in dimethyl sulfoxide (DMSO) at 40 °C. Then, 5 mL of a 1 M aqueous solution tetrabutylammonium hydroxide is added, followed by the required amount of epoxide. The reaction is allowed to proceed at room temperature during several days according to the expected degree of substitution. The reaction medium was dialyzed against a water/ethanol mixture (50/50 v/v) and finally against pure water. The polymer was recovered by freeze-drying the final aqueous solution.

The percentage of modified glucose units was determined by ^{1}H NMR in deuterated dimethyl sulfoxide (Bruker spectrometer, 300 MHz).

Viscometry. Viscometric measurements with aqueous polymer solutions were carried-out using an Ostwald-type capillary viscometer (0.46 mm diameter). 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 required since we verified that the flow time was proportional to the kinematic viscosity. For experiments at different temperatures, the variation of the flow time of water was consistent with the literature data.[32] The densities of the polymer solutions were assumed to be identical to that of pure water within the concentration range explored (up to 80 g/L).

Results

Variation of Solution Viscosity with Polymer Concentration. In this section, the influence of polymer concentration on solution viscosity will be considered, at three different temperatures: 25, 45, and 65 °C.

Native Dextran Solutions. In the dilute domain, the well-known Huggins equation (eq 1) is generally followed by all polymers, provided that electrostatic repulsions are negligible.

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

In eq 1, η and η_s are the viscosity of the solution and of the solvent (Pa·s), respectively, η_{red} is the reduced viscosity of the solution (L/g), η_{sp} is the specific viscosity of the solution, 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. The upper limit of the dilute domain is generally reached for $C[\eta] \approx 1$[19,33−35] for a polymer concentration noted C^* and called the overlap concentration ($C[\eta]$ is the overlap parameter).

For higher concentrations, the variation of the specific viscosity with polymer concentration becomes sharper because of coil overlap and eq 1 is no longer followed.

Some authors determined power-law relations within limited ranges of concentration: dilute, semidilute, unentangled, ... Thus, the overall viscosity-concentration curve is depicted by two or three successive equations.[19,36−38]

Alternatively eq 1 can be expanded by a third term which accounts for overlaps and entanglements (eq 2).

$$\eta_{sp} = C[\eta](1 + k_H C[\eta] + AC[\eta]^B) \quad (2)$$

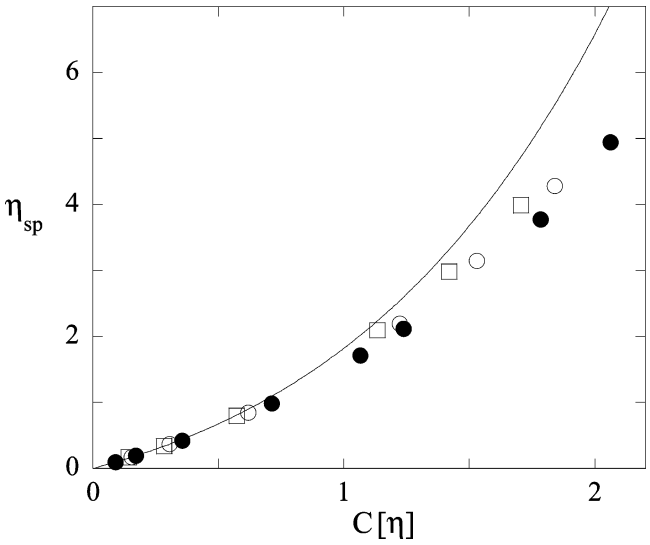

Figure 1. Specific viscosity of dextran T40 aqueous solutions as a function of overlap parameter, at various temperatures: (●) 25 °C; (○) 45 °C; (□) 65 °C. The line is the calculated curve with eq 3 and $k_H = 0.6$.

In eq 2, A and B are experimental coefficients. Generally, B is equal to 3 or more.[27,39−42]

More recently, a polynomial expansion of Huggins equation was introduced, in which all the coefficients are expressed as a function of k_H.[43−46] The Matsuoka−Cowman equation has the form:

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

In eq 3, $k_1 = k_H$, $k_2 = (k_1)^2/2!$, $k_3 = (k_1)^3/3!$ ...

With aqueous dextran solutions, changing temperature in the range 25−65°C has almost no effect on the curve η_{sp} vs C (Figure 1). This is a consequence of the relative invariance of k_H with temperature. Within that temperature range, k_H remains close to 0.6.[33] Only the intrinsic viscosity varies with temperature so the shape of curve is not modified. A similar behavior has been reported for chitosan.[11] Previous studies have shown that the shape of the curve in the semidilute domain ($C[\eta] > 1$) is particularly sensitive to branching of dextran chains.[34] Nevertheless, in that work, we will limit to one dextran sample as starting material. Moreover, we previously showed that the viscometric behavior of the T10, T40, and T500 samples were superimposable.[30]

Amphiphilic Dextran Derivatives. The introduction of hydrocarbon units within the polysaccharide chains induces the establishment of supplementary interactions because of the so-called hydrophobicity of these groups. For low concentrations (i.e., in the dilute domain), intramolecular interactions take place, leading to a contraction of the macromolecules and even to the formation of aggregates combining several macromolecules.[30] Moreover, because of the lower affinity between macromolecules and the solvent, the Huggins constant is higher than for the native polysaccharide (Table 1). Provided that the polymer concentration is enough (i.e., in the semidilute domain), intermolecular interactions settle and result in significantly higher solution viscosities as compared to the solutions of the unmodified polysaccharide.[12] With highly modified polymers (or polymers modified with highly hydrophobic groups), intramolecular interactions remain significant even in the semidilute domain and sometimes limit the thickening behavior.[2,30,47] The transition between dilute and semidilute domains occurs for overlap parameters much lower than unity (contrary to native

Table 1. Viscometric Characteristics of Amphiphilic Dextrans in Water at Various Temperatures (for Symbols See Text)

polymer	temp (°C)	$[\eta]$ (mL/g)	k_H[a]	C^{assn}(L/g)	$C^{assn}[\eta]$	k_1[b]
$DexP_{17}$	25	14.5	1.4	n.d.	n.d.	1.0
$DexP_{33}$	25	10.1	3.2	n.d.	n.d.	3.1
$DexC6_{12}$	25	16.8	1.1	55	0.9	1.1
	45	10.1	4.0	38	0.4	2.3
	65	9.9	3.5	41	0.4	2.5
$DexC6_{38}$	25	8.0	3.7	48	0.4	4.0
	45	8.0	2.8	55	0.4	3.1
$DexC10_{11}$	25	8.1	7.0	38	0.3	4.8
	45	8.8	4.6	31	0.3	3.6
$DexC10_{31}$	25	11.2	0.3	33	0.4	0.7

[a] Huggins constant obtained with the results of the dilute domain. [b] Parameter of eq 3 obtained by curve fitting over the whole concentration range.

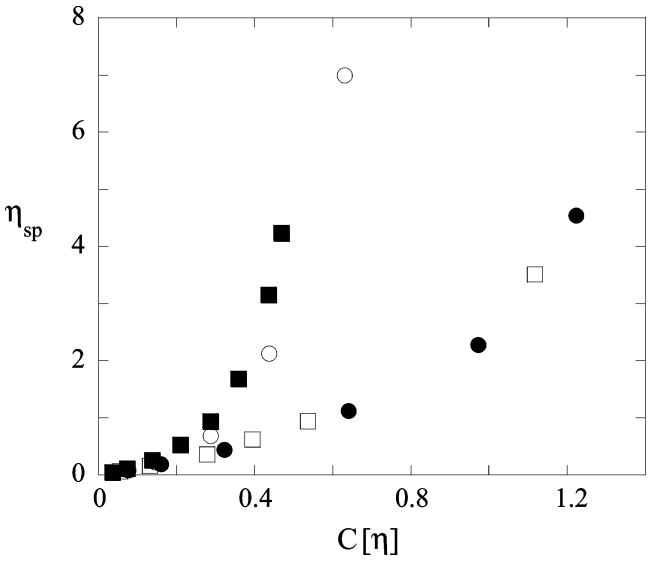

Figure 2. Specific viscosity of dextran derivatives aqueous solutions as a function of overlap parameter at 25 °C: (●) $DexC6_{12}$; (○) $DexC6_{38}$; (□) $DexP_{17}$; (■) $DexC10_{11}$.

polysaccharides). For sufficiently modified polymers it can occur at $C[\eta] \approx 0.4$ (Table 1). The concentration at the upper limit of the dilute domain will be denoted C^{assn}.

The polysaccharides modified with phenoxy and C6 groups give very similar viscometric results over the whole concentration range. On the contrary, when C10 groups are attached to dextran, the viscosity increase is sharper (Figure 2). This can be attributed to the higher hydrophobicity of the C10 groups as compared to phenoxy and C6 ones.

The influence of temperature on the viscometric characteristics was examined between 25 and 65 °C (Table 1). According to the chemical structure of dextran derivatives, two different trends are evidenced. For $DexC6_{12}$, higher temperatures lead to a sharper viscosifying effect. Since the degree is not very high and the hydrocarbon groups are only C6, the intermolecular associations are favored by higher temperatures since the solvent quality is decreased. A similar effect is observed when the ionic strength is increased.[30] For higher degrees of substitution or with more hydrophobic substituents, the reverse effect is observed. Intramolecular associations are probably more significant for $DexC6_{38}$ and $DexC10_{11}$ than for $DexC6_{12}$. As a result, the main effect of increasing temperature is to reinforce intramolecular associations which limit the possibility of establishment of intermolecular ones (which contribute to the viscosity increase). Even if intramolecular associations are also reinforced by higher

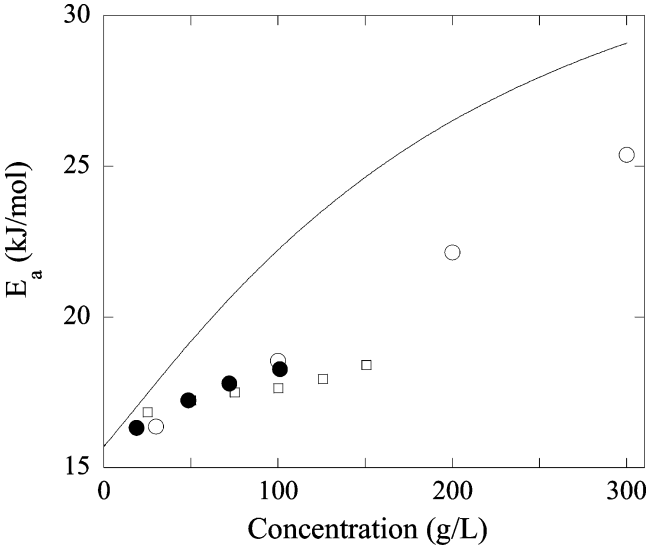

Figure 3. Activation energy of aqueous solutions as a function of solute concentration: (●) T40; (○) T70, data of Phillies et al.;[13] (□) glucose, data of Vázquez Uña et al.[54] The line is the calculated curve for dextran, using eq 5.

temperatures with $DexC6_{12}$ (the intrinsic viscosity is decreased), their impact is much more limited and the overall effect is to strengthen intermolecular associations. Nevertheless, because of the strong decrease of intrinsic viscosity, no thermothickening is observed and the viscosity of the solutions decreases with temperature (see the next section). Thermothickening effect has been reported for acrylamide copolymers containing low amounts of fluorocarbon acrylate units (less than 1 mol %).[47,48] In that case, the presence of hydrophilic spacers was shown to increase the thermothickening effect. Our results are consistent with the conclusions of the authors about the importance of maintaining the hydrophobic groups available for the establishment of intermolecular associations. These amphiphilic copolymers combined low content of hydrophobic units and the presence of hydrophilic spacers, contrary to the dextran derivatives considered here.

Variation of Solution Viscosity with Temperature. This section is devoted to the influence of temperature on the viscosity of polymer solutions in the range 25−65 °C.

Native Dextran Solutions. The viscosity of a native polysaccharide solution generally varies with temperature following a relation similar to that of usual liquids:

$$\eta = A\, e^{E_a/RT} \qquad (4)$$

In eq 4, η is the viscosity of the polymer solution (Pa·s), A is a preexponential factor (Pa·s), R is the gas constant (8.314 J/K.mol), T is the thermodynamic temperature (K), and E_a is the activation energy (J/mol). This relation has been initially introduced by Andrade[49,50] for simple liquids and has been extended later to native polysaccharide solutions.[15,37,51−53] The activation energy depends on shear rate, polymer concentration and polymer molecular characteristics. Here, we will focus on the effect of polymer concentration.

Equation 4 holds for dextran solutions and the activation energy increases with polymer concentration following a roughly linear variation up to 300 g/L (Figure 3). The found values are consistent with those deduced from the results of Phillies et al.[13] which cover a range of polymer concentration higher than ours (between 100 and 300 g/L). On the same graph, we reported, for comparison, the activation energies found for glucose solutions covering the same range of concentrations,

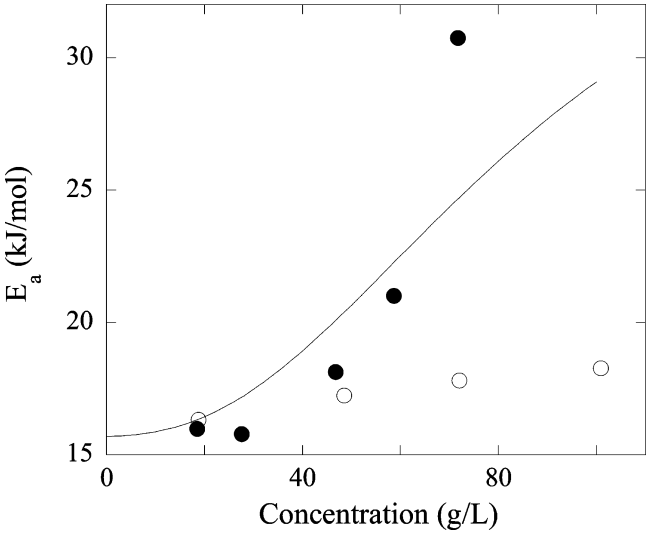

Figure 4. Activation energy of aqueous solutions as a function of polymer concentration: (●) $DexC6_{38}$; (○) T40. The line is the calculated curve using eq 5.

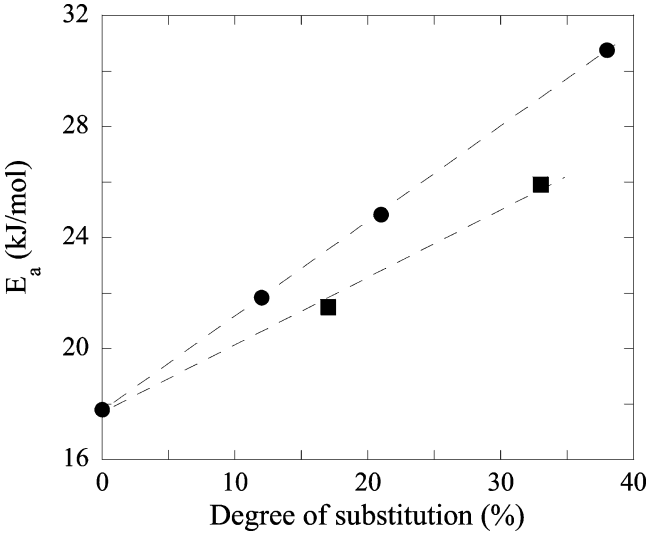

Figure 5. Activation energy of modified dextran aqueous solutions ($C \approx 75$ g/L) as a function of the degree of substitution: (●) $DexC6_\tau$; (■) $DexP_\tau$.

using the results of Vázquez Uña et al.[54] (for kinematic viscosities) and Comensaña et al.[55] (for densities). In the case of glucose solutions, we observe a slight increase of E_a with sugar concentration. It is clear that the activation energy of polysaccharide solutions increases much more sharply with concentration than that of simple sugar solutions. This is a consequence of the macromolecular structure involving permanent links between the repeat units.

Hydrophobically Modified Dextrans. The same kind of experiments was conducted with aqueous solutions of hydrophobically modified dextran samples. For all the solutions, the viscosity decreases with an increase in temperature according to eq 4. The activation energy depends strongly on polymer concentration and, for sufficiently high concentrations, it becomes much higher than that of the native dextran solutions (Figure 4). Moreover, the concentration above which the difference with the native dextran solutions becomes significant is close to the upper limit of the dilute domain, C^{assn} (see previous section). So the sharp increase of the activation energy starts approximately at the same concentration as the establishment of intermolecular associations.

Increasing the degree of substitution of dextran, at a given polymer concentration, brings about a significant increase of the activation energy, with a quasi-linear evolution (Figure 5). At a given degree of substitution (around 33%), the activation energy varies slightly with the nature of the hydrocarbon groups attached to polysaccharide (Table 2). This is very different from what has been reported in the case of telechelic oligomers.[56,57] Nevertheless, for chemically modified chitosan samples, it has been shown that the variation of the activation energy, obtained by rheological measurements, with concentration and nature of hydrocarbon groups is rather complex.[12] The effect of hydrocarbon groups nature in statistically modified polymers differs strongly from that observed for telechelic oligomers.

For associative polymers, the temperature effect on solution viscosity is related to three phenomena: the dissociation of the hydrocarbon groups from the associative junctions, the variation of the effective junction density (i.e., the proportion of intermolecular associations) and the increase of thermal vibrations.[58] As a result, the use of eq 4 should be considered as an approximation since we have no estimation of the effective junction density. Rheological measurements are necessary to determine the three contributions to the variation of viscosity and finally relate the activation energy to the energy of dissociation of hydrocarbon groups from intermolecular associations.[58]

Table 2. Activation Energy of Aqueous Solutions of Modified Dextran Samples with Various Hydrocarbon Groups

polymer	C (g/L)	E_a (kJ/mol)
$DexP_{33}$	73	25.9
$DexC6_{38}$	79	30.8
$DexC10_{31}$	73	20.4

From our experiments, we have shown previously that $DexC10_{31}$ exhibit a viscosifying behavior much less important than $DexC6_{38}$, which can be explained by intramolecular interactions giving dense aggregates with less hydrocarbon groups available for associative junctions.[30] This could explain why the activation energy of the $DexC10_{31}$ solution is below than of $DexC6_{38}$ solution. On the contrary, for the $DexC6_\tau$ and $DexP_\tau$ polymer series, an increase of the substitution degree essentially gives rise to an increase in the number of associative junctions (at least up to 38%) and consequently to an increase of the activation energy (Figure 5). This picture is also consistent with the variation of the Huggins constant (Table 1).

Discussion

Variation of Solution Viscosity with Polymer Concentration. For native dextran, the calculated curve given by eq 3 depicts conveniently the experimental points (Figure 1). Equation 3 holds for many other polysaccharides: dextran,[36,59] pullulan,[60] chitosan,[11] guar,[19,37] xanthan,[27] and hyaluronate[46] (Figure 6). The range of validity of eq 3 appears to be over three decades, on the basis of the experimental data available. Its main practical interest is that it gives a general expression involving only one experimental parameter (k_H) that is determined in the dilute domain. Moreover, a theoretical basis has been proposed for eq 3.[45] The expression in the brackets was interpreted as resulting from the overlap of several hydrodynamic spheres (2, 3, 4, ...) corresponding to the macromolecules. The infinite number of terms in the brackets offers the possibility of an overlap between all the molecules. Nevertheless, a more realistic representation leads to limit the mathematical development to four terms, which correspond to interactions between a maximum of four neighboring macromolecules.[45]

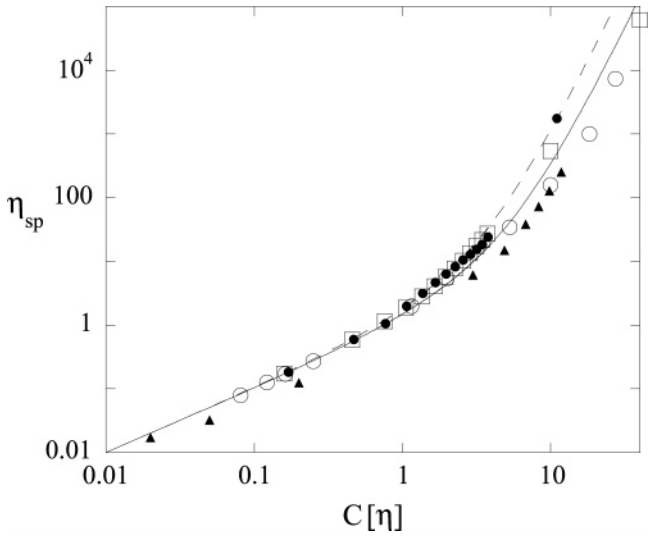

Figure 6. Specific viscosity of polysaccharide aqueous solutions as a function of overlap parameter: (□) xanthan gum in 0.1 M NaCl ($k_H \approx 0.6$), data of Arendt et al.;[27] (●) guar gum in water ($k_H \approx 0.4$), data of Launay et al.;[19] (▲) pullulan in water, data of Lazaridou et al.;[60] (○) chitosan in 0.3 M AcOH/0.05 M AcONa, data of Desbrieres.[11] The lines are the calculated curves using eq 3 and $k_H = 0.4$ (−) or $k_H = 0.6$ (- -).

In the case of hydrophobically modified polysaccharides, eq 3 was shown to depict conveniently the zero-shear viscosity. Moreover, the value of k_1 appears to be close to that of the Huggins constant k_H, even when it becomes much higher than unity.[59] For all the experiments carried-out in the present study, the values of k_1 found by fitting the curves on the overall concentration range are comprised between $0.8k_H$ and k_H (Table 1). For Huggins constants higher than 3, eq 3 tends to overestimate the specific viscosity so that the k_1 value, obtained by direct curve fitting, gets close to $0.8k_H$.

As a result, in a limited range of concentration, the viscosifying behavior of amphiphilic dextrans can be accounted for by the higher value of k_H which results from the increased tendency of interaction between the macromolecules and using eq 3 to take into account the effect of polymer concentration.

Variation of Solution Viscosity with Temperature. Assuming that the viscosity of polysaccharide solutions follows eq 3 (previous section) and that the influence of temperature is given by eq 4, it is possible to derive an expression for the activation energy of the solution:

$$E_a = E_{a,s} + R\left(\frac{T_1 T_2}{T_1 - T_2}\right) \ln \left[\frac{1 + C[\eta]_2 (1 + k_{1_2} C[\eta]_2 + k_{2_2} (C[\eta]_2)^2 + k_{3_2} (C[\eta]_2)^3 + k_{4_2} (C[\eta]_2)^4)}{1 + C[\eta]_1 (1 + k_{1_1} C[\eta]_1 + k_{2_1} (C[\eta]_1)^2 + k_{3_1} (C[\eta]_1)^3 + k_{4_1} (C[\eta]_1)^4)}\right] \quad (5)$$

In eq 5, T_1 and T_2 are the temperatures between which the variation of solution viscosity is examined, $E_{a,s}$ is the activation energy accounting for the variation of solvent viscosity in the same interval, $[\eta]_1$, $[\eta]_2$, k_{i_1} and k_{i_2} are the polymer intrinsic viscosities and the coefficients of eq 3 ($i = 1-4$) at the two temperatures T_1 and T_2 (respectively).

The polymer intrinsic viscosity varies with temperature in a similar way as indicated by eq 4: $[\eta] = Be^{E_{a,int}/RT}$. This fact has been documented for aqueous and organic solutions of polysaccharides.[61] In the case of dextran, we find $E_{a,int} \approx 4$ kJ/mol. This value is consistent with the results of Güner,[62] which lead to $3.7 \leq E_{a,int} \leq 6.2$ kJ/mol for dextran samples having molecular weights between 40 000 and 500 000 g/mol. The results of Mohapatra et al.[63] give significantly higher values around 12 kJ/mol in a similar range of molecular weights. We do not have any explanation for that discrepancy. In the case of chitosan, a value close to 5 kJ/mol was reported by Desbrieres,[11] and for hyaluronate, the data of Fouissac et al.[64] give about 4 kJ/mol.

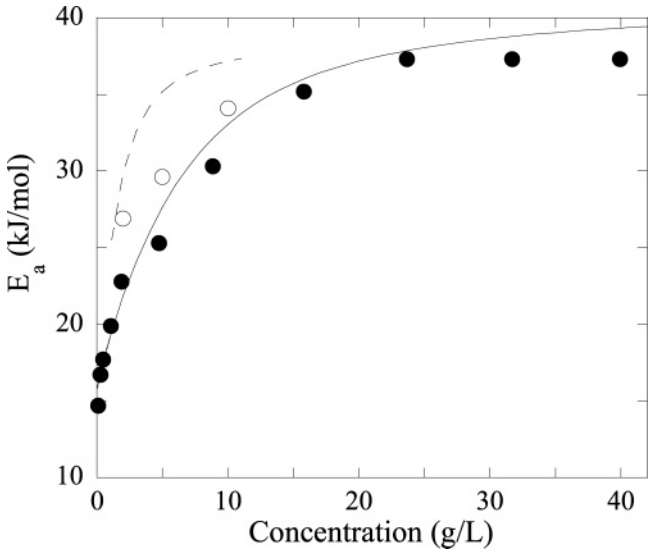

Figure 7. Activation energy of aqueous solutions as a function of polysaccharide concentration: (●) chitosan in 0.3M AcOH/0.05 M AcONa, data of Desbrieres;[11] (○) hyaluronate in 0.1 M NaCl, data of Fouissac et al.[64]

As for the activation energy corresponding to the solvent, with reference values,[32] we find $E_{a\ s} = 15.7$ kJ/mol within the explored temperature range.

The calculated values are fairly consistent with the experimental ones (Figure 3). Using values corresponding to chitosan aqueous solutions published by Desbrieres,[11] as well as values for hyaluronate solutions calculated from the results of Fouissac et al.,[64] we show that eq 5 gives values rather consistent with experiments (Figure 7). The strong difference between the activation energies found for dextran solutions and those corresponding to chitosan and hyaluronate solutions, is simply explained by the much higher intrinsic viscosities of the last two polysaccharides as compared with dextran. At a given concentration, the overlap between macromolecules is much higher in the case of chitosan and hyaluronate, than for dextran (for the considered samples). Cowman et al.[46,65] mentioned that the temperature dependence of hyaluronate solutions was consistent with eq 3. We demonstrate here that this equation is rather general for polysaccharides.

We can imagine that eq 5 could be generalized to polymers in good solvent since eq 3 has been shown to hold in numerous cases. Nevertheless more data are required to ascertain critically this assumption. This would be an efficient way to easily estimate the activation energy of polymer solutions. Obviously, eq 3 is valid only for solutions in which electrostatic interactions can be ignored (neutral polysaccharide or high enough ionic strength).

We now attempt to depict the temperature effect on solution viscosity of amphiphilic dextran derivatives using eq 5. The latter include both the variation of k_H (i.e., the variation of hydrophobic effect with temperature) and that of the intrinsic viscosity (i.e., the balance between intramolecular aggregation and solvent hydration). So a semiquantitative prediction of the

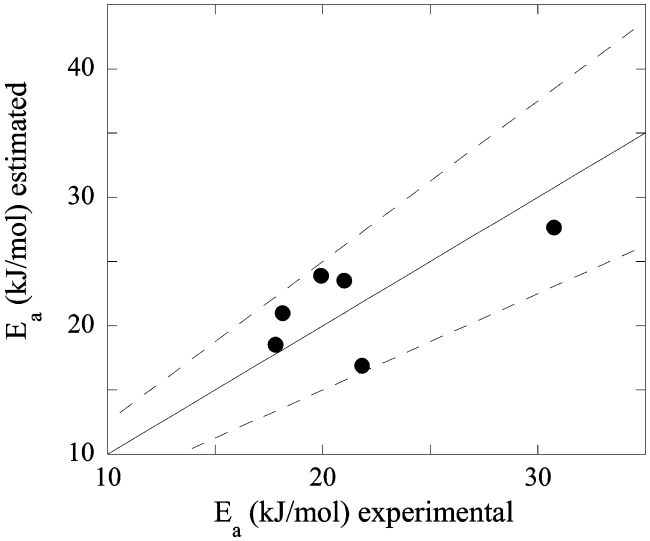

Figure 8. Estimated activation energy as a function of the experimental value for various modified dextran solutions in water. The lines represent the curves: $E_{a\ est.} = E_{a\ exp.}$ (−), $E_{a\ est.} = 0.75 \times E_{a\ exp.}$ (- -) and $E_{a\ est.} = 1.25 \times E_{a\ exp.}$ (- -).

temperature effect could be expected in that way. For $DexC6_{38}$ solutions, the experimental variation of E_a with polymer concentration is approximately depicted by the calculated values (Figure 4). Moreover, the calculated activation energies for various polymer solutions are ±25% the experimental values (Figure 8).

As a result, we can conclude that the temperature effect on the aqueous solutions of amphiphilic dextrans is consistent with eqs 3 and 5. This gives a first semiquantitative way to estimate activation energies of aqueous solutions of amphiphilic polysaccharides. Nevertheless, it is clear that more experimental data are necessary to examine how general are the results presented in that section.

Conclusion

The present work was dedicated to the effect of temperature on the viscometric characteristics of amphiphilic polysaccharides derived from dextran. An increase in temperature appears to lower solvent quality and consequently to strengthen intermolecular and intramolecular associations. The balance between the two kinds of interactions depends significantly on the chemical structure of the modified dextrans. The influence of the degree of substitution and of the nature of hydrocarbon groups was examined. A polynomial extension of Huggins equation (Matsuoka−Cowman equation) was shown to depict conveniently the viscometric results for native and modified dextrans and at all temperatures and over the whole concentration range (dilute and semidilute domains). For all the polymer solutions, the viscosity decreased with temperature following a Arrhenius type equation. The activation energy varies with polymer structure and concentration. The activation energies determined experimentally in the 25−65°C temperature range are fairly consistent with the predictions based on the Matsuoka−Cowman equation either for native or for hydrophobically modified dextrans. These conclusions have been extended to other polysaccharides like chitosan or hyaluronan.

Amphiphilic dextrans will be used as polymeric stabilizers in various processes involving temperatures significantly above room temperature. The result obtained in that work will be useful for the understanding and the improvement of such processes.

Moreover, the results concerning the activation energy of polymer solutions could probably be extended to synthetic polymers and organic solvents. They give a basis for a more general work on that topic for which no general approach is currently available.

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