Transport Properties of Some Cationic Amphiphilic Polysaccharides: Effects of the Side-Chain Length and Solvent Polarity

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ABSTRACT: The transport properties of polyelectrolytes with N-alkyl-N,N-dimethyl-N-(2-hydroxypropyl)ammonium chloride pendent groups (alkyl = octyl, dodecyl, or cetyl) randomly distributed along a polysaccharide backbone (dextran) in solutions were studied with viscometry and conductometry. This investigation mainly considered the influence of the side-chain length and the solvent polarity on the polyelectrolyte behavior in salt-free aqueous solutions. The viscometric data indicated that all the copolymers exhibited polyelectrolyte behavior, and they were plotted in terms of the Rao equation. The viscosity of the polycation with dodecyl as alkyl substituent was also measured in solvent mixtures of water and methanol. The conductometric behavior of these cationic polysaccharides was found to be influenced by the alkyl side-chain length and the solvent polarity. A nonlinear dependence of the equivalent conductivity on the dielectric constant of the solvent was observed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 3031–3038, 2009

Key words: electrochemistry; polyelectrolytes; polysaccharides; solution properties; viscosity

INTRODUCTION

The synthesis and characterization of amphiphilic polymers, that is, polymers which contain both hydrophilic and hydrophobic structural components, have been the subject of fundamental and applied research for many years. Their behavior in aqueous solutions has attracted much interest because of their resemblance to biological macromolecules. On the other hand, they are suitable for many applications in various areas, including medicine, biotechnology, water and soil treatment, enhanced oil recovery, and latex paint technology.[1–5] This widely extended range of potential applications is a result of their tendency to undergo self-organization in aqueous environments to form well-defined assemblies because of intramolecular and/or intermolecular hydrophobic interactions.[6–11] Studies have included both neutral and charged polymers. Charged polymers, called *amphiphilic polyelectrolytes*, exhibit solution properties resulting from the competition between the hydrophobic and electrostatic interactions. Dilute solution properties of amphiphilic polyelectrolytes are influenced by many factors related to the molecular variables that are characteristic of the polymers chains (the chain length, charge density,

polyelectrolyte concentration, length and content of hydrophobic groups, and sequence distribution of charged groups and hydrophobic units along the polymer chain), the counterion nature (size and valence), and the medium properties (pH, temperature, and dielectric constant).[12–28] Increasing interest has now been focused on ionic polysaccharides, which present the advantage of being nontoxic and hence involved in many processes in molecular biology.[29] In this context, this work centers on the effects of the alkyl side-chain length and dielectric constant of the medium on the behavior of some ionic polysaccharides in salt-free aqueous solutions. The amphiphilic polyelectrolytes are new cationic polysaccharides based on a dextran with pendent quaternary ammonium groups [N-alkyl-N,N-dimethyl-N-(2-hydroxypropyl)ammonium chloride] randomly distributed along the polymer backbone (alkyl = octyl, dodecyl, or cetyl). Viscometric and electrolytic conductivity data are discussed. These polymers have been recently studied for their self-aggregation in water, but the aforementioned transport properties of their aqueous solutions were marginally evaluated.[11,30] These polyelectrolytes, with a very well established and controllable structure, are useful in probing the relationship between the molecular architecture and physicochemical properties. On the basis of viscometric and conductometric measurements, we attempted to obtain information on the balance of competing hydrophobic and
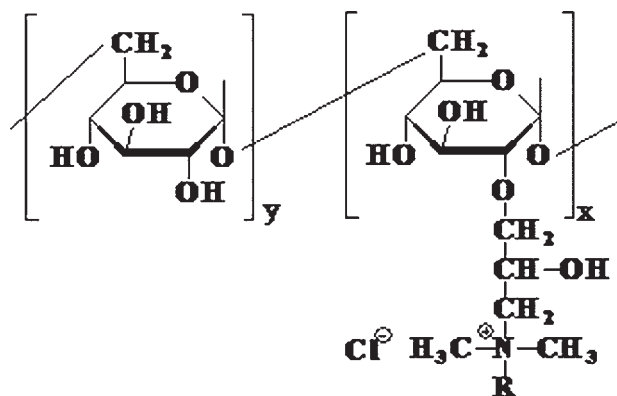
Scheme 1 General chemical structure of polycations based on dextran (D40-RX).

electrostatic interactions, which is primarily a function of the number of hydrophobes and charges in the polymer as well as the size of the hydrophobe. Moreover, the electrolytic conductivity is a property that is often used to determine the critical micellar concentration (cmc) of charged surfactants as well as the critical aggregation concentration (cac) of amphiphilic polyelectrolytes.[31–34] We undertook these experiments with the hope that the viscometric and conductometric measurements could give us more useful information about the behavior of these cationic polysaccharides in solution so that the proper cationic polysaccharide could be chosen for certain applications.

EXPERIMENTAL

Materials

Cationic polysaccharides with pendent quaternary ammonium groups were synthesized by the chemical modification of dextran samples (Sicomed S.A., Bucharest, Romania) with a weight-average molecular weight of 40,000 g/mol, as determined by capillary viscometry and static light scattering in aqueous solutions. The procedure for the synthesis of these polymers has been described elsewhere.[11] The reaction mixture was a perfect solution over the entire modification process, and no micellization of the reagents took place. These reaction condition allowed an even (statistical) distribution of the charged groups along the polysaccharide chains. The polymers were extensively purified by repeated precipitation and dialysis against 0.1N HCl and water and finally recovered as a white powder by lyophilization. The chemical structure, shown in Scheme 1, was proved by ^{1}H-NMR and elemental analysis. The polymer code is D40-RX, where D indicates dextran, 40 is the molar mass of the dextran (kg/mol), R is the substituent at the amino group, and X is equal to DS ± 2 mol%. DS is the degree of substitution and

is expressed as moles of amino groups per 100 glucopyranosidic units [i.e., DS = $100x/(x + y)$, where x and y are the molar fractions of substituted and unsubstituted glucosidic units, respectively].

The content of amino groups (DS) was determined from the nitrogen content (elemental analysis) and chloride-ion content (potentiometric titration with a 0.02N AgNO$_3$ aqueous solution). The values obtained by the two methods were in good agreement. Table I lists several properties of the cationic polymers.

Methods

Viscometric measurements of the polyelectrolyte solutions were carried out with an Ubbelohde viscometer with internal dilution at 25 ± 0.03°C; the viscometer provided reliability of the flow times with an accuracy of 0.03 s. Conductivity measurements were performed with an InoLab 1 conductometer (WTW GmbH, Weilheim, Germany) with a TetraCon 325 conductivity cell (cell constant = 0.1 cm^{-1}). The conductometer ensured direct-current electrical conductivity measurements, and the cell electrodes were made of platinum and coated with platinum black to minimize electrode polarization. All measurements were carried out at 20 ± 0.03°C under a nitrogen atmosphere. The temperature was adjusted by the use of a vessel with a jacket connected to a thermostat. The electrolytic conductivity of the pure solvents, which were carefully freed of dust by repeated filtration, ranged from 2 to 2.5 × 10^{-6} S/cm for water and from 1.5 to 2 × 10^{-6} S/cm for methanol. The dielectric constants of the water/methanol mixtures were obtained, with both the dielectric constant values for the pure solvents[35] and their mass fractions (w/w %) in the mixture taken

TABLE I
Characteristics of the Polycation Samples

Sample	Cl$_i$[a] (mequiv/g)	Quaternary amino groups (mol %)	b (nm)[b]	ξ (20°C water)[c]
D40-Oct35	1.27	35	1.47	0.48
D40-Dod35	1.32	35	1.47	0.48
D40-Cet35	0.91	35	1.47	0.48

[a] Cl$_i$ refers to chloride ion content.
[b] Average spacing between two vicinal ionized groups on the polyion. It is based on a repeating unit length of 0.515 nm for the D-glycopyranose unit.[52]
[c] ξ was calculated as follows: [53,54]

$$\xi = e^2/\varepsilon kTb$$

where e is the elemental charge, ε is the dielectric constant of the solvent, k is the Boltzmann constant, and T is the temperature (K).
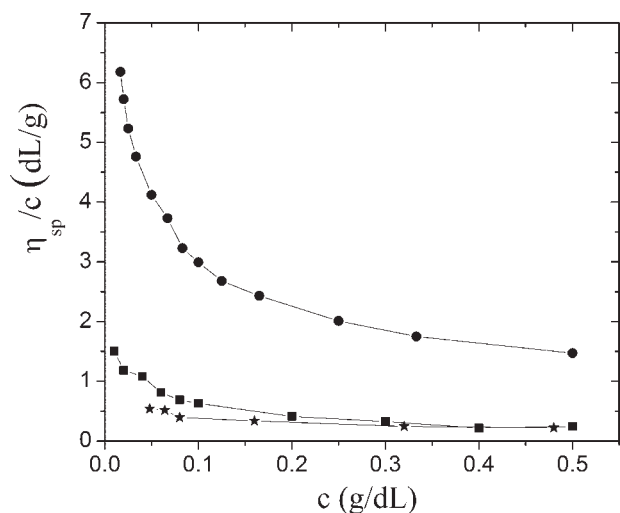
Figure 1 Dependence of η_{sp}/c on c at 25°C for (●) D40-Oct35, (■) D40-Dod35, and (★) D40-Cet35.

into account. The concentration of the stock solutions of the polycations [c (g/dL) and c_p (monomol/L)] was determined by potentiometric titration of the chloride counterion and from the solid content. In the case of polyelectrolyte solutions, the equivalent was related to one monovalently charged monomer unit, and the equivalent conductivity (Λ) was therefore given in S cm²/monomol. The different temperatures at which the measurements of the electrolytic conductivity (20°C) and the viscosity (25°C) were performed were not critical because the resulting variations of the structural, molecular, and medium parameters had an influence only within the experimental error range. Polymer solutions were made up in double-distilled water, water/methanol mixtures, and pure methanol. All viscosity and conductivity measurements were repeated at least twice to check the reliability of the data, which was within ±3%.

RESULTS AND DISCUSSION

Viscometric measurements

Figure 1 presents the variation of the reduced viscosity (η_{sp}/c) with the polymer concentration (c) in saltless aqueous solutions. The behavior of all the copolymers is that of typical polyelectrolytes, with an increase in the η_{sp}/c values upon a decrease in c due to both the intramolecular and intermolecular electrostatic interactions. Furthermore, the η_{sp}/c values at a constant value of c decrease as the hydrophobe chain length increases because the balance between electrostatic and hydrophobic interactions switches in favor of the latter. This results in increased chain contraction with an increase in the R chain length.

Next we present the behavior of D40-Dod35 in binary solvent mixtures of water and methanol (Fig. 2). A glance at this figure shows that D40-Dod35 presents polyelectrolyte behavior with all employed compositions of the mixed solvents; this means that the ionizable groups on the polymer side chain can dissociate in these solvents with a lower polarity. On the other hand, the greater η_{sp}/c values for the polyelectrolyte in mixtures of water and methanol reflect the greater solvation power of the mixed solvents for D40-Dod35 in comparison with the pure solvents. Among the mixed solvents, the 50 : 50 water/methanol mixture produces a higher viscosity, perhaps because it has the best balance of the good solvents for the polysaccharide backbone (water) and amphiphilic side chains (methanol).

Because of the upward concavity of the η_{sp}/c–c curves, it is not possible to extrapolate η_{sp}/c to the zero concentration to determine the intrinsic viscosity ([η]). This problem can be solved either through screening of charges by the addition of a low-molar-mass electrolyte or by means of empirical equations, such as the Fuoss equation[36] or Fedors equation[37] modified by Rao,[38] which is applicable for describing the viscosity of diluted to moderately concentrated neutral polymer solutions and relative viscosity (η_r) values of 1 to about 100. As the η_r values for all the samples under study lie in this range, the curves shown in Figures 1 and 2 were linearized with the Rao equation:

$$\frac{1}{2\left(\eta_r^{1/2} - 1\right)} = \frac{1}{[\eta]\, c} - \frac{a-1}{2.5} \tag{1}$$
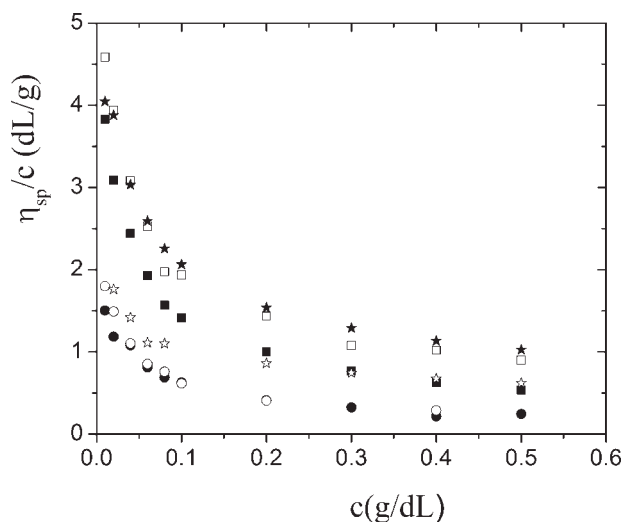

Figure 2 Dependence of η_{sp}/c on c for D40-Dod35 in water/methanol mixtures at 25°C: (●) water, (○) 90 : 10 water/methanol, (■) 60/40 water/methanol, (□) 50 : 50 water/methanol, (★) 40 : 60 water/methanol, and (☆) methanol.
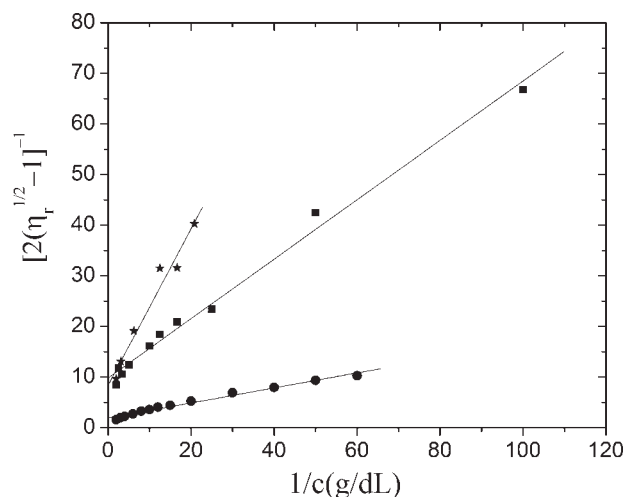
Figure 3 Representation of the viscosity data in terms of the Rao equation for (●) D40-Oct35, (■) D40-Dod35, and (★) D40-Cet35.

where a is a constant for a given polymer–solvent system. As can be observed in Figures 3 and 4, straight lines have been obtained for all polycations in both water and water/methanol mixtures, showing that the Rao equation is suitable for describing the viscometric behavior of these samples and estimating the $[\eta]$ values in salt-free solutions. The $[\eta]$ values so obtained can serve for a semiquantitative comparison of the viscometric behavior of salt-free polyelectrolyte solutions. The applicability of the Rao equation to describing the viscosity of polymer solutions has also been found for other polyelectrolytes.[39–42]

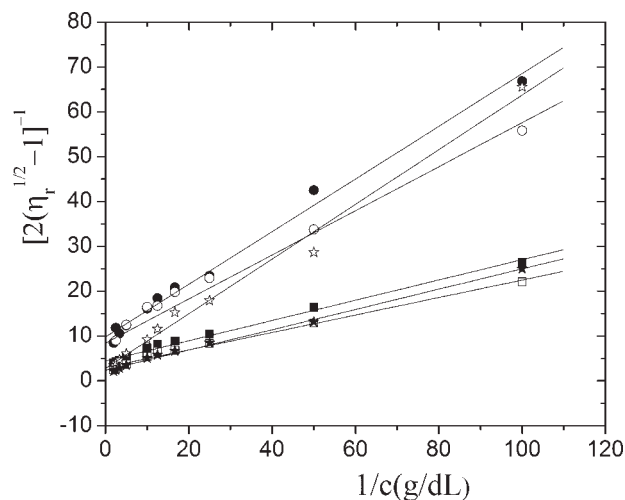It is a well-known fact that polyelectrolyte molecules are highly expanded in salt-free solutions, and

Figure 4 Representation of the viscosity data in terms of the Rao equation for D40-Dod 35 in water/methanol mixtures: (●) water, (○) 90 : 10 water/methanol, (■) 60/40 water/methanol, (□) 50 : 50 water/methanol, (★) 40 : 60 water/methanol, and (☆) methanol.

TABLE II
$[\eta]$, c^*, and R^* for Amphiphilic Polysaccharides in Water Solutions

Sample	$[\eta]_{Rao}$ (dL/g)	c^* [g/dL (10^2 monomol/L)]	R^*
D40-Oct35	6.71	0.15 (0.78)	0.992
D40-Dod35	1.70	0.587 (2.76)	0.995
D40-Cet35	0.65	1.54 (6.63)	0.98

R^* is the squared regression coefficient of linear fits to experimental data.

consequently, the overlap concentration (c^*), which is the limit between dilute and semidilute regimes, is very low in polyelectrolyte solutions.[43] The concentration range involved in the viscometric measurements (8.6×10^{-4} monomol/L $< c < 2 \times 10^{-2}$ monomol/L) may be considered to include c^*. We have roughly evaluated the c^* values as follows:[44]

$$c* = 1/[\eta] \qquad (2)$$

$[\eta]$ and c^* values of the cationic polysaccharides under study are summarized in Tables II and III.

The decrease in $[\eta]$ and the anticipated increase in the c^* values confirm the decrease in the hydrodynamic dimension of the macromolecular coils due to the intramolecular hydrophobic interactions. As shown in Table II, this effect is stronger as the side-chain length increases. Likewise, an increase in either the methanol or water content in the mixture leads to a decrease in the $[\eta]$ values as the solvent composition approaches that of the pure solvent (Table III). The estimation of c^* values helped us to set up the conductivity measurements to maintain them in the dilute domain.

TABLE III
$[\eta]$, c^*, and R^* for D40-Dod35 in Water/Methanol Mixtures

Water/methanol (%, w/w)	$[\eta]_{Rao}$ (dL/g)	c^* [g/dL (10^2 monomol/L)]	R^*
100/0	1.70	0.587 2.76	0.995
90/10	2,03	0.491 2.31	0.964
60/40	4.42	0.225 1.05	0.995
50/50	5.13	0.194 0.91	0.993
40/60	4.42	0.226 1.06	0.997
0/100	1.62	0.609 2.86	0.995

R^* is the squared regression coefficient of linear fits to experimental data.
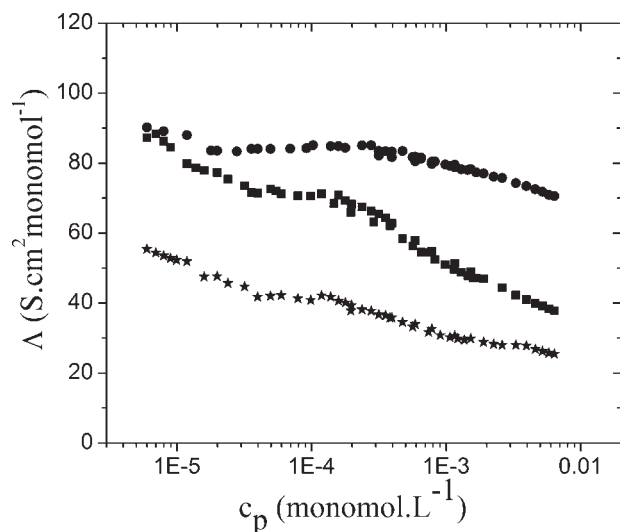
Figure 5 Dependence of Λ on c_p in H_2O at 20°C for (●) D40-Oct35, (■) D40-Dod35, and (★) D40-Cet35.

Conductivity measurements

The conductivity investigations were performed by the measurement of the specific conductivity as a function of the polymer concentration. The specific conductivity includes the contributions of counterions, co-ions, and polyions to the current transport and depends on both the number of ions per unit of volume and their mobility.[45] We have used the values of the specific conductivity to obtain the experimental Λ values of polyelectrolyte solutions according to ref. 46:

$$\Lambda = (\kappa - \kappa_0)/c_p = \Lambda^0 + \phi(c_p) \qquad (3)$$

where κ and κ_0 are the electrolytic conductivity of the solution and the solvent, respectively; c_p is the concentration of the polyelectrolyte solution; Λ^0 is the equivalent conductivity at infinite dilution; and $\phi(c_p)$ represents the effect of interionic interaction on the conductivity.

The experimental conductivity data in Figure 5 for the D40-RX copolymers in water emphasize the influence of the concentration on Λ of ionic polysaccharide solutions. Although the concentration effect on the conductometric behavior of the polyelectrolytes under study is not considered in detail in this article, some aspects are presented.

Thus, for all the investigated systems, the conductometric data show the usual behavior of polyelectrolytes with $\xi < \xi_{cr} = 1$ (ξ is the charge density parameter, and ξ_{cr} is the critical charge density parameter) when counterion condensation is not expected; that is, there is a linear increase in Λ values with dilution over almost the entire concentration range. One may further remark that some regions have different breaks, which suggest that

some associations are taking place in the system. More information in this respect can be obtained from the dependence of the specific conductivity on the polymer concentration [Fig. 6(a–f)].

The measurement of the specific conductivity is a conventional method of determining the cmc of surfactants; the cmc value can be obtained from the intersection of the tangent lines before and after a break in conductivity. Figure 6(a) shows a significant difference in the conductivity slopes over the entire c_p range; that is, the slopes decrease with increasing polymer hydrophobicity. By plotting the experimental data from Figure 6(a) in narrower concentration ranges [Fig. 6(b–f)], one can notice the presence of segments of different slopes, and the breaking points can be assigned to different degrees of amphiphilic polymer self-aggregation (generally called cac). The presence of several cac values is due to a less sharp and cooperative polymer self-aggregation process (in comparison with classical surfactants). This aggregation process sometimes stretches over several decades of polymer concentration.[11] In Table IV, the values of cac obtained by conductivity measurements are given as well as those obtained by fluorescence measurements.[11] These values sometimes fall in the same range of concentration; sometimes they differ by at least 1 order of magnitude (especially cac_1 for D40-Dod35 and D40-Cet35). The difference may be due to the fact that conductivity measurements are less sensitive than fluorescence ones; hence, cac may not be rigorously determined by the former measurements.

The occurrence of micelles in an ionic surfactant solution always results in a less rapid increase of the conductivity with the concentration, mainly because a large fraction of the counterions are bound to the micelle. The degree of counterion dissociation (α) can be calculated by Frahm's method as follows:[47]

$$\alpha = S_2/S_1 \qquad (4)$$

where S_2 and S_1 refer to the slopes of the conductance plot above and below cmc, respectively. In a similar way, we have calculated the fractions of counterions dissociated in different aggregation states of the amphiphilic polyelectrolytes. The results are also given in Table IV. In the case of the polymers, reference slope S_1 does not describe the complete dissociation state of counterions, as for classical surfactants, but instead describes an intermediate dissociation state related to the macromolecular nature of the polyion, which is able to bind counterions regardless of the association state of the hydrophobic side chains.[32]

An analysis of the curves in Figures 5 and 6 also indicates that for the same charge density and concentration, Λ and the specific conductivity decrease
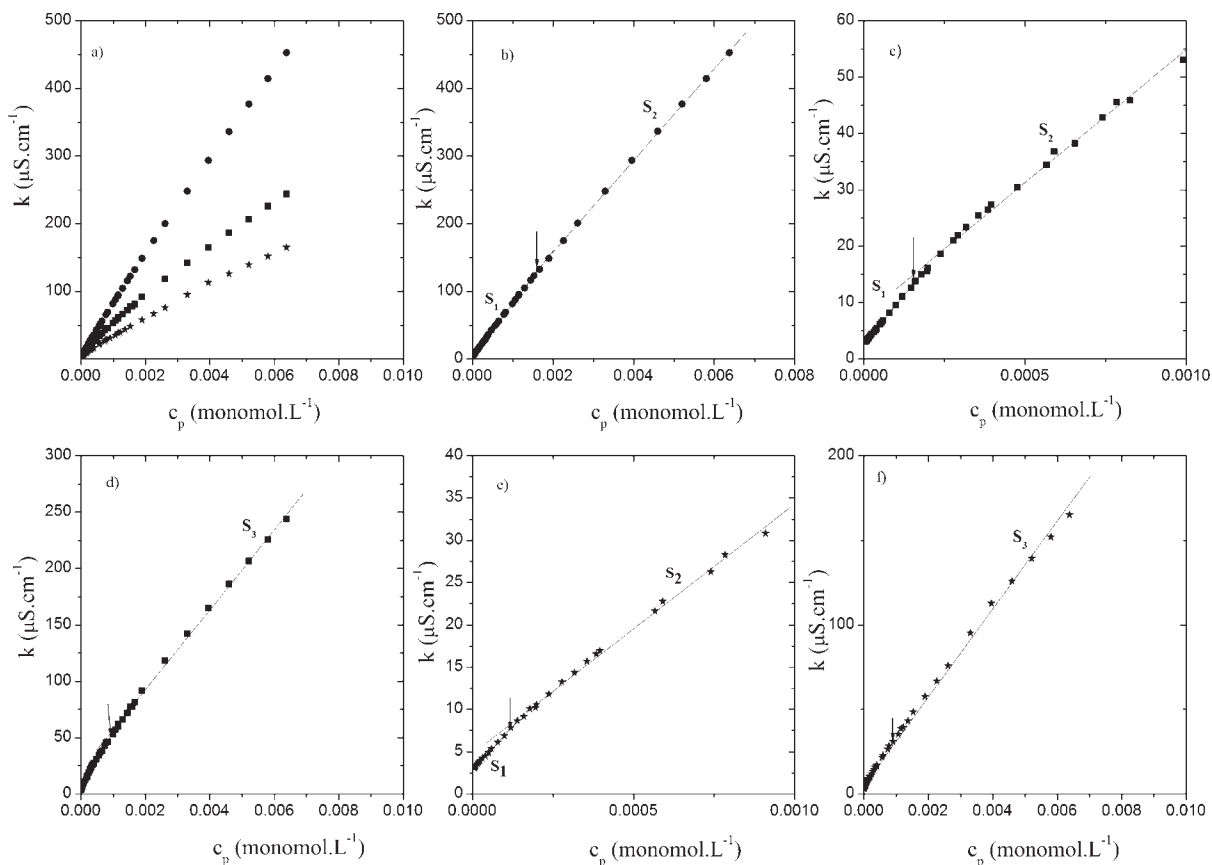
Figure 6 Dependence of the specific conductivity (k) on c_p in H$_2$O at 20°C: (a) (●) D40-Oct35, (■) D40-Dod35, and (★) D40-Cet35; (b) D40-Oct35; (c,d) D40-Dod35; and (e,f) D40-Cet35.

as the alkyl chain length of substituent R attached to the quaternary N atoms increases. This behavior is in agreement with Manning's counterion condensation theory, which predicts a decrease in Λ values when the chain radius increases as a more bulky hydrophobic substituent reduces the mobility of the polyion and hence Λ. Also, the results given by the values of α_1 and α_2 show the influence of the polyelectrolyte hydrophobicity on the degree of counterion binding.

The effects of adding methanol to systems such as these are complex and by no means easy to elucidate. Thus, the Λ value behavior for D40-Dod35 in water/methanol mixtures exhibits the same trend as that in water, that is, a continuous increase with dilution in the whole range of concentrations under study (Fig. 7).

However, it is worth noticing that the profile of the conductivity curve obtained in water is similar only to those obtained in the 90/10 and 60/40 solvent mixtures. For the higher methanol content in the mixture, a well-defined curvature can be observed that is characteristic of polyelectrolytes with $\xi > \xi_{cr} = 1$; Λ exhibits at first a slight increase with decreasing concentration, and this is followed by a greater increase at higher dilution. In this case,

TABLE IV
cac and α Values Determined from Fluorescence and Conductivity Data for the Amphiphilic Polysaccharides

| | cac (mmol/L) | | | | | |
| | Fluorescence | | Conductivity | | Conductivity[a] | |
Sample	cac$_1$	cac$_2$	cac$_1$	cac$_2$	α_1	α_2
D40-Oct35	3.81	38.1	1.67	—	0.87	—
D40-Dod35	0.0118	0.848	0.159	0.99	0.68	0.52
D40-Cet35	0.0021	0.273	0.119	0.909	0.72	0.61

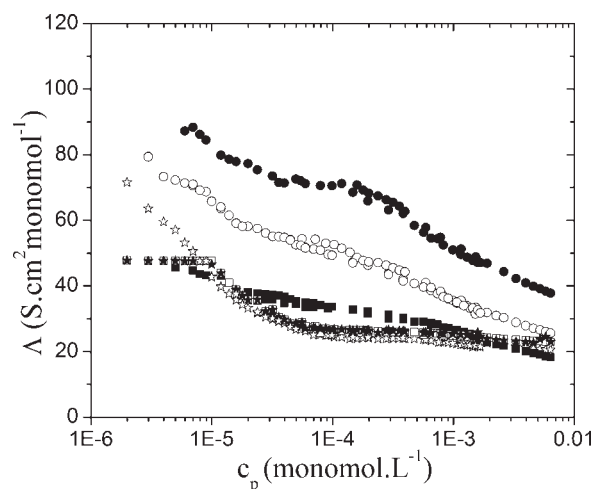[a] $\alpha_1 = S_2/S_1$ and $\alpha_2 = S_3/S_1$ (as shown in Figure 6).

Figure 7 Dependence of Λ on c_p in water/methanol mixtures for D40-Dod35 at 20°C: (●) water, (○) 90 : 10 water/methanol, (■) 60/40 water/methanol, (□) 50 : 50 water/methanol, (★) 40 : 60 water/methanol, and (☆) methanol.

Figure 8 Log Λ of D40-Dod35 as a function of the dielectric constant of the solvent (ε) for different polyelectrolyte concentrations: (○) $1.19 \times 10^{-5}M$, (●) $5.964 \times 10^{-5}M$, (□) $1.47 \times 10^{-4}M$, (☆) $1.15 \times 10^{-3}M$, and (■) $5.66 \times 10^{-4}M$.

counterion condensation, within the Manning theory, takes place. This theory states that condensed counterions do not participate in electrical conduction, whereas free counterions behave as in a simple salt solution. On dilution, more counterions are far away from the polyion and have greater mobility, thus increasing Λ. From the conductometric data, we can assume that the condensation of counterions takes place not only in methanol when $\xi > 1$ (Table V) but also in solvent mixtures when $\xi < 1$, that is, in 50 : 50 and 40 : 60 solvent mixtures. The hypothesis of counterion condensation on both sides of the critical value of ξ has also been reported for other polyelectrolytes.[41,48–50]

Moreover, for a given concentration, the experimental point values decrease with the decrease in the dielectric constant. As the methanol content increases, a weaker electrolytic dissociation of the ionizable groups along the polyion backbone takes place, and so the number of conducting counterions is small. The strongest decrease takes place until a 50 : 50 solvent mixture, the values of Λ being practically the same for the rest of the solvent mixtures. This is more clearly shown in Figure 8, which shows that the dependence of log Λ on the dielectric con-
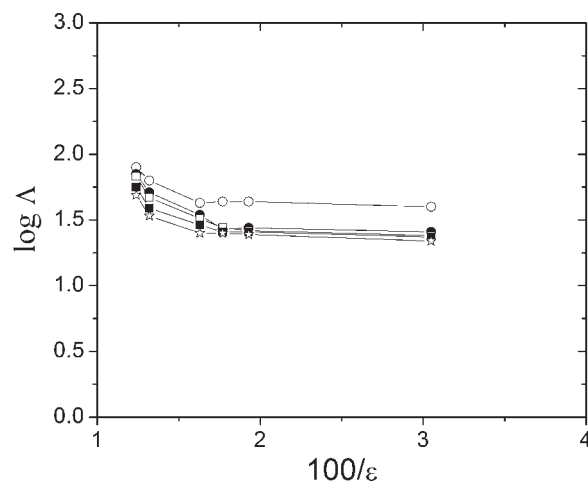
stant, at different polymer concentrations, is not linear as reported for other polyelectrolytes.[23,51]

CONCLUSIONS

These experiments highlight the strong influence of the length of the pendent alkyl chain and dielectric constant of the solvent on the transport properties (viscosity and electrolytic conductivity) of D40-RX cationic polysaccharides. A longer R alkyl substituent of quaternary N atoms brought about an intensification of the intramolecular hydrophobic interactions between side chains, which resulted in chain contraction and hence lower [η] values. D40-Dod35 showed polyelectrolyte behavior in all employed compositions of the water/methanol mixed solvents, having the highest [η] value in the 50 : 50 solvent mixture.

The experimental values obtained for Λ in water show for all cationic polysaccharides under study a behavior similar to that of polyelectrolytes with $\xi < \xi_{cr} = 1$, that is, a linear increase in Λ values with dilution over almost the entire concentration range. For the same charge density and concentration, Λ values decrease as the alkyl chain length of the R substituent attached to the quaternary N atoms increases according to Manning's counterion condensation theory. The profile of the specific conductivity variation with c_p supports the significant influence of the polymer hydrophobicity on the polyion counterion condensation ability. The profile of the Λ curve is similar to that obtained in water for D40-Dod35 only in the 90 : 10 and 60 : 40 solvent mixtures. With a higher methanol content in the mixture, a well-defined curvature can be observed that is characteristic of polyelectrolytes with $\xi > \xi_{cr}$,

TABLE V
Dielectric Constant (ε) and Charge Density Parameter (ξ) Values for D40-Dod35 in Water/Methanol Mixtures

Water/methanol (%, w/w)	ε	ξ
100/0	80.10	0.48
90/10	75.27	0.51
60/40	61.08	0.63
50/50	56.35	0.68
40/60	51.62	0.74
0/0	32.71	1.18

at which counterion condensation takes place. This points to counterion-charged group associations on both sides of ξ_{cr}.

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