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Intrinsic viscosities of polyelectrolytes in the absence and in the presence of extra salt: Consequences of the stepwise conversion of dextran into a polycation

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ABSTRACT

Viscosities of dilute polymer solutions were measured in capillary viscometers for samples varying in their fraction *f* of charged units from 0.00 to 0.90. The dependence of the logarithm of the relative viscosity on polymer concentration *c* is in all cases reproduced quantitatively by three characteristic parameters: $[\eta]$, the intrinsic viscosity; *B*, a viscometric interaction parameter (related to the Huggins constant); $[\eta]^\bullet$, a parameter required only for polyelectrolytes at low concentrations of extra salt. In pure water $[\eta]$ increases more than 80 times as the fraction *f* rises from zero to 0.90 and $[\eta]^\bullet$ starts from zero and goes up to ≈71 mL/g. Upon the addition of NaCl $[\eta]$ decreases by at least one order of magnitude (depending on the value of *f*). The observed dependences of log $[\eta]$ on log c_{salt} can be modeled quantitatively by Boltzmann sigmoids.

1. Introduction

The outstanding importance of polyelectrolytes is undoubted. Biological systems abound in polyelectrolytes, such as nucleic acids or proteins and synthetic polyelectrolytes play an important role in technical applications, like water purification, stabilization and destabilization of dispersions, surface modification, thickening of solutions etc. Despite increasing theoretical and experimental efforts over the past several decades, our understanding of solution properties of polyelectrolytes is still limited (Dautzenberg et al., 1994; Förster & Schmidt, 1995; Gampert, Wilkes, & Eich, 1999; Hara, 2001; Hodgson & Amis, 1991; Ise, 1998; Mandel, 1993; Oosawa, 1971; Rice & Nagasawa, 1961; Schmitz, 1993; Van Leeuwen, Cleven, & Valenta, 1991; Wandrey & Hunkeler, 2002). Charging macromolecules introduces new length scales, such as the Debye screening length and the Bjerrum length. As a consequence the scaling laws, so useful for the description of neutral systems, are difficult to apply for polyelectrolyte solutions. Moreover, the long-range Coulomb interactions lead to a rich variety of effects qualitatively different from those of neutral polymers with respect to, for example, their scattering properties and viscosity behavior (Dobrynin & Rubinstein, 2005).

In the case of intrinsic viscosities $[\eta]$ the problem may be solved through screening of charges by addition of salt (low molar mass electrolytes). The value obtained under this condition depends on the salt concentration; the more salt is added, the lower is the electrostatic repulsive force and, hence, the lower is also $[\eta]$ (Deboudt, Delporte, & Loucheux, 1995; Eisenberg & Pouyet, 1954; Liaw, Shiau, & Lee, 1992; Zhuomei, Xuein, Yuanpei, & Yuanzhen, 1992). Experimentally, $[\eta]$ has been often found to be proportional to $c_s^{-1/2}$ (Fisher, Sochor, & Tan, 1977; Muroga, Amano, Katagiri, Noda, & Nakaya, 1995; Nagasawa, Izumi, & Kagawa, 1959; Reed, Ghosh, Medjahdi, & Francois, 1991). In some cases, no linear relationship between $[\eta]$ and $c_s^{-1/2}$ was observed (Lee & Tsai, 1994; McCormick & Salazar, 1993; Rushing & Hester, 2004; Sorci & Reed, 2002; Vink, 1970). Other attempts to circumvent the problems with the traditional extrapolation to infinite dilution in the absence of extra salt use empirical equations (Fedors, 1979; Fuoss & Strauss, 1948; Juan, Dougherty, & Stivala, 1972; Lovell, 1989; Rao, 1993; Yang, 2004). Tobitani and Ross-Murphy (1997) examined the validity of several models for predicting $[\eta]$ of polyelectrolytes by comparison with experiments and concluded there was no consensus on the method which worked best and proposed a new empirical model.

The following relation (1) (Wolf, 2007) starting from purely phenomenological consideration, has turned out to model the viscosities of polymer solutions as a function of the solute content (c = mass/volume) in the range of pair interaction between the polymer coils quantitatively. It is equally

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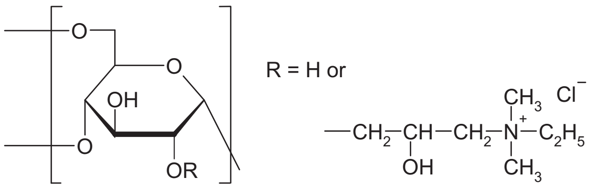

Scheme 1. Repeating units of dextran and of its derivatives. R is N-ethyl-N,N-dimethyl-N-(2-hydroxypropyl) ammonium chloride instead of H.

applicable to charged and uncharged, linear or non-linear macromolecules:

$$\ln \eta_{\mathrm{rel}} = \frac{c[\eta] + Bc^2[\eta][\eta]^\bullet}{1 + Bc[\eta]} \tag{1}$$

The intrinsic viscosities $[\eta]$ of the polymers represent the initial slope of $\ln \eta_{\mathrm{rel}}$ vers. c; B and $[\eta]^\bullet$ are adjustable parameters. Eq. (1) replaces the well known Huggins relation (2) usually employed for the determination of intrinsic viscosities:

$$\frac{\eta_{\mathrm{rel}} - 1}{c} = [\eta] + k_{\mathrm{H}}[\eta]^2 c \tag{2}$$

In this case the $[\eta]$ values are obtained from the y-intercept in plots of $(\eta_{\mathrm{rel}} - 1)/c$ vers. c; k_{H} is the so-called Huggins constant, a viscometric interaction parameter. The reason for the use of Eq. (1) instead of Eq. (2) is due to the fact that Eq. (2) fails for solutions of polyelectrolytes containing no extra salt or only insufficient amounts of it.

So far Eq. (1) has been applied successfully for salt free aqueous solutions of poly (N-butyl-4-vinylpyridinium bromide samples with different quaternization degree (Wolf, 2007), sodium polystyrene sulfonate (Eckelt, Knopf, & Wolf, 2008), peripherically charged dendronized poly(methyl methacrylate) and carboxymethyl guar (Badiger, Gupta, Eckelt, & Wolf, 2008). Furthermore we have recently measured the intrinsic viscosities of the present dextran based polycations in salt free mixed solvents containing water plus methanol (Ghimici, Nichifor, & Wolf, 2009).

The main goal of the present contribution was to check the ability of Eq. (1) to quantitatively describe the transition in the viscometric behavior of DEX-*f* from the uncharged dextran to cationic polyelectrolytes both in pure water (no salt added) and in the presence of variable salt concentration. A quantitative evaluation of the influence of the mentioned variables was performed by calculation of the hydrodynamic parameters: intrinsic viscosity $[\eta]$, hydrodynamic interaction parameter B (a measure of polymer–polymer segment interactions), and the characteristic specific hydrodynamic volume $[\eta]^\bullet$. A comparison of these parameter values as influenced by f and c_s was also entended. For this purpose, we have used polymers with different content in permanently charged units (strong cationic charges) alternating with neutral units (Scheme 1). In this way we avoided the possible interference of the self-ionization often observed when the charge density is modified only by partial ionization of weak polyelectrolytes, or by partial quaternization of weak polybases such as polyvinylpyridine.

2. Experimental part

2.1. Materials

The cationic polysaccharides with pendent quaternary ammonium groups required for the present study were synthesized by chemical modification of dextran (Sicomed S.A., Bucharest, $M_r \approx 40$ kg/mol, polydispersity index $M_w/M_n = 1.12$). The procedure has already been described (Nichifor, Stanciu, & Simionescu, 2010). The samples were extensively purified by repeated precipitation and dialysis against 0.1 N HCl and water and finally recovered as a white powder by freeze drying. The chemical structure of the polymers (shown in Scheme 1) was proved by ^{1}H NMR analysis. The fraction f of monomer units bearing positive charges was calculated from the measured contents of nitrogen (elementary analysis) and chloride ions (potentiometric titration with 0.02 N $AgNO_3$ aqueous solution) with an accuracy of ±2 mol/%.

Table 1
Characteristics of the polycation samples; c_{Cl^-} is the chloride ion content, b is the spacing between two vicinal ionized groups on the polyion, based on a repeating unit length of 0.515 nm for the D-glycopyranose unit (Pass & Hales, 1981), and ξ is the charge density parameter, calculated according to references (Manning, 1969, 1975).

f	c_{Cl^-} (meq/g)	b (nm)	ξ_{water} (20 °C)
0.11	0.63	4.68	0.15
0.24	1.19	2.14	0.33
0.74	2.56	0.70	1.01
0.90	2.86	0.57	1.24

The salts used for the present study, NaCl and NaBr, were analytical grade products and used without further purification.

2.2. Methods

Viscometric measurements of the polyelectrolyte solutions were carried out with an Ubbelohde capillary viscometer for dilution sequences (size 0a, capillary diameter of 0.53 mm) in combination with an automatic viscosity measurement system AVS 300 (Schott Instruments, Mainz, Germany), at 25 °C. All polyelectrolytes were dissolved in highly purified deionized water from a Milli-Q PF (Millipore, Switzerland). All viscosity measurements were repeated at least twice in order to check the reliability of the data.

3. Results and discussion

Dextran is a well known polysaccharide where the glucose units are normally either α-1-6 or α-1-4 linked; branching starts mainly form α-1-3 linkages. The polymers under investigation are random copolymers, differing in the fraction f of monomer units. The reaction mixture was a homogeneous solution over the entire modification process, allowing an even (statistical) distribution of the charged groups along the polysaccharide chains. The reaction conditions were mild and did not affect the integrity of the polymer backbone. Relevant data of the polycations under investigation are collected in Table 1; it is interesting to note that the inverse of the average spacing between two vicinal ionized groups on the polyion is for the present system related to f by the proportionality $1/b = 1.94f$ and that the charge density parameter ξ (Manning, 1969, 1975) depends on f according to $\xi = 1.37f$.

This chapter is subdivided into three sections: Section 3.1 describes and discusses the viscometric behavior of the aqueous solutions of the different DEX-*f* samples in the absence of extra salt and Section 3.2 the changes caused by the addition of salt. Section 3.3 deals with the question whether the effects induced by an alteration of the charge density along the polymer chain (variable f) as compared with additional charges in the solvent (variable salt concentration) can be described with the same mathematical expressions.

3.1. Viscosities in the absence of salt

Fig. 1 displays $\ln \eta_{\mathrm{rel}}$ as a function of c according to Eq. (1). The initial slopes of these dependencies yield the intrinsic viscosities $[\eta]$; the parameters B and $[\eta]^\bullet$ determine the curvature of this function.

The parameters obtained from the evaluation of the dependencies shown in Fig. 1 are collected in Table 2 together with averaged

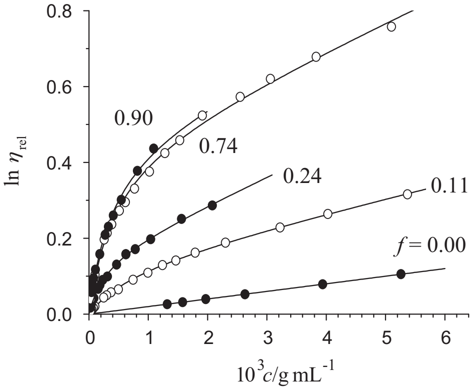

Fig. 1. Natural logarithm of the relative viscosities as a function of the polymer concentration, c, for aqueous solutions at 25 °C. The numbers at the curves display the fraction f of charged units the different DEX-f samples contain.

Table 2
Fractions f of charged monomer units (of mass M_o) and parameters of Eq. (1) describing the composition dependence of the viscosities of the aqueous solutions in the absence of extra salt.

f	M_o	$[\eta]$ (mL/g)	B	$[\eta]^\bullet$ (mL/g)
0.00	162.0	20	−0.05	0
0.11	180.2	205	5.92	37
0.24	201.7	642	4.80	72
0.74	284.4	1140	2.10	71
0.90	310.9	1629	(2.00)	(70)

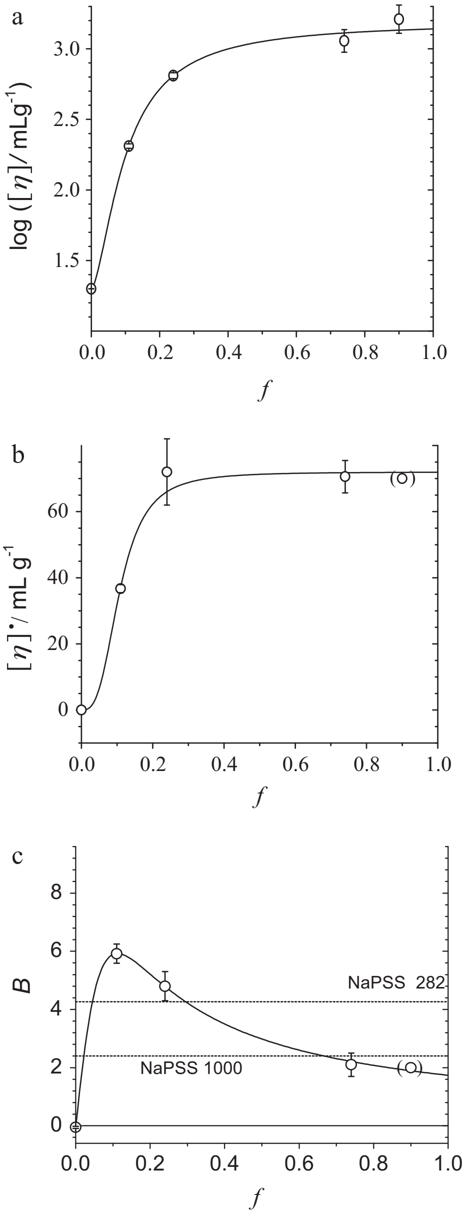

Fig. 2. Viscometric parameters of the different samples of DEX-f as a function of f, the fraction of charged monomeric units. (a) Intrinsic viscosity; the data are fitted by a logistic curve.[1] (b) $[\eta]^\bullet$ of Eq. (1); the data are connected by a logistic curve. (c) Viscometric interaction parameter B (Eq. (1)); the full curve is calculated according to Eq. (4) using the parameters of Table 3. The dotted horizontal lines indicate the B values measured for aqueous solutions of the sodium salt of polystyrene sulfonate of the indicated molecular weights (Eckelt et al., 2008) (in kg/mol) in the absence of external salt.

molar masses of the monomer units of the different DEX-f samples. The accuracy of the intrinsic viscosities is in all cases reasonable as shown in Fig. 2a. The errors for $[\eta]^\bullet$ (cf. Fig. 2b) and B (cf. Fig. 2c) are, however, larger than normal for f = 0.24 and f = 0.90; the data for the latter polymer are put into parenthesis because they are estimates only based on the systematic change in the shape of the individual curves of Fig. 1.

Fig. 2a visualizes how the intrinsic viscosities increase as f rises, i.e. as the fraction of charged monomer units grows. Within experimental error this result, obtained with newly prepared DEX-f samples, match earlier measurements concerning intrinsic viscosities in mixed solvents (Ghimici et al., 2009). Moreover, the intrinsic viscosities for a set of polymers with a similar charge density range were previously calculated also by Rao model, and the results were close (Ghimici et al., 2009). Fig. 2b and 2c depict how the other two parameters of Eq. (1) depend on the charging of the polymer. The parameter $[\eta]^\bullet$ increases with rising f like $[\eta]$. The starting point of this dependence is zero (uncharged dextran) and the ordinate scale is linear and not logarithmic as with $[\eta]$.

B, the third parameter required for the quantitative description of the viscosities of polyelectrolyte solutions in the absence of extra salt, quantifies the viscometric interaction between polymer segments belonging to different macromolecules. The comparison of the Taylor series of Eq. (1) with Eq. (2) within the region of pair interaction (i.e. up to the square of the concentration) yields the following interdependence of B and the Huggins constant k_H:

$$B = \frac{0.5 - k_H}{1 - ([\eta]^\bullet/[\eta])} \tag{3}$$

With the application of the above relation it is important to keep in mind that the composition range of pair interaction is far smaller for the polyelectrolytes than for uncharged macromolecules, for which the second term in the denominator is always zero.

Fig. 2c shows how B changes upon an increased charging of monomer units; the curve starts at the low value typical for uncharged polymers, passes a pronounced maximum in the vicinity of f = 0.1 and thereafter falls to a value which is typical for polyelectrolytes of this molar mass (Eckelt et al., 2008).

The experimental data of Fig. 2c can be described by the following relation. The numerical values of the parameters of Eq. (4) are given in Table 3:

$$B = \frac{B_{f=0}(1 + Af^E) + (1 + A)(B_{f=1} - B_{f=0})f}{1 + Af^E} \tag{4}$$

The pronounced maximum in the dependence $B(f)$ for comparatively low f values is in accord with similar extrema in the case of

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[1] Logistic equation: $\log[\eta] = \frac{A_1+A_2}{1+(\log f/\log f_0)^p} + A_2$.

Table 3
Parameters of Eq. (4) describing the dependence of the parameter *B* on *f*.

$B_{f=0}$	$B_{f=1}$	A	E
−0.05 ± 0.16	1.73 ± 0.11	65.2 ± 10	1.82 ± 0.08

second osmotic virial coefficients (Morariu et al., 2011) and polymer densities. These observations are tentatively attributed to the formation of clusters by the charged monomer units and their consequences for the thermodynamic and viscometric behavior of such systems.

We now raise the question, to which extent the electrolyte concentration, $c^{(\,)}_{\mathrm{salt}}$, in an isolated coil of partly charged macromolecules (no salt added) depends on *f*. This quantity can be calculated from their intrinsic viscosities and molar masses according to the following relation, obtained by dividing the moles of charges per one mole of polymer (equal to *f* times the degree of polymerization) by the molar volume of the polymer coils at infinite dilution ([*η*]*M*):

$$c^{(\,)}_{\mathrm{salt}} = \frac{zf}{[\eta]M_o} \qquad (5)$$

In this relation M_o is the average mass of a polymer segment and *z* is the maximum number of charges per monomer unit (here unity). The numerical values obtained for $c^{(\,)}_{\mathrm{salt}}$ on the basis of (5) vary only little with *f* (cf. Table 4). Allowing for over-all errors of the parameters on the right hand side of Eq. (5) on the order of 10–20% this could mean that an isolated polyelectrolyte molecule swells in pure water until a certain characteristic salt concentration is reached, irrespective of the particular value of *f* (≠ 0).

3.2. Viscosities in the presence of salt

The composition dependence of the viscosities for solutions of the DEX-*f* samples in water, containing different amounts of NaCl, is shown in Fig. 3a for *f* = 0.11, in Fig. 3b for *f* = 0.24, and in Fig. 3c for *f* = 0.90. In order to check to which extent the special chemical nature of the added salt changes the salt effects we have also performed some orienting measurements replacing NaCl by NaBr; Fig. 4 shows the results.

How the intrinsic viscosities of the different samples change upon adding salt to the solvent is displayed in Fig. 5a, summarizing all data obtained from the four preceding plots. This double logarithmic graph demonstrates that the sensitivity of the specific hydrodynamic volume of the polymer (related to the volume the isolated coils occupy) with respect to the addition of salt to the solvent becomes highest (points of inflection) in the range of milli molar concentrations. Expectedly the effects are most pronounced for the highest *f* values.

The curves in Fig. 5a are calculated by adjusting the parameters of the Boltzmann sigmoid formulated in Eq. (6):

$$\log\,[\eta] = \log\,[\eta]_{c_{\mathrm{salt}}\to\infty} + \frac{\log\,[\eta]_{c_{\mathrm{salt}}=0} - \log\,[\eta]_{c_{\mathrm{salt}}\to\infty}}{1+\exp\{\log(H(c_{\mathrm{salt}}/c^{\mathrm{ip}}_{\mathrm{salt}}))\}} \qquad (6)$$

It is gratifying to see that the intrinsic viscosities extrapolated according to Eq. (6) to infinitely low salt concentrations ($[\eta]_{c_{\mathrm{salt}}=0}$) agree quantitatively with the independently measured [*η*] values presented in the last section. Furthermore it is worthwhile to note that the second limiting value ($[\eta]_{c_{\mathrm{salt}}\to\infty}$) coincides within experimental error with the intrinsic viscosity of the uncharged dextran, irrespective of the *f* value. The particularities of the different DEX-*f* samples are quantified by the parameters *H* and $c^{\mathrm{ip}}_{\mathrm{salt}}$, the salt concentration at the inflection point of the different curves. All data are collected in Table 4, which also states $c^{(\,)}_{\mathrm{salt}}$, the salt concentration inside the isolated polyelectrolyte coil in the absence of extra salt. Differences in the effects of NaCl and of NaBr cannot be observed.

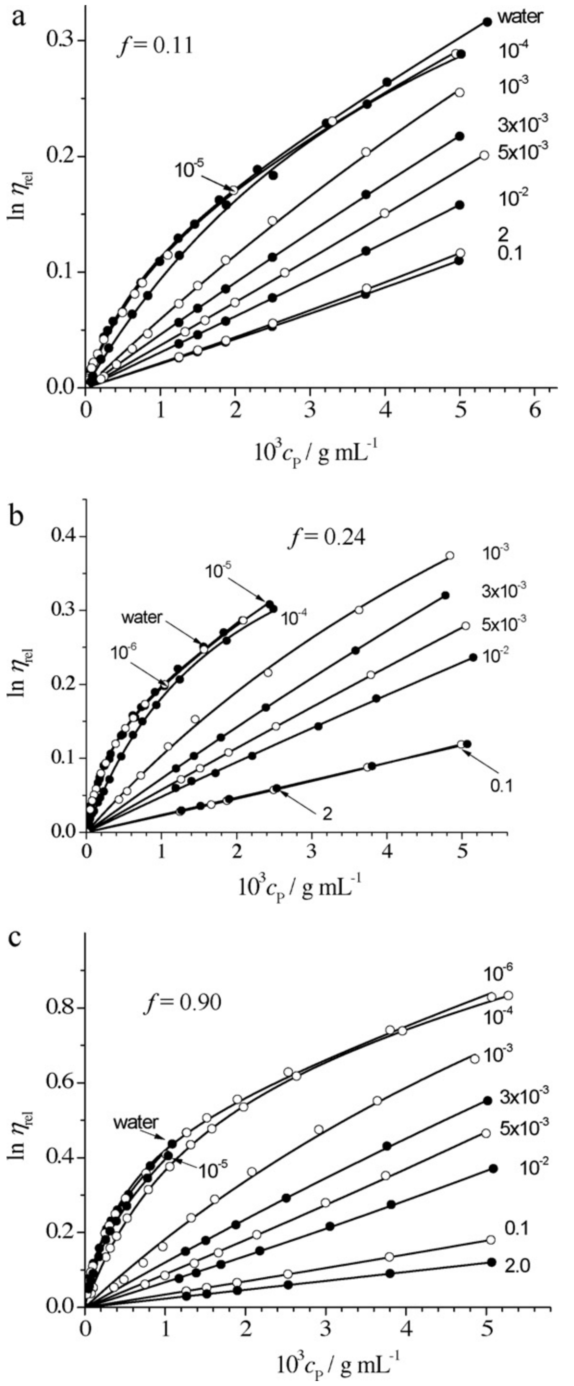

Fig. 3. Evaluation of viscosity data for aqueous solutions of DEX-*f* according to Eq. (1). The uppermost curves give the result for pure water (full circles); the different NaCl concentrations (mol/L) are indicated in the graph. (a) DEX-0.11; (b) DEX-0.24; (c) DEX-0.90.

According to the present findings the parameter $[\eta]^{\bullet}$ is so sensitive with respect to the presence of salt in the solvent that extremely low salt concentrations suffice to bring this parameter down to zero. The study of this transition would require lower salt concentrations than investigated here.

The viscometric interaction parameter *B* changes by the addition of salt (like [*η*] and $[\eta]^{\bullet}$) more obviously as demonstrated in Fig. 5b. This dependence can again be modeled by a Boltzmann sigmoid, but this time the asymptotes for vanishing salt concentration do

Table 4

Parameters of Eq. (6) describing the dependence of the intrinsic viscosities on the concentration of the salt added. c^{ip}_{salt} stands for the salt concentration at the inflection point and $c^{()}_{salt}$ is the average salt concentration inside an isolated polymer coil in the absence of extra salt calculated according to Eq. (5).

f	$[\eta]_{c_{salt}=0}$ (mL/g)	$[\eta]_{c_{salt}\to\infty}$ (mL/g)	H	$\log c^{ip}_{salt}$ (c: mol/L)	$\log c^{()}_{salt}$ Eq. (5) (c: mol/L)
0.11	205	20	1.31	−3.06	−2.52
0.24	642	20	1.27	−2.97	−2.73
0.90	1629	20	1.09	−2.91	−2.75

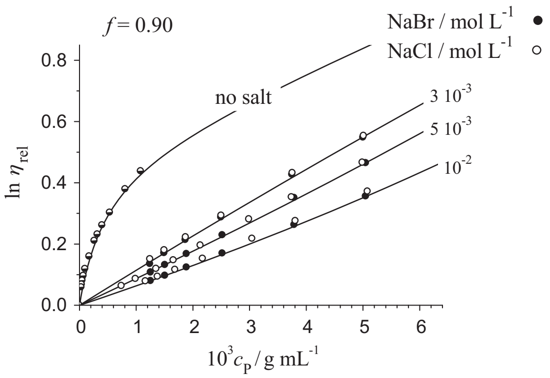

Fig. 4. Evaluation of viscosity data for aqueous solutions of DEX-0.90 according to Eq. (1). The uppermost curve gives the result for pure water; the different NaCl and NaBr concentrations (mol/L) are indicated in the graph. Empty circles: NaCl; full circles: NaBr.

no longer coincide with the directly determined values (cf. Fig. 2c); this observation is probably due to the lack of data for salt concentrations below 10^{-6} mol/L. The mismatch of the asymptotes at high salt concentrations with the B value of the uncharged dextran (dotted line in Fig. 5b), on the other hand, is most likely caused by the fact that the solvents are dissimilar: In the case of the uncharged samples it is pure water but here it is water plus plenty of salt which will likely change the structure of pure water. The substitution of NaCl against NaBr remains without consequences for B, as in the case of the salt dependence of the intrinsic viscosities (cf. Fig. 5a).

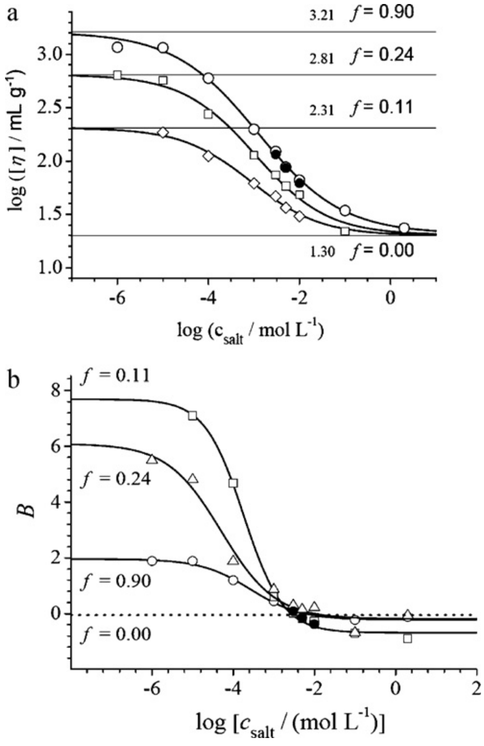

Fig. 5. Dependence of viscometric parameters on the salt concentration in water for the samples differing in the fraction f of charged monomers. Open symbols: NaCl; full symbols: NaBr. The upper asymptotes indicate the $[\eta]$ values in pure water and the lower asymptote states the intrinsic viscosity of the unsubstituted dextran in water. (a) Intrinsic viscosity and (b) interaction parameter B.

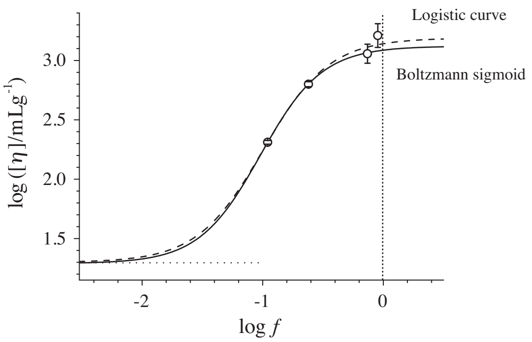

Fig. 6. Dependence of the intrinsic viscosities of DEX-f in pure water on the fraction of charged monomer units. The broken line shows the curve of Fig. 2a as function of log f instead of f. The dotted line indicates the intrinsic viscosity of the uncharged dextran.

3.3. Chain charging versus changes in solvent salinity

The effects of salt on the parameters of Eq. (1) ($[\eta]$, $[\eta]^\bullet$ and B) were modeled by Boltzmann sigmoids of the type formulated in Eq. (6). On the other hand the consequences of an augmentation of charge density along the polymer chain by increasing f were described in terms of a logistic curve. In view of the fact that the coil expansion resulting from the charging of polymer chains in the absence of salt should be equivalent to the coil expansion caused by the reduction of the concentration of external salt at constant f we check to which extent it is possible to describe both phenomena by the same mathematical expressions. In doing so it turns out (Fig. 6) that the Boltzmann sigmoid can model the (still limited information on the) f dependence of the intrinsic viscosities in the absence of salt with a similar accuracy as the previously applied logistic curve.

4. Conclusions/outlook

The most important observation of the present study lies in the ability of Eq. (1) to describe the transition in the viscometric behavior of DEX-f in pure water (no salt added) from the uncharged dextran to cationic polyelectrolytes quantitatively. The continuous rise of the intrinsic viscosities by more than an order of magnitude as a function of the fraction f of charged monomers is well represented by a logistic curve or – more consistently with the other dependencies – by a Boltzmann sigmoid. In contrast to $[\eta]$ the viscometric interaction parameter B passes a pronounced maximum at $f \approx 0.1$. Eq. (1) remains applicable for solvents containing variable amounts of salt. In the limit of high salt concentration the polyelectrolytes perform similar to the unsubstituted dextran.

Additional experiments at very low f values and theoretical considerations are required to decide which of the two expressions is physically more meaningful. Presently the only items speaking for the Boltzmann sigmoid are its more general applicability and the lower slope in the region of large f values; where no experiments have so far been performed for $f > 1$ (more than one charge per monomer unit).

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