# Polyelectrolytes: Intrinsic Viscosities in the Absence and in the Presence of Salt

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ABSTRACT: Intrinsic viscosities were determined at 25 °C for 10 samples of narrowly distributed sodium polystyrene sulfonate (the molecular weights $M$ ranging from 0.9 to 1000 kg/mol) in pure water and in aqueous solutions containing 0.9 wt % NaCl from the slope of $\ln \eta_{\mathrm{rel}}$ versus polymer concentration. In the middle range of $M$, the $[\eta]$ values are in the former case almost 2 orders of magnitude larger than in the latter case. In the absence of salt, the plot of $\log [\eta]$ as a function of $\log M$ exhibits a sigmoidal shape, which can be approximated within the interval $3 < M$ (in kg mol$^{-1}$) $< 30$ by $\log[\eta] = -0.17 + 2.1 \log M$. In the presence of salt, the following relation holds true in the entire regime: $\log[\eta] = -0.13 + 0.86 \log M$. The concentration dependences of $\eta$ of the present polyelectrolyte solutions and of solutions of uncharged polymers in organic solvents taken from the literature can be modeled quantitatively by means of recently reported relations at least up to reduced polymer concentration $c[\eta] = 5$. The physical meaning of the parameters obtained from this modeling is surveyed.

## 1. Introduction

Measurement and theoretical understanding of the intrinsic viscosities of polyelectrolytes in salt-free solvents have attracted considerable interest in the past.[1−7] We have recently come back to that topic and used an uncommon, alternative definition of the intrinsic viscosity to obtain experimental access to this quantity. In the preceding publication[8] we have applied the novel concept to viscosity data that were published in current text books for aqueous solutions of two sets of poly(*N*-butyl-4-vinylpyridinium bromide) samples differing in the extent of quaternization. The main idea of the new approach is the following: As long as the viscosity $\eta$ of the solutions constitutes a variable of state, the intrinsic viscosity $[\eta]$ is given by the initial slope of the dependence of the natural logarithm of the relative viscosity $\ln \eta_{\mathrm{rel}}$ ($\eta_{\mathrm{rel}}$ = viscosity of the solution/viscosity of the solvent) on polymer concentration $c$ (mass/volume). Under these conditions we can write

$$\mathrm{d} \ln \eta = \left(\frac{\partial \ln \eta}{\partial c}\right)_{T,p,\dot\gamma} \mathrm{d}c + \left(\frac{\partial \ln \eta}{\partial T}\right)_{c,p,\dot\gamma} \mathrm{d}T + \left(\frac{\partial \ln \eta}{\partial p}\right)_{c,T,\dot\gamma} \mathrm{d}p + \left(\frac{\partial \ln \eta}{\partial \dot\gamma}\right)_{c,T,p} \mathrm{d}\dot\gamma \quad (1)$$

This equation describes the relative change of $\eta$ as a function of concentration $c$ (mass per volume), temperature $T$, hydrostatic pressure $p$, and shear rate $\dot\gamma$ and enables the introduction of a *generalized* intrinsic viscosity $\{\eta\}$ according to

$$\left(\frac{\partial \ln \eta}{\partial c}\right)_{T,p,\dot\gamma} = \{\eta\} \quad (2)$$

The intrinsic viscosity itself is then defined as

$$\lim_{\substack{c \to 0 \\ \dot\gamma \to 0}} \{\eta\} = [\eta] \quad (3)$$

$[\eta]$ represents the specific hydrodynamic volume of *isolated* polymer coils, in contrast to $\{\eta\}$, which quantifies the specific hydrodynamic volume at a given polymer concentration $c$. The second and the third partial derivatives of eq 1 yield the activation energy and the activation volume of the viscous flow, and the fourth quantifies the shear influences on $\eta$.

For the discussion it is convenient to normalize the concentrations $c$ by multiplying them with the intrinsic viscosity

$$c[\eta] = \tilde{c} \quad (4)$$

in this manner we obtain $\tilde{c}$, a dimensionless reduced concentration. This quantity is sometimes wrongly called the coil overlap parameter. Such a naming would only be correct for the special case $\{\eta\} = [\eta]$. In the normal case it is mandatory to multiply $c$ by $\{\eta\}$, the specific hydrodynamic volume at the particular concentration, to obtain a general measure for the coil overlap and not by its limiting value $[\eta]$. The hydrodynamic volume a polymer molecule occupies at a certain finite concentration $c$ divided by that at infinite dilution represents another quantity that helps discussion. To this end we can directly use $\{\eta\}/[\eta]$ because the molar mass of the polymer, by which the specific volumes must be multiplied to obtain molar volumes, cancels. That ratio provides information on the changes in the hydrodynamic volume of an individual macromolecule induced by the presence of other polymers.

It is the goal of this contribution to demonstrate by means of well-defined samples of the sodium salt of polystyrene sulfonic acid (Na−PSS) how to obtain $[\eta]$ values for their solutions in pure water by means of eqs 1−3 and to establish the corresponding $[\eta]/M$ relation. For the sake of comparison, the same kind of measurements are also performed with water containing 0.9 wt % NaCl; data concerning solutions of uncharged polymers in different organic solvents are taken from the literature. Particular attention is being paid to the modeling of viscosities for all systems up to the reduced concentration on the order of 5, i.e., well beyond the region of pair interaction between the solute molecules and to the changes in coil dimensions associated with the increase in polymer concentration.

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**Table 1. Molecular Weights of the Different Sodium Salts of Polystyrene Sulfonates and Parameters of Equation 6, Describing the Composition Dependence of the Viscosity in Aqueous Solutions**

| $M$/kg mol$^{-1}$ | $[\eta]$/mL g$^{-1}$ | $[\eta]^{\bullet}$/mL g$^{-1}$ | $B$ |
|---|---|---|---|
| 0.91 | 2.29 | | 182.00 |
| 3.60 | 9.08 | 3.00 | 56.20 |
| 6.53 | 35.50 | 6.08 | 28.80 |
| 14.90 | 204.00 | 18.70 | 13.18 |
| 26.10 | 955.00 | 19.60 | 8.50 |
| 63.90 | 3 800.00 | 90.00 | 3.16 |
| 145.00 | 5 620.00 | 197.00 | 1.62 |
| 282.00 | 11 750.00 | 119.00 | 0.63 |
| 666.00 | 10 000.00 | 255.00 | 0.46 |
| 1000.00 | 12 560.00 | 1100.00 | 0.38 |

The present approach is a purely phenomenological one; we have made no attempt to establish or discuss scaling laws or molecular theories of polyelectrolyte solutions. Nevertheless the new method for the unequivocal determination of the intrinsic viscosities for solutions of charged molecules in pure water should be helpful for further studies in this field.

## 2. Experimental Part

**2.1. Substances.** Sodium salts of polystyrene sulfonates (Na−PSS) were kindly donated by Polymer Standard Service (Mainz, Germany). Their molar masses and the parameters of eq 6 used to model the concentration dependence of viscosities of aqueous solutions are collected in Table 1. The samples with narrow molecular weight distributions ($M_w/M_n < 1.1$) were prepared from anionically synthesized precursors (characterized by light scattering, viscometry, and GPC) by sulfonation and complete neutralization. The thus obtained polymer was purified by precipitation and exhaustive dialysis. According to NMR analysis, the degree of substitution is in all cases 100%. The samples were used shortly after preparation.

Water was thoroughly purified for the present measurements. By means of osmosis (Elix 10) and the Millipore deionization system (Schwalbach, Germany), a resistivity of 18.2 MΩ at 25 °C could be reached. Before use, the water was degassed to remove oxygen and $CO_2$. Sodium chloride was obtained from Fluka (Buchs, Switzerland) and of puriss. p.a. quality.

**2.2. Viscometry.** The experiments were performed at 25 °C using Ubbelohde capillary viscometers for dilution sequences of type Oa with a capillary diameter of 0.53 mm, in combination with AVS 310 (Schott, Mainz, Germany). Hagenbach corrections were applied. The viscometric measurements were carried out either in pure water or in 0.9 wt % NaCl aqueous solutions. All samples were freed of dust by means of filters with a pore diameter of 0.45 $\mu$m (Spartan 30/B, Schleicher&Schuell, Dassel, Germany). Only freshly prepared samples were used.

Possible influences of the shear rate on the measured viscosities were checked for the solutions of the highest molecular weight sample in pure water using three capillaries with different diameters to realize wall shear rates between 70 and 270 s$^{-1}$. These experiments have shown that the resulting viscosities do not depend on $\dot{\gamma}$ as long as the polymer concentrations remains below $[\eta]^{-1}$ even in case of this highest molecular weight sample. Because of the fact that the intrinsic viscosities obtained by means of the new approach stem from the *initial* slope of ln $\eta_{rel}$ versus $c$ (i.e., from data for $c \ll [\eta]^{-1}$), possible influences of shear rate at high concentrations remain inconsequential. Furthermore we have made sure that the viscosity of the solutions does not change with time, for instance due to the uptake of carbon dioxide from the atmosphere.

## 3. Data Evaluation

**3.1. ln $\eta_{rel}$ versus $c$.** For the mathematical representation of text book data[8] for the concentration dependence of the relative viscosities of aqueous solutions of polycations, the following two relations turned out to be equally apt. They read

$$\ln \eta_{rel} = A(1 - e^{-([\eta]-[\eta])} \pm c/A) + [\eta]^{\pm}c \tag{5}$$

and

$$\ln \eta_{rel} = \frac{c[\eta] + Bc^2[\eta][\eta]^{\bullet}}{1 + Bc[\eta]} \tag{6}$$

where $A$, $B$, $[\eta]^{\pm}$ and $[\eta]^{\bullet}$ are constants. Both require one parameter more than the relations normally used to obtain intrinsic viscosities for uncharged polymers. The values of these constants can be easily determined on a PC from a sufficiently large number of viscosity measurements at different polymer concentrations by any fitting program.

In terms of ln $\eta_{rel}$, the most widely used Huggins equation (determining $[\eta]$ by extrapolating $(\eta_{rel} - 1)/c$ as a function of $c$ to infinite dilution) reads

$$\ln \eta_{rel} = \ln(1 + [\eta]c(1 + k_H[\eta]c + ...)) \tag{7}$$

where $k_H$ is the Huggins coefficient. The comparison of this relation with eqs 5 and 6 demonstrates that one additional parameter is required for polyelectrolytes, namely, $[\eta]^{\pm}$ with eq 5 and $[\eta]^{\bullet}$ with eq 6; these parameters are mandatory because of the experimental observation that ln $\eta_{rel}$ approaches a linear dependence on $c$ again at sufficiently high polymer concentrations. In that context it is interesting to note that eqs 5 and 6 are capable of modeling the experimentally observed maxima in $(\eta_{rel} - 1)/c$ as a function of $c$ as demonstrated for instance by Figure 4 of ref 8 and shown for the present data in Figure 4.

A Taylor series of the above three expressions for ln $\eta_{rel}$ yields equations of the same mathematical form. For the range of pair interaction, they can be written in terms of $\tilde{c}$ (eq 4) as

$$\ln \eta_{rel} = \tilde{c} - k\tilde{c}^2 - ... \tag{8}$$

where $k$ is

$$k = \left(1 - \frac{[\eta]^{\pm}}{[\eta]}\right)^2 \frac{1}{2A} \tag{9}$$

for eq 5

$$k = \left(1 - \frac{[\eta]^{\bullet}}{[\eta]}\right) B \tag{10}$$

for eq 6 and

$$k = \frac{1}{2} - k_H \tag{11}$$

in the case of the Huggins relation.

For the common evaluation of all experimental data, covering $\tilde{c}$ values up to 5, this series expansion is no longer suitable and eqs 5 or 6 must be used. During the application of relations to the present measurements, encompassing a much larger range of molar masses of the polyelectrolytes than that of ref 8, it became clear that eq 5 fails to model the results for Na−PSS consisting of less than approximately 70 monomeric units, in contrast to eq 6 which still works. Within the range of the truly high-molecular weight polyelectrolytes, the two fit curves are so similar in graphs of the type of Figure 3 that they cannot be distinguished with the naked eye. However, this does not imply that the $[\eta]$ values obtained from them are identical because the exact value of the limiting slope of ln $\eta_{rel}$ might still differ. This situation is very similar to that observed with uncharged polymers, where the $[\eta]$ values resulting from Huggins, Schulz−Blaschke, or Martin plots from the same data are normally not identical.[9] For the present systems, eq 6 yields slightly larger intrinsic viscosities than eq 5. The evaluation of the data for sufficiently low polymer concentration according to the relations in eqs 2 and 3, i.e., the direct determination of the initial slope of ln $\eta_{\mathrm{rel}}$ versus $c$, yields $[\eta]$ values which are free from any assumption. In the following section we present the experimental data together with their modeling by means of eq 6. The slightly different $[\eta]$ values obtained with eq 5 and that resulting from the direct evaluation are reproduced in Figure 5, showing the Kuhn−Mark−Houwink relation for aqueous Na−PSS solutions.

**3.2. $\{\eta\}$ versus $c$.** The specific hydrodynamic volume of the polyelectrolyte at arbitrary concentration $\{\eta\}$ can be used to obtain information on the shrinkage or expansion of the polymer coils, as compared with their extension at infinite dilution, induced by the presence of further solute molecules. For the ratio $\{\eta\}/[\eta]$ we obtain the following expression from eq 5

$$\frac{\{\eta\}}{[\eta]} = (1-q)\exp[-\tilde{c}/A(1-q)] + q \quad \text{where} \quad q = \frac{[\eta]^{\pm}}{[\eta]} \tag{12}$$

Equation 6 yields

$$\frac{\{\eta\}}{[\eta]} = \frac{1 + 2Br\tilde{c} + B^2 r\tilde{c}^2}{1 + 2B\tilde{c} + B^2\tilde{c}^2} \quad \text{where} \quad r = \frac{[\eta]^{\bullet}}{[\eta]} \tag{13}$$

and eq 7 results in

$$\frac{\{\eta\}}{[\eta]} = \frac{1 + 2k_{\mathrm{H}}\tilde{c}}{1 + \tilde{c} + k_{\mathrm{H}}\tilde{c}^2} \tag{14}$$

It appears worthwhile to note the similarity of eqs 13 and 14; the former expression referring to polyelectrolytes and the latter, being valid for uncharged macromolecules, differ only by a quadratic term of $\tilde{c}$ in the numerator.

In order to obtain information concerning the limiting behavior in the range of small reduced concentration, the above relations are again developed in Taylor series. The expansion of eq 12 yields

$$\frac{\{\eta\}}{[\eta]} = 1 - \frac{(1-q)^2}{A}\tilde{c} - \frac{(1-q)^3}{2A^2}\tilde{c}^2 - \ldots \tag{15}$$

from eq 13 we obtain

$$\frac{\{\eta\}}{[\eta]} = 1 - 2B(1-r)\tilde{c} - 3B^2(1-r)\tilde{c}^2 - \ldots \tag{16}$$

and the Huggins expression (eq 14) leads to

$$\frac{\{\eta\}}{[\eta]} = 1 - (1-2k_{\mathrm{H}})\tilde{c} - (3k_{\mathrm{H}} - 1)\tilde{c}^2 - \ldots \tag{17}$$

For typical polyelectrolytes and for uncharged polymers, the bracket term in front of $\tilde{c}$ results in a positive value; this finding indicates that the polymer coils are normally shrinking upon the addition of further macromolecules, i.e., upon an increase of the polymer concentration.

**3.3. Average Ionic Strength Within Isolated Coils.** For the assessment of salt effects on the intrinsic viscosities of polyelectrolytes, it is interesting to compare the salt concentrations of the solvent with the concentration of ions within the realm of isolated coils. For that reason we estimate $n_{\mathrm{I}}$, the molar concentration of ions, by setting the volume of the individual macromolecules equal to $[\eta]M$ and assume that each monomeric unit bears one charge and that the number of counterions leaving the coil remains negligible. Under these premises we obtain the following expression

$$n_{\mathrm{I}} = \frac{1}{[\eta]M_{\mathrm{o}}} \tag{18}$$

in which $M_{\mathrm{o}}$ is the molar mass of the monomeric unit. According to this equation, the charge density inside an isolated coil depends inversely on the intrinsic viscosity and approaches zero for infinitely long chains.

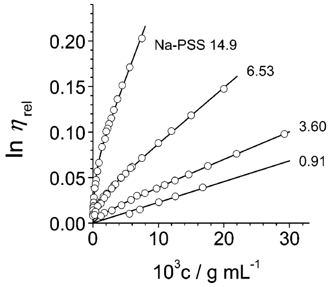

**Figure 1.** Relative viscosities of the solutions of the four lowest molecular weight samples of Na−PSS in pure water as a function of the unreduced polymer concentrations at 25 °C. The molecular weight (kg/mol) is given in the graph. Lines: Calculated according to eq 6 by means of the parameters of Table 1.

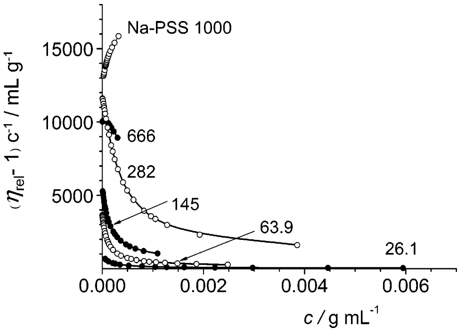

**Figure 2.** Huggins plots for aqueous solutions of the different Na−PSS samples indicated in the graph. The lines are guides for the eye only.

## 4. Results and Discussion

**4.1. Na−PSS in Pure Water. Composition Dependence of Viscosities.** The primary data obtained from capillary viscometry are presented in the following graphs. Figure 1 shows the concentration dependence of ln $\eta_{\mathrm{rel}}$ for the four lowest molecular weight samples of Na−PSS in unreduced form.

Before starting with the evaluation of the results for the truly high-molecular weight samples of Na−PSS according to eq 6 and in terms of reduced concentrations, we represent these data (cf. Figure 2) also in terms of Huggins plots. A more detailed analysis of the information obtained from such graphs is given in the context of Figure 4, comparing on an adequate scale the traditional approach with the present approach for Na−PSS 666, the only sample exhibiting a maximum in the Huggins plot.

The very different composition ranges of Figure 2 are in Figure 3 harmonized by using reduced concentrations. For the assessment of Figure 3, it should be kept in mind that the ordinate scale is approximately 10 times larger than in Figure 1.

The curves shown in Figures 1 and 3 are calculated by fitting the parameters of eq 6 to the data points. The most obvious

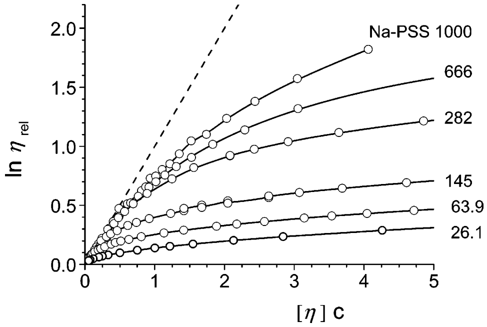

**Figure 3.** Like Figure 1 but as a function of the reduced polymer concentration. Lines: Calculated according to eq 6 by means of the parameters of Table 1. Broken line: ln $\eta_{rel} = [\eta]c$.

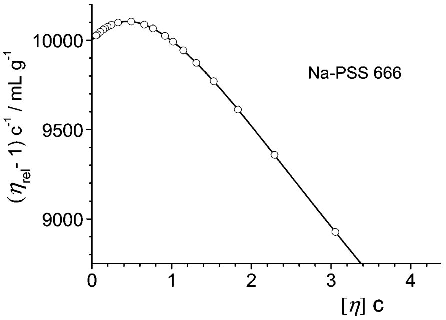

**Figure 4.** Evaluation of the viscosity data shown in Figure 3 for Na−PSS 666 in terms of a Huggins plot. Points, experimental data; line, calculated by means of eq 6 using the parameters of Table 1.

result consists in the extremely large *M*-dependence of the viscosity increase resulting from an augmentation of the polymer concentration. Only for the longest polyelectrolyte chains, the linear increase of ln $\eta_{rel}$ (anticipated on the basis of the idea that the relative increase in viscosity d$\eta$/$\eta$ should be proportional to d*c*) extends noteworthily into the region of higher $\tilde{c}$ values. This observation is, however, plausible in view of the fact that the charge density within isolated coils decreases with increasing [$\eta$] (eq 18). This means that the shielding of the electric charges resulting from a certain fixed degree of coil overlap and leading to a reduction of {$\eta$} becomes less important the higher the molar mass of the polyelectrolyte becomes.

In Figure 2 we have evaluated the current viscosity data in the traditional manner, i.e., by plotting the reduced viscosities as a function of polymer concentration. In such graphs one often observes maxima, as reported and discussed extensively in the literature (see e.g. refs 10 and 11). In the present case of aqueous polystyrene sulfonate solutions, only one sample exhibits such a behavior within the normal concentration range (up to $c[\eta] \approx 6$), namely, Na−PSS 666. For the higher molecular weight sample, the slope of the Huggins plots is always positive, whereas it is always negative for $M \leq 282$ kg/mol. This finding implies that the Huggins coefficient changes its sign from negative to positive within the interval $282 < M$( in kg mol$^{-1}$) $< 666$. All curves are well represented by the new approach. Figure 4 demonstrates that eq 6 is also capable of describing the viscosities as a function of composition in a classical Huggins evaluation quantitatively, even if this dependence passes a maximum.

**[$\eta$]/*M* Relations.** Different evaluation methods often yield nonidentical [$\eta$] values[9] as already mentioned in section 2. This situation is demonstrated for the present system in Figure 5, showing the data obtained by means of the eqs 5 and 6 plus the values resulting form the purely phenomenological evaluation (the initial slope of the ln $\eta_{rel}$ on *c*). Also incorporated into this graph are literature data[12] obtained by means of traditional evaluation methods (i.e., employing an extrapolation of the zero-divided-by-zero type) from measurements at extremly high dilution.

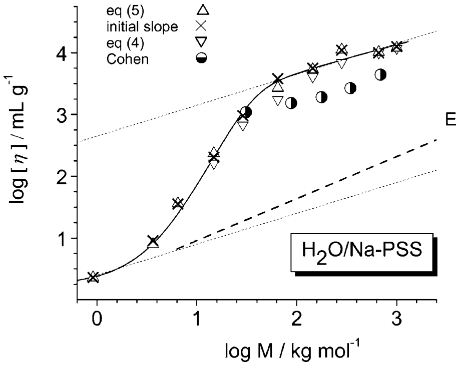

**Figure 5.** Kuhn−Mark−Houwink plot for the system $H_2O$/Na−PSS. The intrinsic viscosities in pure water were obtained by the different methods of data evaluation indicated in the graph. The solid line is drawn as a guide for the eye only; the dotted lines have a slope of 0.5. Also shown are literature data[12] reported for the same system (◑) and the [$\eta$]/*M* relation[13] for ethylbenzene/polystyrene (broken line). All data refer to 25 °C.

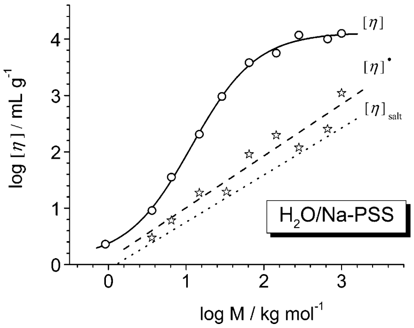

**Figure 6.** Comparison of [$\eta$], the intrinsic viscosities of the system $H_2O$/Na−PSS (Table 1), with $[\eta]^\bullet$ and with $[\eta]_{salt}$, the intrinsic viscosities in the saline solvent. Solid line, modeled by means a Boltzmann equation (cf. text); broken line, least-square fit to $[\eta]^\bullet$ (Table 1); and dotted line, taken from Figure 11.

The data obtained by means of eq 6 agree best with the model free values resulting from the initial slope. According to the present results, the Kuhn−Mark−Houwink dependence of the system $H_2O$/Na−PSS exhibits a sigmoidal shape, starting at low *M* values with a slope of $^1/_2$ and ending with the same slope at high *M* values (dotted lines). Only the literature value reported[14] for the lowest molecular weight of Na−PSS matches the present results, whereas the intrinsic viscosities of all other samples are only approximately half as large as those measured here. The most probable explanation lies in the high shear rates[12] applied by these authors. As it looks, the employed $\dot{\gamma}$ (600 s$^{-1}$) was low enough to avoid shear thinning in the case of the short chain sample but not so with the higher molecular weight material. Figure 5 also demonstrates by means of the data for the system ethylbenzene/polystyrene that the intrinsic viscosities of Na−PSS in pure water are, due to electrostatic repulsion between the individual segments of a given macromolecule, up to 2 orders of magnitude larger than that of the uncharged molecules of the same molar mass in thermodynamically good solvents.

Both relations used for the modeling of ln $\eta_{rel}$ as a function of *c* do not only yield [$\eta$] but also a further characteristic specific hydrodynamic volume, namely, $[\eta]^\pm$ (eq 5) or $[\eta]^\bullet$ (eq 6). In Figure 6 we compare $[\eta]^\bullet$ with the [$\eta$] values of Na−PSS in aqueous solutions obtained from the initial slope; the solid curve shown in this plot is a fit by means of the Botzmann equation.

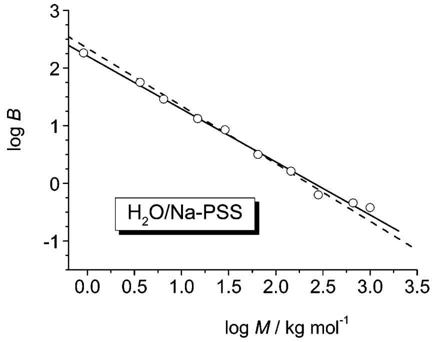

**Figure 7.** Molecular weight dependence of $B$ (eq 6). Full line, least-square adjustment with a slope of −0.92; broken line, adjusted with a fixed slope of −1.

In the molecular weight range $3 < M$ (in kg mol$^{-1}$) $< 30$ the curve can be well approximated by the relation $\log[\eta] = -0.17 + 2.1 \log M$.

In order to obtain the solid line of Figure 6 (Kuhn−Mark−Houwink relation for the solutions of Na−PSS in pure water), the parameters of eq 19 (Boltzmann equation) were adjusted to data points by means of a PC.

$$\log[\eta] = \frac{\mathrm{A2} + (\mathrm{A1} - \mathrm{A2})}{1 + \exp\left[\frac{\log M/M_0}{D}\right]} \tag{19}$$

These parameters assume the following values: A1 = 0.093, A2 = 4.116, $M_o = 1.071$, and $D = 0.415$. The $[\eta]^\bullet$ values shown in Figure 6 scatter considerably more than $[\eta]$, probably because of the too small range of $\tilde{c}$ values covered by the present experiments. These specific hydrodynamic volumes, which are approached at large reduced polymer concentration in the salt free water, are still markedly larger than those measured in the saline solvent. The dependencies of $[\eta]^\bullet$ and of $[\eta]_{\mathrm{salt}}$ on $M$ are comparable.

The third parameter required for the description of ln $\eta_{\mathrm{rel}}$ as a function of composition in the case of pure water, $B$ in the case of eq 6, corresponds to the Huggins coefficient of eq 7. Figure 7 shows how $B$ depends on $M$.

Unlike $k_{\mathrm{H}}$, which normally varies only moderately with $M$,[15] the parameter $B$ decreases rapidly as the molar mass of the polyelectrolyte rises. This behavior is again a consequence of the charge density within an isolated coil being inversely proportional to $[\eta]$ (eq 18). Within the experimental uncertainties, the present data are in agreement with an exponential decay of $B$ upon an augmentation of $M$.

**Composition Dependence of the Specific Hydrodynamic Volume.** The situation concerning the higher degree of coil shrinkage caused by the elevation of polymer concentration outlined in the preceding paragraph becomes directly visible in terms of the generalized specific hydrodynamic volume. Figure 8 shows the results in terms of the relative hydrodynamic coil volumes as a function of the reduced polymer concentration. This graph indicates that a reduced polymer concentration of less than 0.5 suffices to half the coil volume of Na−PSS 14.9 as compared with that at infinite dilution, whereas the coil volume of Na−PSS 1000 is practically still unaltered at the same $\tilde{c}$ value.

**4.2. Na−PSS in Saline Aqueous Solutions and Solutions of Uncharged Polymers.** In this section we compare the viscosities for three samples of Na−PSS in the presence of salt and that of some solutions of uncharged macromolecules in organic solvents with the behavior of Na−PSS in pure water discussed so far. All measurements reported here refer to reduced polymer concentrations below unity.

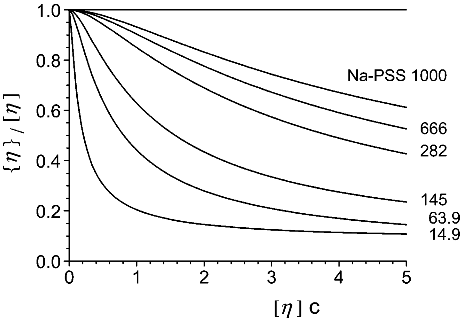

**Figure 8.** Reduced specific hydrodynamic volumes as a function of the reduced polymer concentrations for solutions of Na−PSS with the indicated molar masses in pure water as calculated by means of eq 13 and the parameters collected in Table 1.

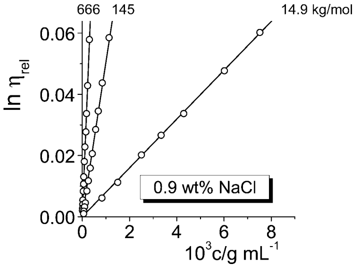

**Figure 9.** Like Figure 1 but with water containing 0.9 wt % NaCl instead of pure water. The numbers at the lines state the molar masses of Na−PSS. Lines: least-square fits.

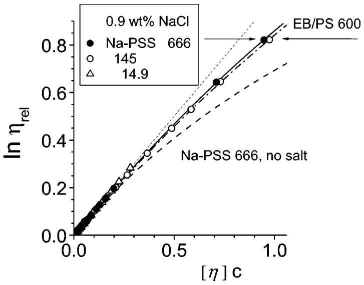

**Figure 10.** Like Figure 9 but for a much higher polymer concentration and as a function of $\tilde{c}$. Also shown are the data for Na−PSS 666 in pure water (broken line) and results[15] for the system ethyl benzene/polystyrene with a comparable molar mass (dot−dashed line).

**Composition Dependence of Viscosities.** Figure 9 shows the composition dependence of ln $\eta_{\mathrm{rel}}$ for some samples of Na−PSS in saline aqueous solution obtained at very high dilution; these data are in Figure 10 reproduced as a function of a much wider range of the reduced polymer concentration and supplemented by data published[15] for the system ethyl benzene/polystyrene. For comparison, that graph also displays the results obtained with Na−PSS 666 in the absence of salt.

The polymer concentrations of Figure 9 are extremely low and correspond to $\tilde{c}$ values of only 0.05−0.08; correspondingly the ln $\eta_{\mathrm{rel}}$ range is more than a magnitude smaller than that of Figure 10. It is particularly worthy to note that the intrinsic viscosities obtained from the slope of the data referring to such high dilution agree very well with the data resulting from the entire composition range up to $\tilde{c} \approx 1$, despite the fact that the viscosity data plotted in Figure 9 are totally unsuitable for an evaluation in Huggins plots, because of the extreme scattering of $(\eta_{\mathrm{rel}} - 1)/c$ resulting from the zero-divided-by-zero situation.

The curves shown in Figure 10 for Na−PSS 666 in the saline solvent and for polystyrene 600 in ethyl benzene are hardly

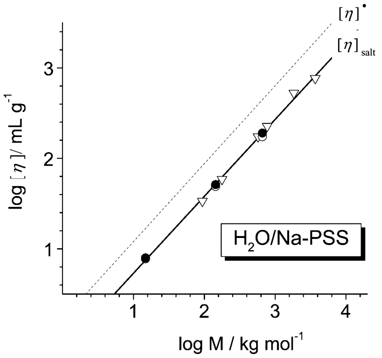

**Figure 11.** Like Figure 5 but with water containing 0.9 wt % NaCl instead of pure water. ●, Present measurements (dilute regime, Figure 9); ○, present measurements (entire regime, Figure 10); ▽, data reported in the literature[16] for water containing 0.2 m NaCl. Full line: least-square fit to all $[\eta]_{salt}$ data. Dotted line: *M*-dependence of $[\eta]^\bullet$ as shown in Figure 6.

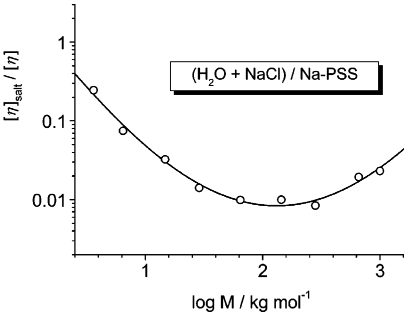

**Figure 12.** Intrinsic viscosities of Na−PSS in saline solution, normalized to the intrinsic viscosities in pure water as a function of their molecular weight. Line: fitted Gauss curve.

distinguishable. Both sets of viscosity data can also be evaluated in Huggins plots and yield the same value $k_H = 0.32$; the small shift is likely due to the differences in the Kuhn−Mark−Houwink relations of these two systems. The considerably slower increase of ln $\eta_{rel}$ with increasing $\tilde{c}$ values for the solutions of the polyelectrolyte in pure water reflects the pronounced reduction of the hydrodynamic specific volume caused by the charges of the increasing number of neighboring macromolecules.

**[η]/*M* Relations.** Figure 11 gives the Kuhn−Mark−Houwink plot for the solutions of Na−PSS in water containing 0.9 wt % NaCl (corresponding to isotonic conditions and 0.154 mol/L) together with literature values[16] for the same system but a salt concentration of 0.200 mol/L. The results of the two sets of experiments fall on the same line and their common evaluation yields the following relation if [η] is given in mL g$^{-1}$ and *M* in kg mol$^{-1}$, $\log [\eta] = -0.13 + 0.86 \log M$. The dotted line of this graph, displaying the result for $[\eta]^\bullet$ of Figure 6, manifests that the molecular weight dependence of $[\eta]^\bullet$ is very similar to that of $[\eta]_{salt}$ and fundamentally different from that of the intrinsic viscosities of Na−PSS in pure water.

Figure 12 evinces to which extent the hydrodynamically equivalent polymer coils of Na−PSS of different chain length shrink from their dimensions in pure water when the solvent is replaced by water containing 0.9 wt % NaCl. The sample of lowest molar mass loses about two-thirds of its initial volume, whereas that value goes down to about 99% as *M* rises. This situation can be rationalized by keeping in mind that the charge density within isolated coils is still comparatively high for short chains (cf. eq 18) whereas it approaches zero as *M* and consequently also [η] tend to infinity. Accordingly the efficiency of added salt increases to the extent the coils contain less "charges of their own" per volume. The Gauss curve modeling the data points shown in Figure 12 exhibits a minimum. Presently it is unclear whether there really exists a reversion in the effect of salt on coil extension because of only two data points beyond this minimum. One could, however, argue that the average distance between non-neighboring charges of a polyelectrolyte chain becomes so large for large *M* that the electrostatic repulsion does no longer contribute noteworthily to the volume an individul molecule occupies. This situation would imply that the addition of salt remains inconsequential because of the lack of electrostatic repulsion from the very beginning.

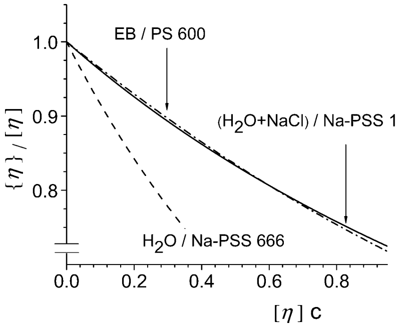

**Figure 13.** Comparison of the reduced specific hydrodynamic volumes as a function of the reduced polymer concentrations for different systems. Full line, Na−PSS 145 in water containing 0.9 wt % NaCl; dot−dashed line, polystyrene 600 kg/mol in ethyl benzene; broken line, Na−PSS 666 in pure water.

**Composition Dependence of the Specific Hydrodynamic Volumes.** Figure 13 constitutes a blowup of Figure 8 and compares the behavior of different types of systems in the range of moderate polymer concentrations up to $\tilde{c} \approx 1$. This graph shows that the coil shrinkage of the polyelectrolytes upon an increase in $\tilde{c}$ is in the presence of salt much less pronounced than in its absence.

The effect of salt can be rationalized on the basis of microphase equilibria[17,18] established between the mixture contained in the realm of the individual polymer coils with the pure solvent (water or water plus NaCl) surrounding them. The amount of salt taken up into the mixed phase according to the Donnan equilibrium[19,20] baffles the effects of the additional charges resulting from the increasing coil overlap as the polymer concentration rises. The functionalities of {η}/[η] versus $\tilde{c}$ of polyelectrolytes in saline aqueous solutions and that of ordinary uncharged macromolecules in organic solvents are practically indistinguishable.

In order to obtain more information on the concentration influences on the viscometrically decisive coil volumes we compare in Figure 14 additional literature data for solutions of uncharged polymers with the behavior of Na−PSS in the presence of salt. These results and numerous data for other systems testify to two general qualitative features: (i) The second derivative of ln η is almost always negative, no matter whether the polymer is charged or not, with the exception of solutions in thermodynamically poor solvents and (ii) for a given polymer and a given good solvent, the influences of $\tilde{c}$ on {η}/[η] decrease in all cases with increasing chain length.

Ad (i): The concentration influences on the specific hydrodynamic volume can be rationalized by considering two effects, namely, the increasing interpenetration of coils associated with an augmentation of polymer concentration and the thermodynamically governed predominance of solvent/segment or (intermolecular) segment/segment contacts. The overlap of different coils reduces the energy dissipation per molecule and the

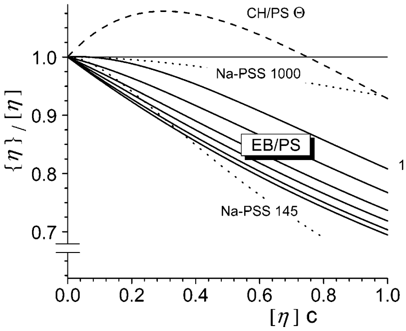

**Figure 14.** Like Figure 13 but for solutions of polystyrenes[15] (PS) with different molecular weight, in either ethyl benzene (EB) at 25 °C or in cyclohexane (CH) at the Θ temperature and two representatives of the system Na−PSS (cf. Figure 8).

increase in the number of intersegmental contacts, associated with a reduction of solvent power, forces the solute molecules to move conjointly (pull along effect[21,22]) and increases the viscosity of the system. Under thermodynamic Θ-conditions, the latter effect dominates in the region of low $\tilde{c}$ values as can be seen from Figure 14. With this special case of solvent quality, intersegmental contacts are preferred to the extent required to compensate the excluded volume contributions. Θ-conditions are normally defined by the requirement that the second osmotic virial coefficient (second member of a series expansion of the osmotic pressure with respect to $c$) be zero, irrespective of the molecular weight of the polymer. By analogy to this particular *thermodynamic* behavior, it is possible to introduce a *viscometric* Θ state, for which the second term in the power series of ln $\eta_{\mathrm{rel}}$ (cf. eq 8) vanishes, i.e., $k$ becomes 0. For typical solutions of uncharged polymers in organic solvents, this condition is equivalent to $k_{\mathrm{H}} = 0$. In contrast to the thermodynamic Θ temperature, which does not depend on $M$, the viscometric Θ temperature varies considerably with chain length. For the endothermal system cyclohexane/polystyrene it decreases markedly with increasing molecular weight;[15] one can speculate that the viscometric Θ temperature approaches Θ as $M \rightarrow \infty$. The curve shown in Figure 14 for the system cyclohexane/polystyrene refers to the thermodynamic Θ temperature and applies to all molecular weights, because the curves $k_{\mathrm{H}}$ ($T$; $M$) exhibit a common intersect[15] at this temperature.

Ad (ii): The diversification of the curves shown in Figure 14 for a given system and different molecular weights of the polymer reflects the changes in the coil dimensions of an individual macromolecule, which are for thermodynamic reasons resulting from an increase in chain overlap. For good solvents, the coils shrink from their expanded state at high dilution down to the unperturbed dimensions prevailing in the pure melt. Because of the higher concentration of segments belonging to a certain molecule within the volume it occupies, the coil shrinkage is for short chains more pronounced than for long ones. This situation implies that $\{\eta\}/[\eta]$ decreases more rapidly for low $M$ than for high $M$ as $\tilde{c}$ rises. In plots of $\{\eta\}/[\eta]$ as a function of $\{\eta\}c$ (the true coil overlap parameter) instead of $[\eta]c$ (the reduced polymer concentration) these differences become even more obvious.

## 5. Conclusions

The measurements presented here demonstrate that the analysis of the concentration dependence of the viscosities of polymer solutions in terms of ln $\eta_{\mathrm{rel}}$ versus $c$ (instead of the traditional Huggins plots or similar evaluations) provides a general facility to obtain intrinsic viscosities. The method works for aqueous solutions of polyelectrolytes in the absence and in the presence of salt as well as for solutions of uncharged polymers in organic solvents. Qualitative dissimilarities between the different systems are absent; the distinctions are of quantitative nature only. For thermodynamically sufficiently good solvents, the viscosities increase less than exponential with concentration, where these effects become larger as the solvent quality rises and as the molecular weight of the polymer falls.

The new method also provides easy access to $\{\eta\}$, the specific hydrodynamic volume at arbitrary polymer concentrations, introduced in this context. The observations described in the last paragraph signify that the coils shrink the more upon an augmentation of the polymer concentration, the better the solvent, and the shorter the chains. In the special case of thermodynamic Θ conditions, an initial rise in $\{\eta\}$ is followed by the usual decline at higher $\tilde{c}$ values.

It is much to be hoped that the new evaluation tools contribute to a better understanding of the rheological behavior of mixtures containing polyelectrolytes, particularly in view of the fact that such systems are hard to overestimate in their technical and biological importance.

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