

The Viscosity of Polyelectrolytes: Influence of counterion and solvent type

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Abstract

We study the viscosity of polystyrene sulfonate with sodium and tetrabutylammonium counterions in aqueous and organic solvent media. We find that at low concentrations, the Fuoss law ($\eta_{sp} \sim c^{1/2}$) is approximately obeyed, but at higher concentrations an exponential dependence on the polymer volume fraction sets in. These findings are discussed in terms of Fujita's free volume theory.

Charged polymers display complex rheological properties, the understanding of which lags behind that of neutral polymers.¹⁻³ Literature studies on polyelectrolyte dynamics usually focus on aqueous systems. While water is undoubtedly the most important solvent due to its biological and industrial relevance, theories make predictions for the dependence of polyelectrolyte properties on solvent dielectric constant³⁻⁶ which cannot be tested by studying aqueous solutions. The narrow solubility of common polyelectrolytes in non-aqueous media can be overcome by introducing organic counterions, which improve solubility in non-aqueous

media.^{1,7,8} Most literature data deal with dilute or modestly concentrated solutions, but recent studies have shown the emergence of unexpected behaviour at high concentrations,^{9–18} which are poorly understood.

In this letter, we study the viscosity of polystyrene sulfonate with sodium and tetrabutylammonium (TBA) counterions in different solvents. We find that the specific viscosity of solutions can be written as:

$$\eta_{sp} \simeq \left(\frac{c}{c^*}\right)^{1/2} e^{A\phi} \quad (1)$$

where c^* is the overlap concentration, which decreases with increasing dielectric constant of the media, and A is a parameter that depends on the solvent.

The specific viscosity of NaPSS and TBAPSS in DI water is plotted as a function of concentration (c), where c is expressed in moles of monomers per dm^3 in Figure 1a. At low concentrations, both polymers show similar viscosities, which follow the Fuoss law ($\eta_{sp} \sim c^{1/2}$), as indicated by the black line. For $c \gtrsim 0.1$ M, the two datasets diverge and the $\eta_{sp} \sim c^{1/2}$ scaling is no longer obeyed. The Fuoss law, first established experimentally for solutions below or not far above the overlap concentration in salt-free solvents^{20,21} was derived theoretically by de Gennes and co-workers for the semidilute regime.²²

The overlap concentration c^* is estimated as $c^* \simeq 0.006$ M by fitting the data with $\eta_{sp} \geq 1$ to $\eta_{sp} = (c/c^*)^{1/2}$. In figure 1b, the specific viscosity normalised by $(c/c^*)^{1/2}$ (i.e. the black line in part a) is plotted as a function of polymer volume fraction. The relative deviation from the Fuoss law is seen to be similar for the Na and TBA salts of PSS, and to approximately follow an exponential form (see inset). An analogous plot using the mass fraction (x) instead of the volume fraction (ϕ), shown in the supporting information gives better agreement at low concentrations but greater deviation at high ones. The specific viscosity for the two salts is approximately described by: $\eta_{sp} \simeq (c/c^*)^{1/2} e^{14\phi}$. The term in brackets corresponds to the scaling prediction and the exponential term is not, to the best of our knowledge, directly predicted by any polyelectrolyte theory.^{3,5,23,24} We return to the interpretation of this term below.

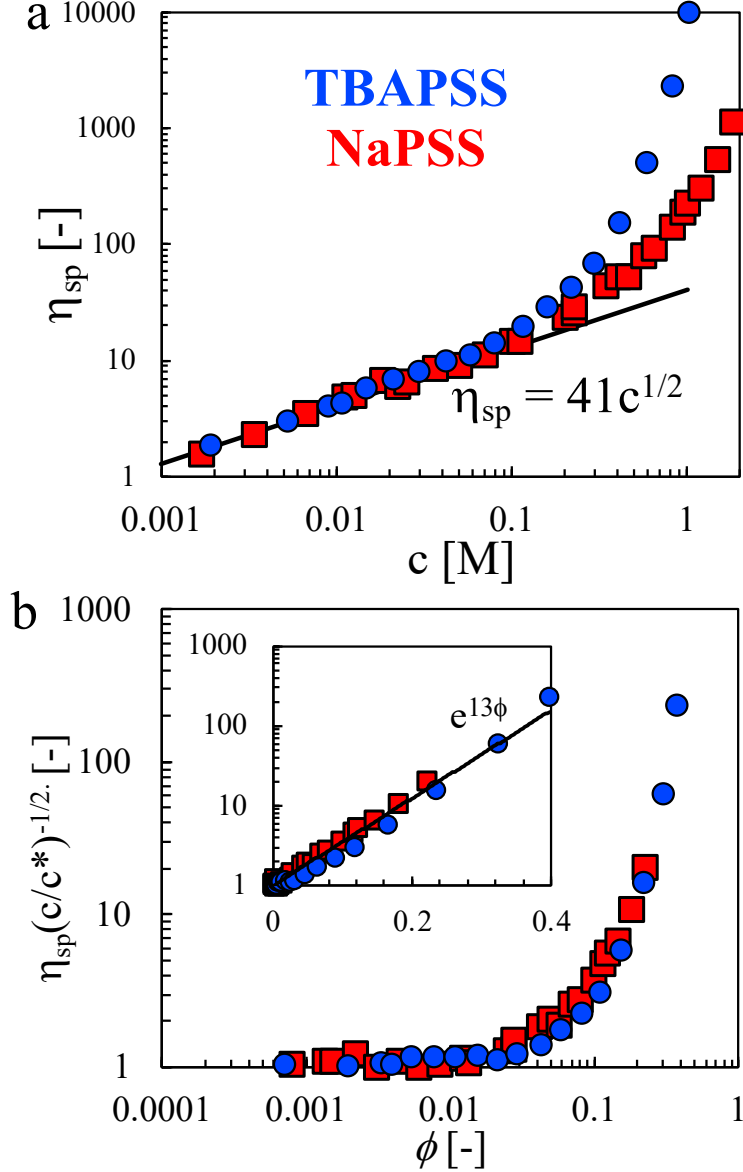


Figure 1: a: specific viscosity of NaPSS and TBAPSS in water as a function of number concentration of repeating units per unit volume. Line is scaling prediction ($\eta_{sp} \propto c^{1/2}$) with the pre-factor as a fit parameter. b: η_{sp} normalised by scaling prediction ($\eta_{sp} = (c/c^*)^{1/2} \simeq 41c^{1/2}$) as a function of the polymer volume fraction (ϕ). Inset shows the data in log-lin representation, line is exponential fit forced to 1 at $\phi = 0$. Data for NaPSS are from¹⁹ and refs. therein.

The specific viscosity of TBAPSS in different solvents is plotted as a function of concentration (c) in figure 2a. At low concentrations, solvents with high dielectric constants display the highest specific viscosities, and the Fuoss law is followed. For the lower permittivity solvents, the $\eta_{sp} - c$ exponent displays values $\simeq 0.6 - 0.8$. At high concentrations, the

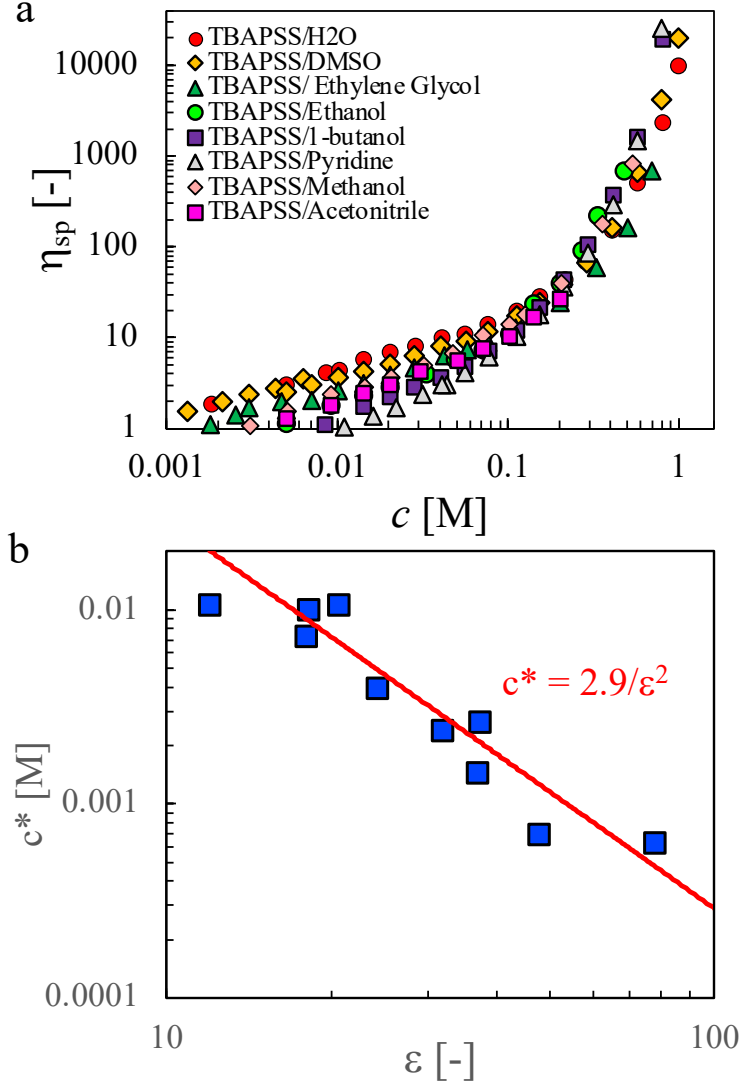


Figure 2: a: Specific viscosity of TBAPSS ($N = 1354$) solutions in different solvents, indicated on the legend. b: Overlap concentration, calculated by fitting $\eta_{sp} > 1$ data to $\eta_{sp} = (c/c^*)^{1/2}$, as a function of solvent's dielectric constant (ϵ). Line is a power-law fit excluding the pyridine ($\epsilon \simeq 12$) datum.

lower permittivity solvents display higher viscosities. The overlap concentration is plotted as a function of dielectric constant in figure 2b. If the pyridine datum is ignored, the c^* data scale inversely with the square of the dielectric constant of the solvent, in agreement with the trends observed for two poly(ionic liquids).^{1,7,25} As expected, for higher permittivities, polymer chains are more expanded due to the larger fraction of dissociated counterions, see¹ for a discussion.

Figure 3a plots the viscosity of TBAPSS in various solvents using the same representation as in figure 1b over the entire volume fraction range studied. An exponential dependence can be observed for all solvents studied. The exponent is seen to depend on the solvent. Solvents with lower dielectric constant such as pyridine ($\epsilon \simeq 12$), 1-butanol ($\epsilon \simeq 18$) and ethanol ($\epsilon \simeq 28$) display stronger exponents ($\sim e^{26\phi}$) than the high permittivity solvents such as water ($\epsilon \simeq 80$) or DMSO ($\epsilon \simeq 48$), for which a weaker relation of $\sim e^{14\phi}$ is observed.

The scaling theory derives the Fuoss law under the assumption that the monomeric friction coefficient ζ is concentration-independent, which is a good approximation for low polymer concentrations. More generally, the viscosity of a polymer solution is expected to follow: $\eta_{sp} = \zeta(\phi)\eta_{sp,0}$, where $\eta_{sp,0}$ is the specific viscosity with a constant monomeric friction factor. Fujita's free volume theory,²⁶ predicts:

$$\zeta(\phi) \sim e^{-1/f(\phi)} \quad (2)$$

where f is the fractional free volume of the solution:

$$f = f_p^0\phi + f_s^*(\phi)(1 - \phi) \quad (3)$$

where f_p^0 is the fractional free volume of the polymer and $f_s^*(\phi)$ is the fractional free volume of the solvent at a polymer volume fraction ϕ . Experimentally, $f_s^*(\phi)$ is found to decrease sharply from its value for the pure solvent case (f_s^0) to a constant value (f_s^+) in solutions of modest or high polymer volume fractions, see.²⁶

Assuming that the solvent free volume term dominates in eq. 3 for the ϕ -range studied here, and equating $\eta_{sp,0}$ with $(c/c^*)^{1/2}$,^{27,28} we plot of $\eta_{sp}(c^*/c)^{1/2}$ as a function of $1/(1 - \phi)$ in figure 3b, which approximately follows an exponential relationship, giving fractional free volumes of $f_s^+ \simeq 0.1$ for the high dielectric constant solvents and $f_s^+ \simeq 0.05$ for the lower ϵ solvents, see table 1. Eqs. 2-3 provide a rational for the result of figure 1b: the change in $\zeta(\phi)$ arises primarily from the decrease in the contribution of the solvent to the fractional

free volume (f) of the solution, and is therefore independent of the counterion type for a fixed value of ϕ .

Estimates for the fractional free volume of the solvents based on applying the Doolittle equation to viscosity data²⁹⁻³² are compiled in table 1. These f_s^0 values are higher than the f_s^* values needed for Eq. 2-3 to account for our experimental results. This is consistent with Fujita and Einaga’s finding that for concentrated neutral polymers $f_s^+/f_s^0 \simeq 2.2 - 4.5$. The ratios for our data H₂O ($f_s^+/f_s^0 \simeq 2.8$), EG ($f_s^+/f_s^0 \simeq 1.5$), methanol ($f_s^+/f_s^0 \simeq 6$), ethanol ($f_s^+/f_s^0 \simeq 6.8$) and butanol ($f_s^+/f_s^0 \simeq 6.3$)³³ are in a similar range, thus suggesting free volume effects as a plausible explanation for the exponential dependence of the viscosity. However, we cannot rule out the influence of other mechanisms.

Measurements of the chain’s self diffusion coefficient (D) in concentrated polyelectrolyte solutions would be useful towards understanding the results reported here. The influence of ζ on D and η_{sp} cancels when the product $\eta_{sp}D$ is considered. For example, Lopez et al showed that $\eta_{sp}D$ for NaPSS in DI water follows the scaling predictions well, even though η_{sp} and D do not.⁹ Diffusion data for the TBAPSS system in different solvents could help resolve whether the exponential term in eq. 1 arises from a ϕ -dependent ζ . Studies on the temperature dependence of the viscosity of polyelectrolyte solutions, which we have been unable to perform due to evaporation, would further allow us to understand the extent to which the concentration dependence of ζ can be accounted for in terms of free volume. Presently, some observations in this report can only be tentatively explained. The supporting information includes a tabulation of all viscosity data, open for further analysis. We hope that the results presented here will stimulate research on concentrated polyelectrolyte solutions.

Chemicals: NaPSS was purchased from Polymer Standard Service (Mainz, Germany). Details of the molar mass determination can be found in¹⁹ and.⁹ TBABr was purchased from Sigma-Aldrich. The solvents were purchased from Sigma-Aldrich or VWR. The solvents used and their associated properties are provided in table 1. Deionised water was from a milli-Q

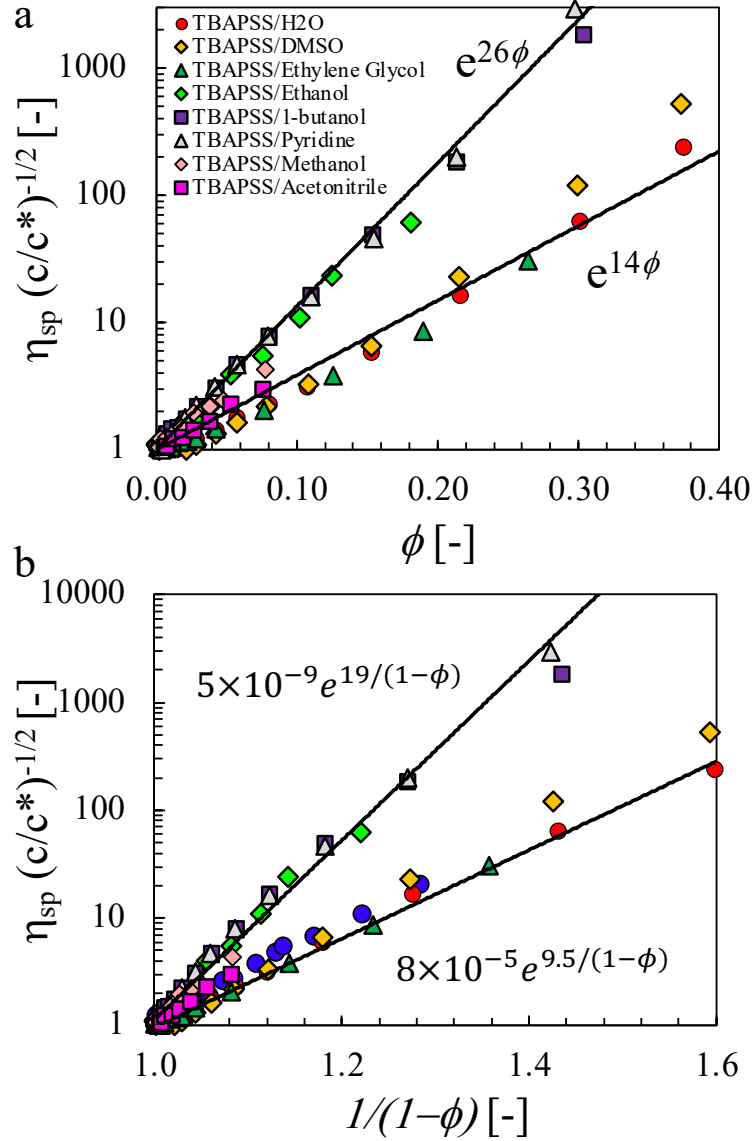


Figure 3: a: Specific viscosity normalised by $(c/c^*)^{1/2}$, as a function of polymer volume fraction. b: same plot as part a but as a function of $1/(1-\phi)$, following eq. 3. Symbols have the same meaning as in part a.

source, it had a conductivity of $2 \mu\text{S}/\text{cm}$ after being exposed to air. The Spectra/Por dialysis tubings used had a MWCO of 12-15 kDa and were procured from VWR.

Polymer and solution preparation: TBAPSS was prepared by dialysing NaPSS with a 50 molar excess of TBABr against DI water until the conductivity of the bath did not increase beyond the value of DI water when exposed to atmosphere for at least 24 hours. Solutions were freeze dried under a vacuum (~ 0.4 mbar) and the resulting polymer was

used to prepare the solutions. Conductivity measurements were carried out with a Mettler Toledo S47 SevenMulti conductivity meter.

Table 1: Solvent properties and TBACMC parameters. Values for ϵ are taken from³⁴ and values of ρ_s , Λ , the solvent density and conductivity at $T = 25$ °C are measured by us. ν is the partial molar volume of TBAPSS. ^a extrapolated from BuOH, PrOH and EtOH. ^b We use a value of $\nu = 0.91$ mL/g. For acetone and IPA, only solutions close to c^* were studied, the choice of ν does not have a significant effect on c^* .

Solvent	ϵ [-]	ρ_s [g/mL]	Λ [μ S/cm]	ν [mL/g]	c^* [mM]	f_s^0 [-]	f_s^+ [-]
Water	80.1	0.997	2	0.9068	0.6	0.29	0.10
DMSO	47.2	1.1	0.5437	0.9105	0.53	-	0.091
Ethylene Glycol	41.4	1.11	0.0836	0.9197	1.7	0.16	0.10
Acetonitrile	36.6	0.786	0.1358	^b	2.9	-	0.067
Methanol	33	0.792	0.8225	^b	2.2	0.32 ^a	0.058
Ethanol	25.3	0.789	0.1475	^b	3.8	0.338	0.050
Acetone	21	0.784	0.301	^b	10.1	-	-
Isopropanol	20.2	0.786	0.0247	^b	9.4	-	-
1-Butanol	17.8	0.810	0.1795	0.9178	7.2	0.34	0.056
Pyridine	13.3	0.982	1.4525	0.9065	9.9	-	0.053

Rheology: The rheology measurements were carried out on a stress-controlled Kinexus-pro rheometer (Netzsch). A cone-plate geometry with a 40 mm diameter ($\theta = 1^\circ$, sample volume $\simeq 0.35$ mL) was used. A solvent trap filled with $\simeq 400$ μ L of the respective solvent was used to prevent evaporation. The measurements were carried out at 25 °C. The rheometer was frequently calibrated by conducting a 20 minute torque mapping in air.

Density measurements: The density measurements were performed using the Anton Paar DMA 5000 densitometer with a least count of 10^{-6} g cm⁻³. The accuracy of the instrument was checked using DI water.

Rolling-ball viscosimetry: A Lovis 2000 M viscometer (Anton Paar) was used for samples with low viscosity. The capillary diameter was 1.59 mm. Details on the calibration and data analysis can be found in.¹⁹

Acknowledgement

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Supporting Information Available

Viscosity and density data are tabulated in the supporting information.

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$c_e \simeq 1.5 \text{ M}$,²⁸ so that entanglement effects should be small in over the concentration range studied. Thus, we identify $(c/c^*)^{1/2}$ with $\eta_{sp,0}$.

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- (32) When the fractional free volume is not available for $T = 25 \text{ }^\circ\text{C}$, we assume f_s varies with temperature as $\Delta f_s = \alpha \Delta T$, where α is the thermal expansion coefficient.
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