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Polyelectrolyte effect in perfluorosulfonated ionomer solutions

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Ubbelohde viscosity measurements were performed on dilute solutions of perfluorosulfonated ionomers (PFSI) in various solvents exhibiting quite different dielectric constants. With aliphatic alcohols as solvents an increase of the reduced viscosity with dilution is evident. This effect is analogous to the so-called 'polyelectrolyte effect' observed for highly charged ionic polymers in polar solvents. The polyelectrolyte effect increases with the dielectric constant for alcohols, is similar in water and in methanol solutions, and disappears for high polarity solvents. This evolution is discussed in terms of an increase of the electrostatic persistence length. The viscosimetric behaviour of PFSI solutions is shown to fit well with the Liberti–Stivala equation.

(Keywords: viscosity; ionomer solutions; perfluorinated ionomer)

Introduction

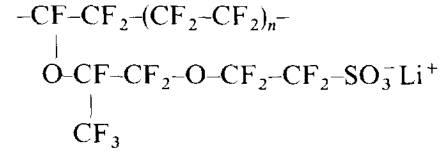
It is only a few years since solutions of high equivalent weight perfluorosulfonated ionomers (PFSI) were first prepared. For example, Nafion 117 (E.I. Du Pont de Nemours) is dissolved by heating for 1 h at 250°C under high pressure in a mixture of water and ethanol[1,2]. While many studies have been concerned with the native membrane[3], very little work has been devoted to PFSI solutions. Small-angle X-ray and neutron scattering experiments have given a first insight into the structure of these colloidal solutions[4–6]. The basic particles were shown to be rod-like with a radius of around 20 Å. The rod consists of several main chains packed close together with the terminal ionic groups of the side chains disposed along the surface.

Moore and Martin[7] studied the concentration dependence of the viscosity of a 50/50 water/ethanol solution of Nafion 117 and found a dramatic increase of the reduced viscosity upon dilution; they attributed this phenomenon to polyelectrolyte behaviour. The concentration range where the effect occurs and its intensity are surprising: although solutions of both polyelectrolyte and model ionomer usually exhibit the polyelectrolyte effect at concentrations ranging from 0.05 to 0.5% volume fractions[8–10], the concentration range for PFSI solutions is 10 times lower. Moreover, the intensity of the effect appears to be 10 times greater compared to other ionomer solutions.

In this communication, the effect of nature of solvent on the PFSI solution viscosity will be examined in order to determine the driving forces of the polyelectrolyte effect.

Experimental

Materials. The long pendent chain perfluorosulfonated ionomer used for the viscosity measurements was Nafion 117 membrane (E.I. Du Pont de Nemours). Its chemical formula is:



$$\begin{array}{l} -\mathrm{CF}-\mathrm{CF_2}-(\mathrm{CF_2}-\mathrm{CF_2})_n- \\ \quad | \\ \quad \mathrm{O}-\mathrm{CF}-\mathrm{CF_2}-\mathrm{O}-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{SO_3^-}\,\mathrm{Li^+} \\ \qquad\quad | \\ \qquad\quad \mathrm{CF_3} \end{array}$$

with $n \approx 6.5$ corresponding to an equivalent weight of 1100 g/eq. The as-received membranes were first cleaned in boiling nitric acid in order to obtain colourless materials. The polymer was then neutralized overnight with 1 M LiCl solution and dissolved in an autoclave in a water/ethanol (50/50) mixture at 250°C for 1 h, according to the standard procedure[1]. The method used to obtain solutions in pure solvent from the hydroalcoholic solution was to evaporate the solvent, crush the residual particles and redissolve the white powder obtained in the desired solvent[11]. However, for water and formamide, dialysis was used.

All the solutions were either filtered or centrifuged in order to remove the largest undissolved particles before introduction into the viscosimeter. The concentration was measured by evaporation and weighing. All the solvents were reagent grade and were used as received.

Apparatus. An Amtec VCD Ubbelohde viscosimeter was used with three different capillary sizes (0.36, 0.38 and 0.45 mm) depending on the viscosity of the solvent. The temperature was regulated at 25.0±0.05°C. The reduced viscosity, η_{red}, is defined as the specific viscosity

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divided by the concentration:

$$\eta_{\mathrm{red}}=\frac{\eta_{\mathrm{sp}}}{c}=\frac{t-t_0}{t_0}\frac{1}{c}$$

where c is the concentration ($\mathrm{g\,dl^{-1}}$), and t and t_0 are the measured flowing times of the polymer solution and of the pure solvent, respectively.

Results and discussion

Figure 1 presents the evolution of the reduced viscosity *versus* concentration for four alcoholic solutions of Nafion 1100 $\mathrm{Li^+}$. A polyelectrolyte effect is clearly observed. The most pronounced increase of η_{red} at low concentrations is observed with methanol and the phenomenon becomes less and less marked when heavier aliphatic alcohols are used, such as ethanol, 2-propanol and 1-butanol. This decrease of the polyelectrolyte effect can easily be attributed to the decrease of the dielectric constant from 32.7 to 17.5. The influence of the dielectric constant was already suggested for lightly sulfonated polystyrene solutions[7].

In order to examine the effect of the dielectric constant of the solvent, the viscosimetric behaviour of PFSI solutions were investigated in water and amides, which are solvents presenting higher ε values. The influence of the dielectric constant on solution viscosity is shown in *Figure 2* using *N,N*-dimethylacetamide (DMA), water, formamide (FA) and *N*-methylformamide (NMF) ($\varepsilon = 37.8$, 78.4, 111 and 182.4, respectively) as solvents. The polyelectrolyte effect is 10 times greater for DMA solutions compared to methanol, of the same order of magnitude for water solutions, and does not appear for FA and NMF solutions. The results for each solvent are listed in *Table 1* and show that the polyelectrolyte effect increases with increasing the dielectric constant up to $\varepsilon \approx 30$, is rather constant between $\varepsilon = 30$–80 (except for DMA) and then disappears for $\varepsilon > 100$. Several solvent parameters, such as solubility parameters and interfacial energies, were checked and could not explain the observed behaviour. The particular affinity of PFSI for DMA as a solvent was also evident when studying the swelling properties of PFSI membranes[12].

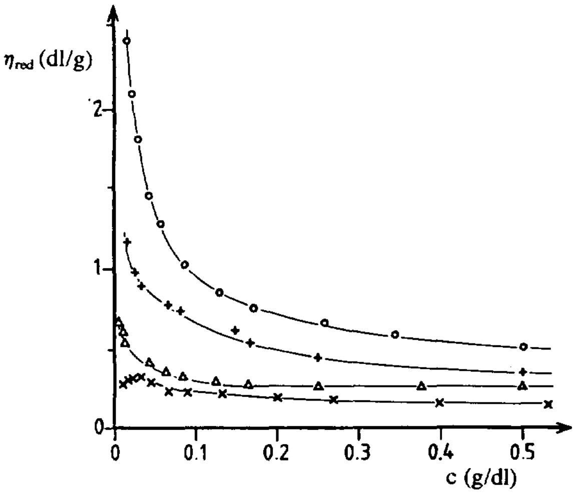

Figure 1 Reduced viscosity *versus* concentration of Nafion 1100 $\mathrm{Li^+}$ dilute solutions in: ○, methanol; +, ethanol; △, 2-propanol; ×, 1-butanol

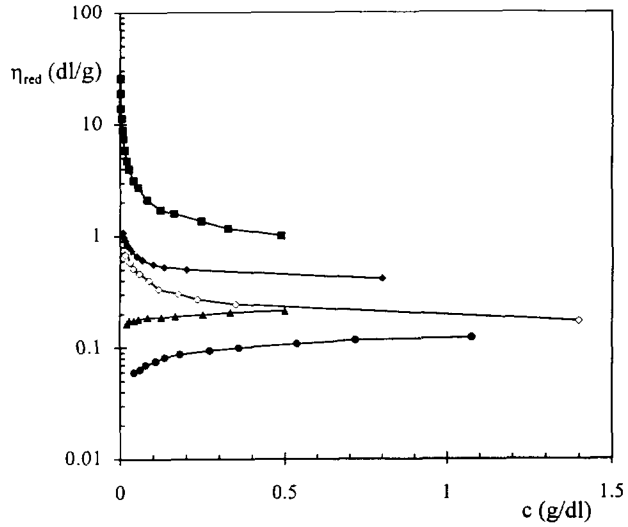

Figure 2 Semi-logarithmic plot of the reduced viscosity *versus* concentration of Nafion 1100 $\mathrm{Li^+}$ dilute solutions in: ■, DMA; ◆, water; ◇, 50/50 water/ethanol mixture; ▲, formamide; ●, NMF

Table 1 Solvents used for viscosity measurements with their dielectric constant, reduced viscosity and intensity of the polyelectrolyte effect, determined as the ratio of the maximum reduced viscosity measured (around $0.01\,\mathrm{g\,dl^{-1}}$) to the reduced viscosity at $0.5\,\mathrm{g\,dl^{-1}}$

Solvent	Dielectric constant	η_{red} at $0.5\,\mathrm{g\,dl^{-1}}$ ($\mathrm{dl\,g^{-1}}$)	Intensity of the effect
1-Butanol	17.51	0.27	1.5
2-Propanol	19.92	0.30	2
Ethanol	24.55	0.35	3.5
Methanol	32.70	0.52	5
N,N-Dimethylacetamide	37.78	1.00	25
Water	78.39	0.45	2.5
Formamide	111.00	0.21	no effect
N-Methylformamide	182.40	0.11	no effect

The effect of the dielectric constant of the solvents can be examined in terms of the persistence length within Odjik's theory[13]. The polyelectrolyte effect is attributed to an extension of the rod-like particles and therefore to an increase of the total persistence length ($L_{\mathrm{t}} = L_{\mathrm{p}} + L_{\mathrm{e}}$). The bare persistence length, L_{p}, corresponding to the persistence length of the neutral analogous polymer, was recently estimated to be around 100 Å from small-angle scattering studies in the presence of an excess of added salt[7]. The electrostatic persistence length, L_{e}, can be estimated using Odjik's theory as[13]:

$$L_{\mathrm{e}}=\frac{1}{16\pi l_{\mathrm{B}} dc}$$

where d is the linear charge density, c is the polymer concentration expressed in number of monomers per cubic angstrom, and l_{B} is the Bjerum length defined as:

$$l_{\mathrm{B}}=\frac{e^2}{4\pi\varepsilon_0\varepsilon kT}$$

The electrostatic persistence length is then proportional to ε/c. For a given solvent, L_{e} increases when the polymer concentration is decreased and therefore the polymer coil extends up to a complete extension. At high dielectric constant, L_e is very large, the particle can be considered as already stretched and consequently no effect appears. From the radius and the specific volume, d is estimated to be around 0.7 Å/charge. L_e can then be calculated and varies from 225 Å in butanol to 3400 Å in NMF. This phenomenological approach is in first approximation consistent with the results obtained for PFSI solutions, but it is difficult to go further in the analysis since the applicability of the worm-like chain theory to particles presenting radii of the order of 20 Å is not straightforward. Odijk's theory includes the counterion condensation concept through the charge parameter $\lambda = l_B/d$. The fraction of uncondensed cations is $1/\lambda$ for λ values larger than unity[14]. This fraction is very small in PFSI solutions and decreases from 22.7% for NMF solutions to 2.2% for butanol solutions. But these theories are based on the hypothesis that the polyion can be replaced by an infinite line charge and this hypothesis is probably not verified for large values of the radius. The main problem of the preceding interpretation is that the viscosity of stretched particles is expected to be large compared to other solvents, but the viscosity of NMF solution appears to be very low (*Figure 2*). Moreover, the evolution of the reduced viscosity, for example at 0.5 g dl^{-1} (*Table 1*), with the dielectric constant of the solvent presents a maximum which is unexplained.

The polyelectrolyte effects in ethanol and in water are 10 times lower and the concentrations at which the effects occur are 10 times greater compared to the results reported by Moore *et al.*[7] in 50/50 water/ethanol mixture. A synergic effect comparable to that used to explain the dissolution in such mixtures could be evoked, but we measured the viscosity in 50/50 water/ethanol mixture and found it to be of the same order as for water and ethanol solutions (*Figure 2*). Therefore no special effect is observed for the mixture as reported by Moore *et al.*

For salt-free polyelectrolyte solutions, an empirical analysis using the Fuoss equation[15]

$$\eta_{\mathrm{red}} = \frac{A}{1 + B\sqrt{c}} + D$$

is usually performed in order to extract the intrinsic viscosity by extrapolation to zero concentration ($[\eta]_{c=0} = A + D$). This data treatment applied to PFSI solutions leads, in most cases, to negative values for the intrinsic viscosities. A similar difficulty has often been met in polyelectrolyte solutions, and several modified Fuoss equations have been proposed, such as the Liberti–Stivala equation[16]:

$$\frac{\eta_{\mathrm{sp}}}{c} = [\eta]_\infty + k\frac{[\eta]_\infty}{\sqrt{c}}$$

where $[\eta]_\infty$ represents the intrinsic viscosity when the charges are shielded to the extent that the macromolecule behaves as a non-charged chain and is determined from the extrapolation to infinite concentration. $[\eta]_\infty$ corresponds to the D parameter in the Fuoss equation.

The plot of η_{sp}/c *versus* $c^{-1/2}$ is presented in *Figure 3* for five different solvents. The viscosity of PFSI solutions is well represented by the modified Fuoss equation since a linear behaviour is obtained, even for solutions presenting no polyelectrolyte effect. The extrapolation to infinite concentration shows that the same limit is obtained for most of the solvents, except water. The difference between PFSI solutions in water and those in other solvents was already evidenced by small-angle scattering experiments[4–6], ^{19}F n.m.r.[17] and electron spin resonance studies[18]. This difference was attributed to a larger interfacial energy which leads to larger radii for the rod-like particles and to the initiation of aggregation.

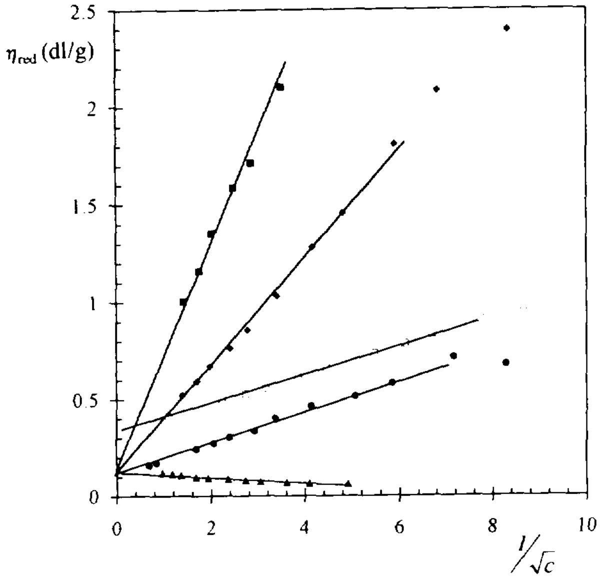

Figure 3 Reduced viscosity *versus* $c^{-1/2}$ of Nafion 1100 Li$^+$ solutions: ■, DMA; ◆, methanol; □, water; ●, 50/50 water/ethanol mixture; ▲, NMF

Conclusions

A polyelectrolyte effect for PFSI solutions was evident in most of the polar solvents. The effect was shown to increase with the dielectric constant of the solvent for low values of ε and to disappear for large values of ε. This evolution can qualitatively be interpreted in terms of the persistence length theory as a transition from a worm-like chain to a rigid chain, but the very low values of the reduced viscosity for solvent presenting high dielectric constants cannot be explained. It would be interesting to confirm the effect of the dielectric constant by studying model polyelectrolytes, such as sulfonated polystyrene, in order to check the disappearance of the polyelectrolyte effect for solvents with high dielectric constant depending on the contour length (i.e. molecular weight). The viscosimetric behaviour of PFSI solutions is shown to fit well with the Liberti–Stivala equation.

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