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Ionomers in solution: 1. Viscometric and chromatographic studies in cononsolvent and cosolvent mixtures

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The viscosity and elution behaviour of polystyrene sulfonate ionomers with varying ionic content has been studied in the pure solvents chloroform (CHL), tetrahydrofuran (THF), dioxan (DIO), ethyl acetate (EA) and dimethylformamide (DMF) as well as in their cononsolvent mixtures CHL/THF (50 : 50), DIO/CHL (75 : 25) and in the cosolvent mixture EA/DMF (50 : 50). In the pure solvents with low dielectric constant the reduced viscosities of ionomers are lower at low concentrations and higher at moderate ones than the respective viscosities of the polystyrene precursor. These results can be explained by formation of intramolecular and intermolecular associations. Moreover, differences in viscosity with the precursor are greater the higher the ionic content of the ionomer, and they are also enhanced in the cononsolvent mixtures. In contrast, ionomers with the highest ionic content behave in DMF as polyelectrolytes. This trend is weakened in the presence of EA, which seems to interact strongly with ionomers; the higher their ionic content the greater is this interaction. Moreover, whereas the ionic part of ionomer is preferentially solvated by EA, the hydrocarbonated part is solvated by DMF. Secondary exclusion mechanisms invert the order in elution volumes of ionomers when changing the eluent and/or the chromatographic gel. © 1997 Elsevier Science Ltd.

(Keywords: polystyrene sulfonate ionomers; cosolvent mixtures; cononsolvent mixtures)

INTRODUCTION

Ionomers can be defined as macromolecules containing a small percentage of ionic groups (typically less than 10 mol%) chemically bound and distributed in non-ionic backbone chains. In contrast to polyelectrolytes, where major interest has been concentrated on the study of their solution properties[1,2], in the case of ionomers attention has been focused on their properties in the solid state[3], with few publications on their properties in solution, despite the properties of solid ionomers depending on the solvents used during their preparation[4]. The addition of charged groups to a non-polar chain can drastically modify its properties. As an example, the tensile strength of an ionomer and its miscibility with other polymers can be greatly increased[3,5–8]. The presence of low levels of charged groups also has large effects on the properties of the polymer when it is in solution. Some of these novel effects have led to new applications of ionomers: these range from adhesives and compatibilizers for oil-based and gas drilling fluids to viscosity modifiers and stabilizers[5]. The aim of this paper is a better understanding of the properties of ionomers in solution by using cononsolvent[9] and cosolvent mixtures[10,11].

In single non-polar solvents, ionomers such as sulfonated polystyrene are in the form of ion pairs, and because of the attraction between ion pairs tend to form aggregates. However, whereas at low ionomer concentrations the reduced viscosities of ionomer solutions are lower than those of the polystyrene precursor[12], due to the dominant intramolecular ion pair association, at high ionomer concentrations the reduced viscosities of ionomers are larger than those of polystyrene, intermolecular ion pair association now being the dominant effect. Both intra- and intermolecular association effects are of course enhanced with increasing ion content. Regarding solvent mixtures, the cononsolvency phenomenon appears when a macromolecule is dissolved in a mixture of two good solvents (usually two non-polar solvents, both with low dielectric constants) with negative excess free energy ($G^E < 0$). Under these conditions, the favourable interactions between the components of the solvent mixture make the solvent mixture behave as a poor solvent for the polymer, reducing its dimensions, as shown for polystyrene in its cononsolvent mixtures tetrahydrofuran (THF)/chloroform (CHL) and 1,4-dioxan (DIO)/CHL[13]. In this paper the behaviour of sulfonated polystyrene with different ion contents in the above cononsolvent mixtures is compared to that of the polystyrene precursor and to those in the pure solvents.

In contrast to the above, ionomers behave as polyelectrolytes in polar solvents, and diverse experiments[14–17] show the parallelism between the former solutions and the polyelectrolyte/water ones[1,2]. Thus, the reduced viscosities of ionomers increase with decreasing polymer concentration[12], and this polyelectrolyte character is enhanced by increasing ion content. When a polymer is dissolved in a mixture of two poor solvents (generally a polar one plus a non-polar one) with $G^E > 0$

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the unfavourable interactions between the components of the solvent mixture make the solvent mixture behave as a good solvent for the polymer, increasing its dimensions with respect to those in the pure solvents. This is the cosolvency phenomenon, manifested for polystyrene by the mixture dimethylformamide (DMF)/ethyl acetate (EA)[9]. The polyelectrolyte properties of ionomers in a polar solvent as opposed to the cosolvent ones make it interesting to study the behaviour of sulfonated polystyrene with different ion contents in the above cosolvent mixture. The results obtained from such a study are reported in this paper and compared to those for the polystyrene precursor and to those in the pure solvents.

EXPERIMENTAL

Materials

Sulfonated polystyrene samples were kindly supplied by Exxon Research and Engineering Co. (New Jersey, USA). They were prepared by sulfonation of a standard polystyrene (from Polymer Laboratories Ltd) with narrow molecular weight distribution ($I \leq 1.05$) and $M_W = 105\,000\,\mathrm{g\,mol^{-1}}$. Their ionic contents, as stated by the supplier, were 0.62, 1.38 and 3.18 mol%.

Methods

Reduced viscosities in diverse solvents for uncharged and charged polymers were performed with an AVS440 automatic Ubbelhode viscometer from Schott Gërate (Hofheim, FRG) at 25.0°C. Size exclusion chromatography (s.e.c.) measurements were carried out at room temperature on Waters LC equipment as described elsewhere[18,19]. Three μ-Styragel 10^3, 10^4 and 10^5 Å columns were used with THF and THF/CHL mixtures as eluents, and a Spherogel TSK PW4000 column from Beckman Instruments (Galway, Ireland) with an EA/DMF mixture as the eluent.

RESULTS AND DISCUSSION

The viscosity results of S–xSSNa ($M_w \approx 105\,000$) ionomers in the low-polarity solvents THF, CHL and DIO and in the cononsolvent THF/CHL (50/50 v/v) and CHL/DIO (75/25 v/v) mixtures are shown in *Figure 1*.

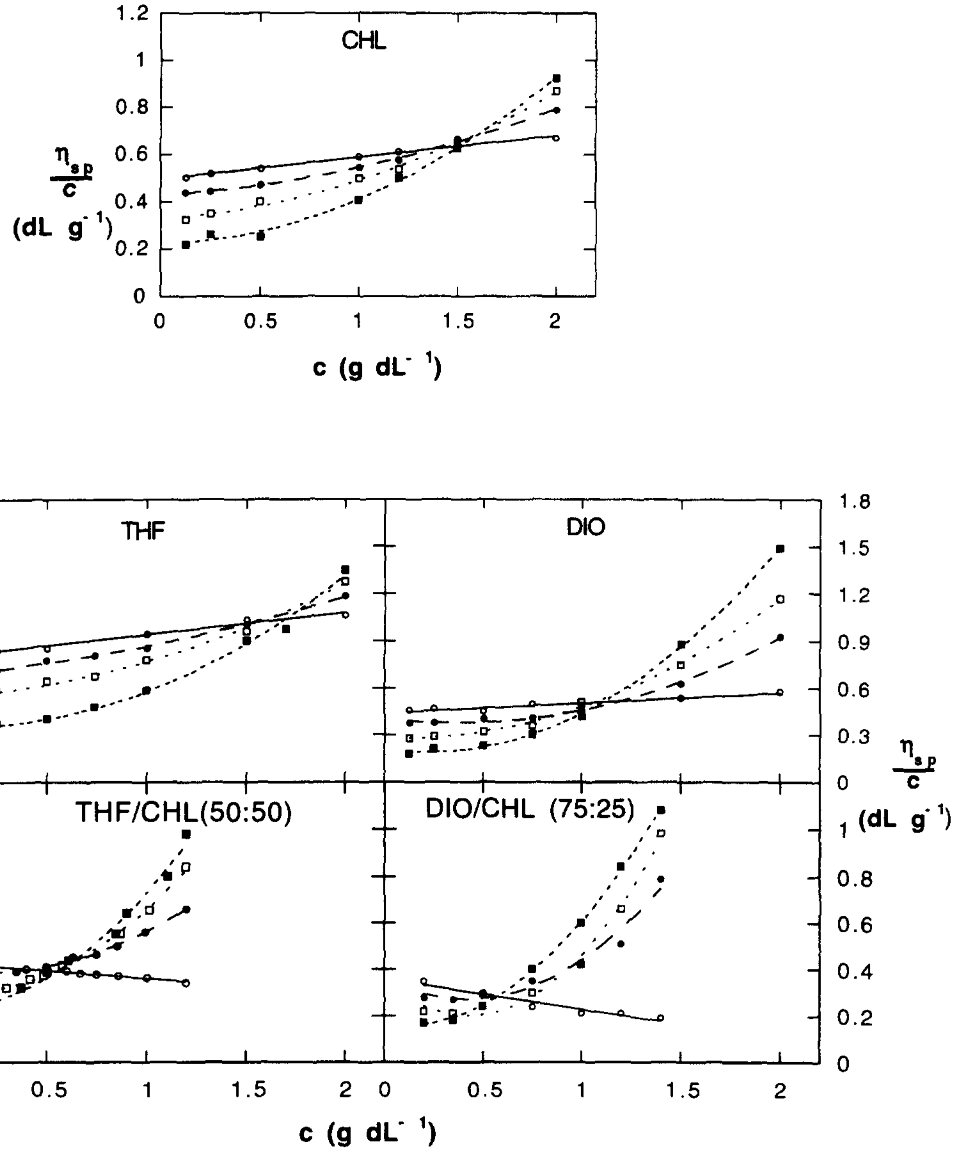

Figure 1 Dependences on polymer concentration of reduced (η_{sp}/c) viscosities in the pure solvents and cononsolvent mixtures shown for S–xSSNa ionomers with the following ionic contents (mol%): ○, 0; ●, 0.62; □, 1.38; ■, 3.18

The above ionomer nomenclature is based on that proposed by Eisenberg[2] where S stands for polystyrene and xSSNa indicates the x mole fraction of sodium styrenesulfonate. The results for pure solvents in *Figure 1* agree with those in the literature[12,20]. At low polymer concentrations the reduced viscosities of ionomer solutions were lower than those of S, and, as for other similar results in low dielectric constant media, are interpreted in terms of intramolecular ion pair association[12,21–24]. In contrast, at high polymer concentrations the viscosities of ionomers were higher than those of the S precursor due to intermolecular associations, and increase with increasing polymer concentration. Both effects are of course enhanced with increased ionic content of the ionomer, as shown in *Figure 1* or even better in *Figure 2*, where a decrease in the intrinsic viscosity $[\eta]$ (reduced viscosity at $c \rightarrow 0$) at low ($c \rightarrow 0$) ionomer concentration and an increase in reduced viscosity at moderate ionomer concentrations can be observed. Comparison among viscosity results in the three pure solvents confirm the above. Thus, $[\eta]$ values in DIO for ionomers with the same sulfonation degree are lower than in CHL and in THF, in agreement with its lower dielectric constant value, $\epsilon_{\mathrm{DIO}}^{25^\circ\mathrm{C}} = 2.0$ against $\epsilon_{\mathrm{CHL}}^{22^\circ\mathrm{C}} = 4.8$ and $\epsilon_{\mathrm{THF}}^{25^\circ\mathrm{C}} = 7.6$, and as a result stronger intramolecular associations. On the other hand, intermolecular associations will be also stronger in DIO, as indicated by the steeper η_{sp}/c *versus* c dependence.

THF/CHL and CHL/DIO mixtures show cononsolvent effects for S. Maximal effects were displayed at a volumetric composition of 50/50 in the former and 75/25 in the latter, with respective excess free energy values of about $-1.0\,\mathrm{kJ\,mol^{-1}}$ and $-0.8\,\mathrm{kJ\,mol^{-1}}$[13]. In the THF/CHL (50/50) mixture, mean decreases of $[\eta]$ and second virial coefficients (A_2) values from those in the pure solvents were 16 and 30%, respectively[9]. In the CHL/DIO mixture $[\eta]$ and A_2 decreased by about 11 and 23%, respectively[9]. As can be seen in *Figure 1*, the cononsolvent character of the mixtures makes the intramolecular association of the ion pairs increase at low polymer concentrations, as shown by the lower values of the reduced viscosities with respect to those in the pure solvents. On the other hand, at high ionomer concentrations, viscosities in the mixtures were higher than those in the pure solvents, as expected with increasing intermolecular associations. It holds again in the mixtures that both kinds of associations are stronger the higher the ionic content of the ionomer, as shown in *Figure 2*.

Besides viscometry[20], aggregates caused by intermolecular interactions have also been detected by static and dynamic light-scattering techniques[25,26] through the determination of apparent weight-average molecular weights, second virial coefficients or apparent diffusion coefficients. Here, aggregate formation was detected by the s.e.c. technique. As is known, the elution volume of a macromolecular solute in a set of chromatographic columns, V_e, is related to the size (hydrodynamic

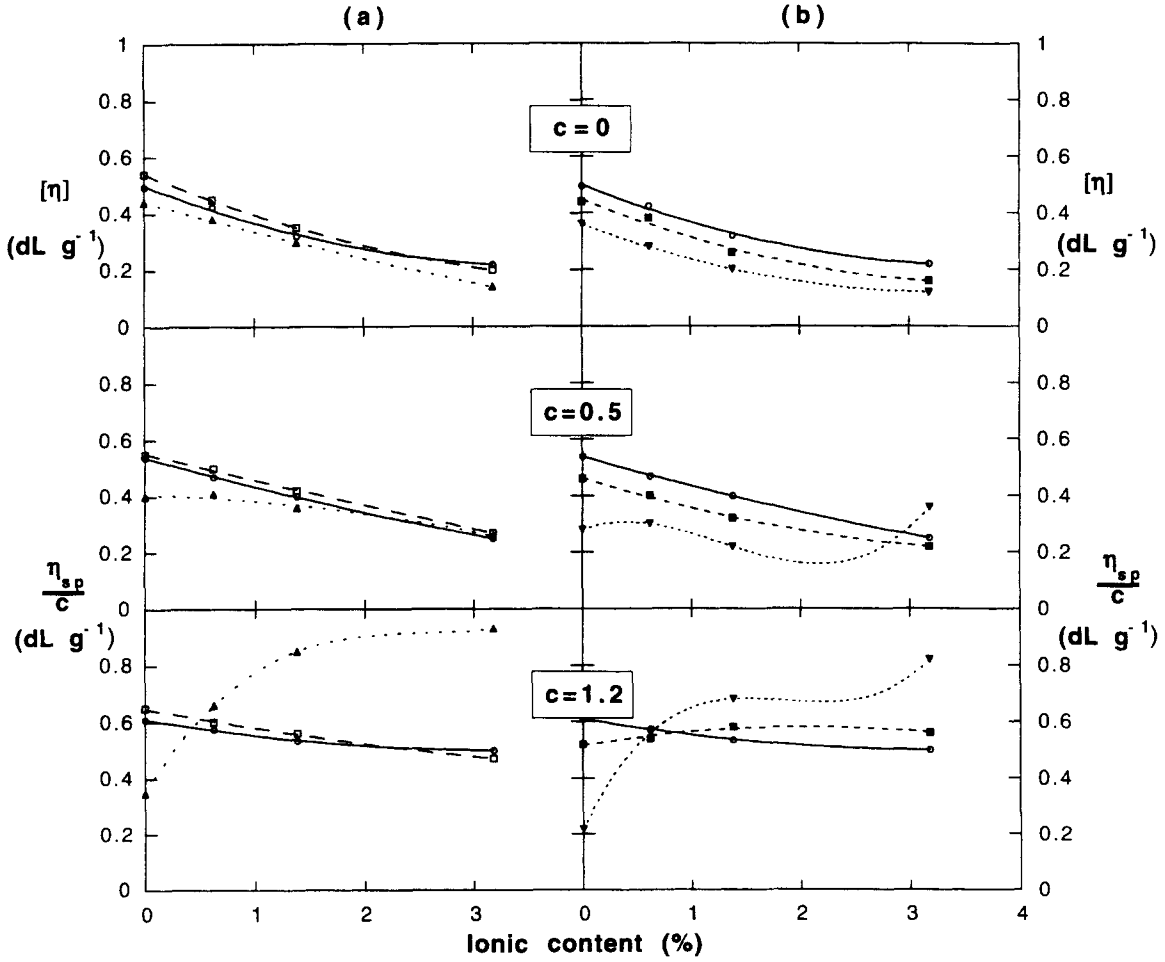

Figure 2 Dependences on x (ionomer content) of intrinsic $[\eta]$ and reduced (η_{sp}/c) viscosities of S-xSSNa ionomer solutions at concentrations c for pure solvents and cononsolvent mixtures. (a) ○, CHL; □, THF; ▲, THF/CHL (50/50); (b) ○, CHL; ■, DIO; ▼, DIO/CHL (75/25)

volume, V_h) of the macromolecular coil. In the upper part of *Figure 3* the elution volume dependences on solute concentration for S and its ionomers in THF are shown. As is well established, besides other effects such as viscous fingering the main causal agent of V_e retardation is the coil shrinkage that occurs with increasing concentration. The elution behaviour of S and of the ionomer with the lowest ionic content (xSSNa = 0.62%) is that expected for neutral polymers suffering concentration effects[27–32], as shown by the approximate linear correlation between elution volume and concentration. However, the elution behaviour of ionomers with higher ionic content is more complex. At low solute concentrations, effects due to coil shrinkage are negligible, and, as a result, elution volumes decrease with solute concentration in agreement with the increase in reduced viscosities shown in *Figure 1* and explained by intermolecular association. At moderate and high concentrations two opposite effects seem to govern elution volumes, the above concentration effects and those derived from interchain association. The former retard V_e, while the latter tend to anticipate it. At moderate concentrations both effects tend to compensate for each other, and at high concentrations the association effects are dominant. This complex behaviour is better seen in the cononsolvent THF/CHL mixture in which intramolecular association phenomena at low solute concentration appear also for the lowest ionic content ionomer. At moderate concentrations shrinkage effects seem to be larger than association effects, which at the highest concentrations seem again to govern elution volumes, in agreement with the enhancement of intermolecular association in the cononsolvent mixture shown by reduced viscosities in *Figure 1*. V_e values at infinite dilution deserve some comment. V_e values at an infinite dilution ($c \rightarrow 0$) of S and ionomers are very different both in THF and in the THF/CHL cononsolvent mixture, which in s.e.c. indicates very different hydrodynamic volumes. However, the higher the ionic content the poorer the solvent and the more favoured the solute–chromatographic gel interactions[33–36], retarding V_e. These secondary elution effects prevent the possibility of comparison among the elution volumes of the different ionomers in order to obtain any conclusion on their sizes or on their hydrodynamic volumes.

As indicated in the introduction, cosolvent mixtures for non-polar polymers are often those formed by a polar and by a non-polar solvent. Here, the viscosity behaviour of S–xSSNa ($M_w \approx 105\,000$) ionomers in the solvents EA and DMF and in the cosolvent mixture EA/DMF (50/50 v/v) for S[9,13] is studied. In *Figure 4* viscosity results are shown for ionomers with diverse ionic content. Results in EA for the ionomer with the higher ionic content, namely 3.18%, are omitted because the ionomer is not soluble in EA. The results obtained in EA are those expected for low dielectric constant solvents ($\epsilon_{EA}^{25°C} = 6.0$) although intermolecular associations as manifested by viscosity values seem to be weaker for the same ionomer than those found in solvents with similar dielectric constants, as can be seen by comparing viscosity values for EA in *Figure 4* and the corresponding ones in *Figure 1* for THF and/or CHL. These differences in association are probably due to the different nature of ion pairs in the aforementioned solvents. Thus, interactions between the ionic group of the ionomer and EA molecules should lead to the formation of ion pairs separated by solvent

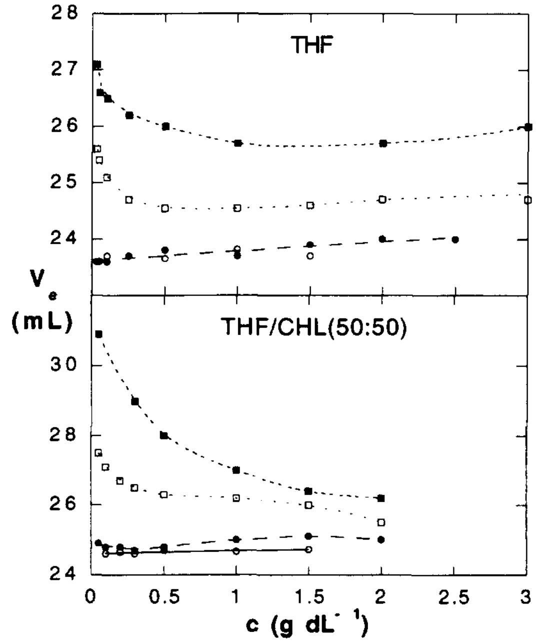

Figure 3 Elution volumes (V_e) in the THF and in the cononsolvent mixture THF/CHL (50/50) of S–xSSNa ionomers with different ionic content as a function of ionomer concentration c. Symbols are as in *Figure 1*

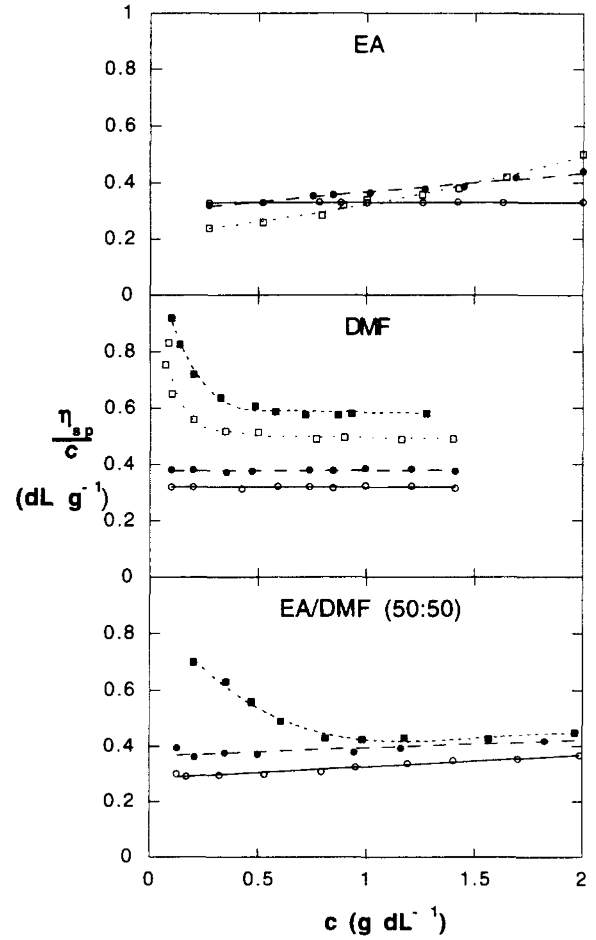

Figure 4 Dependences on polymer concentration of reduced (η_{sp}/c) viscosities in the pure solvents and cosolvent mixture shown for S–xSSNa ionomers with different ionic contents. Symbols are as in *Figure 1*

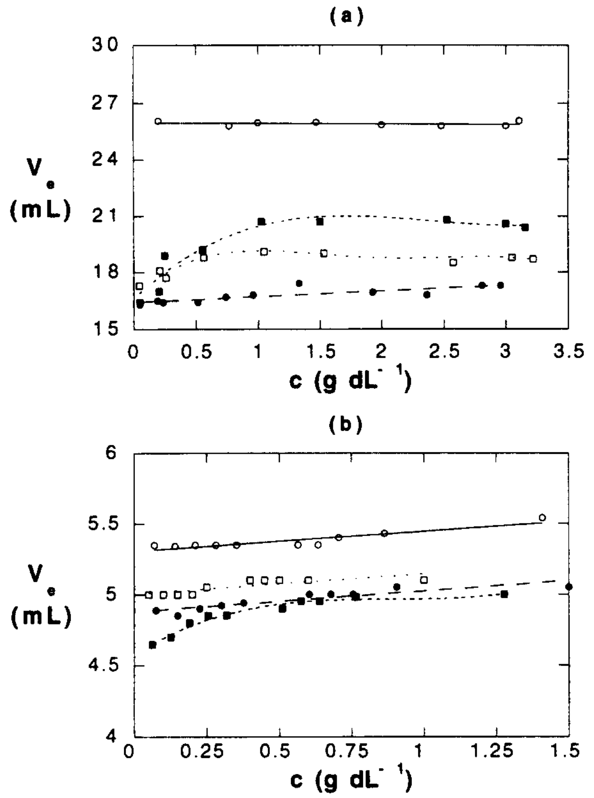

Figure 5 Elution volumes (V_e) as a function of ionomer concentration of S–*x*SSNa ionomers with different ionic contents. (a) μ-Styragel columns with DMF as the eluent. (b) TSK column with DMF/EA (50/50) as the eluent. Symbols are as in *Figure 1*

molecules or to a global strong solvation of the contact ion pairs. In both cases the close approach of ion pairs is impeded, resulting in a weaker intermolecular interaction. In order to test the different association powers of EA and THF, viscometer efflux times of ionomer solutions in THF and in a mixture THF/EA (80/20 v/v) have been compared. As an example, for solutions with $c = 0.603\,\mathrm{g\,dl^{-1}}$ for the ionomer with 3.18% ionic content the efflux time in THF decays from 610.71 to 566.62 s in the THF/EA (80/20) mixture, the reduced viscosity going from $\eta_{sp}/c = 0.327$ in THF to $\eta_{sp}/c = 0.246\,\mathrm{dl\,g^{-1}}$ in the mixture. These results confirm the ability of EA to impede aggregates, probably due, as suggested above, to strong specific interactions of the solvent with the ionic moieties of the ionomer.

The results in *Figure 4* for DMF are those expected for solvents with a high dielectric constant ($\epsilon_{DMF}^{25°C} = 36.7$), where ionomers behave similarly to polyelectrolytes, their reduced viscosities sharply decreasing with increasing polymer concentration. The effect is more pronounced the higher the ionic content of the ionomer, and it is caused by the dissociation of ion pairs with the corresponding presence of negative charges along the polymer backbone and upon the corresponding chain elongation[3,37,38]. The viscosity results for the cosolvent EA/DMF mixture, also shown in *Figure 4*, are intermediate between the above two different behaviours in the pure solvents. Starting with S and with the lowest ionic content (0.62%) ionomer, the intrinsic and reduced viscosities in the mixture are higher than in the pure solvents, as expected from the cosolvent character of the mixture. On the other hand, the trend followed by the viscosity of the ionomer with the highest ionic content (3.18%) in the mixture is one of compromise between the contradictory ones in the pure solvents. Thus, the $[\eta]$ value in the mixture is higher than in EA but lower than in DMF, and the polyelectrolytic behaviour followed by the reduced viscosity in DMF is also observed in the mixture but attenuated, probably due again to the specific interaction of the ionic groups with EA.

The elution volume dependences on solute concentration for S and its ionomers in DMF through μ-Styragel are shown in *Figure 5a*. As mentioned above when discussing elution results in THF and in its mixture with CHL (*Figure 3*), secondary effects prevent comparisons among the elution volumes of the different ionomers in order to deduce any conclusion on their relative sizes. The results in *Figure 5a* show that S elutes later than ionomers and no perceptible concentration effects are observed, in agreement with the viscosity results in *Figure 4*. Ionomers with high ionic content show at low concentrations an increase in V_e with c, also in agreement with the viscosity results in *Figure 4*, but the order of elution is the reverse expected from their viscosity values. As said before, secondary effects due to the different solute–gel interactions are responsible for these apparent anomalies. Similar elution results to those in *Figure 5a* are shown in *Figure 5b*, but now elution is through a TSK column in the cosolvent mixture EA/DMF (50/50). Once again, V_e values for S are higher than those for ionomers, but the order of appearance of ionomers is changed to that in μ-Styragel, and is not the expected one from viscosity results. In addition to the intricate secondary mechanisms depending on the simultaneous balance of solute–eluent, solute–gel and eluent–gel interactions, there is another aspect of the elution behaviour of ionomers that deserves some comment. In the chromatograms of S and the lowest ionic content ionomer in EA/DMF solutions, a 'vacant peak' appears after the polymer peak[39–41], due to an EA excess with respect to the eluent mixture, which indicates preferential sorption of solutes by DMF[42]. However, when the solutes are the ionomers with high ionic content the vacant peak is now of DMF, as these ionomers are preferentially solvated by EA. These facts seem to confirm once more the apparent strong affinity of EA for ionic groups of ionomers.

In conclusion, whereas the viscometric and elution behaviour of ionomers in the cononsolvent mixtures can be interpreted in terms of enhanced inter- and intramolecular associations with respect to those in the pure solvents, in cosolvent mixtures appear on the one hand polyelectrolyte effects and on the other preferential sorption effects, which make interpretation of viscometric and elution behaviour difficult. It seems that in the sulfonated systems studied here the hydrocarbonated moiety is preferentially solvated by DMF, whereas the ionic one is preferentially solvated by EA. Quantification of the above preferential sorption effects, through the evaluation of preferential sorption parameters and their dependences on ionomer ionic content and composition of solvent mixtures, deserves further study.

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