Electro-optical and viscometric behaviour of sodium polystyrene sulphonate in formamide

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Unusual electro-optical signals have been recorded on sodium polystyrene sulphonate in formamide. It was shown that such signals largely arise from the positive birefringence of the solvent being superimposed on the negative birefringence of the polyion. On the basis of conductimetric experiments, the residual content of ammonium formate caused by hydrolysis of formamide was estimated. Commercial formamide of analytical grade was shown to contain rather large amounts (0.02 M) of ammonium formate, sufficient to very strongly decrease the polyelectrolyte effect. The persistence length in these conditions is equal to 80Å, quite similar to that determined in 2×10^{-2} M NaCl aqueous solution. At a lower ammonium formate content (7×10^{-4} M), the degree of extension of the polyion at infinite dilution, calculated from the relaxation time of the birefringence, is identical to that measured in 6×10^{-4} M NaCl. The influence of the nature of the solvent and the ionic strength on the electric polarizability and the optical anisotropy factor was also analysed and compared with the results obtained in water. The latter parameter was discussed in terms of the so-called form anisotropy of the solvent and the intrinsic optical anisotropy of the polyion.

(Keywords: polyelectrolytes; electro-optics; birefringence; viscosity; polystyrene sulphonate; formamide)

INTRODUCTION

Until now, most of the studies on the solution behaviour of polyelectrolytes have been performed in aqueous media of variable ionic strength ranging from pure water to salt concentrations of the order of one mole per litre. Fewer studies have been devoted to polyelectrolytic behaviour in polar organic solvents and the majority of them were concerned with the cationic polyelectrolytes such as the polyvinylpyridinium salts in a wide variety of organic solvents of high dielectric permittivity, including aliphatic alcohols, nitroalkanes, aliphatic amides, dimethylsulphoxide etc.... Owing to their lower solubility in organic solvents, the anionic polyelectrolytes have been less studied. Barabanov *et al.*[1,2] examined the influence of the solvent, essentially dimethylformamide and acetone, on the ionization and solvation processes of polymethacrylic acid and its copolymers neutralized to different degrees, and estimated the overall ionization constant from conductimetric experiments[2]. The alkaline salts of polystyrene sulphonic acid have been investigated only in water/organic solvent mixtures and, to our knowledge, no results have been published so far on their behaviour in pure organic solvents of very high dielectric constant, such as formamide or *N*-methylformamide.

In their study of the electric birefringence of potassium polystyrene sulphonate (PSSK), Nakayama and Yoshioka[3] observed in water/dioxane mixtures that the specific Kerr constant decreased with increasing dioxane content, i.e. with decreasing dielectric constant. This effect was attributed to a lowering of the electric polarizability due to the coiling of the polyion. In water/ethylene glycol and water/glycerol mixtures, the non-Kerr behaviour observed[3] was explained by considering that a saturation of the electric polarizability appears at relatively low fields[4]. In addition, some thermodynamic aspects were directly approached by Vesnaver and Dolar[5] in their studies on the osmotic coefficients of polystyrene sulphonates in water/dioxane mixtures, in the presence of monovalent and divalent counterions.

Preliminary experiments in our laboratory showed that the electric birefringence of solutions of polystyrene sulphonic acid salts in formamide is positive at high field strength and that unusual transients are often encountered. On the contrary, the electric birefringence of these polysalts in water always remains negative, whatever the concentration and the field strength[6]. The purpose of the present work is to study, with the aid of electro-optical and viscometric techniques, the polyelectrolytic behaviour of sodium polystyrene sulphonate in formamide. We shall try to seek the origin of the change of sign of the optical anisotropy and to compare the values of the electric and conformational parameters in formamide and in water.

MATERIALS AND METHODS

Samples

Sodium polystyrene sulphonate samples were purchased from Pressure Chemical (Pittsburgh, Pa) where they were prepared by sulphonation of polystyrene standards of low polydispersity. They showed number average molecular weights $\bar{M}_n$, determined from osmometry

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in 1 M Na_2SO_4, of 31.5×10^4, 67.2×10^4, 1.0×10^5, 2.04×10^5, 4.0×10^5 and 7.65×10^5 for samples A, B, C, D, E and F respectively. The polydispersity indices of the parent polystyrenes are of the order of 1.05 and the degrees of sulphonation determined by X-ray fluorescence for sulphur are 0.88, 0.89, 0.89, 0.81, 0.70 for samples A, B, C, D, F respectively[6]. All these samples have been exhaustively dialysed against deionized water.

Two potassium polystyrene sulphonates (H and K), obtained by courtesy of the laboratory of Professor M. Mandel (Leiden, The Netherlands), have been prepared by polymerization of potassium styrene sulphonate with potassium persulphate as initiator. Their degree of sulphonation was thus equal to unity and their viscometric average molecular weights, calculated according to the relation of Takahashi *et al.*[7] were equal to 1.5×10^5 (H) and 8.85×10^5 (K) respectively. The monomeric model compound sodium paratoluene sulphonate (pTSNa) from Merck–Schuchardt (Darmstadt) was purified by recrystallization with the solvent/non-solvent system methanol/ethanol.

Solvents

Carefully deionized water was degassed under nitrogen and kept free from carbon dioxide contamination; it showed a conductivity of the order of 2.20×10^{-6} Ω^{-1} cm^{-1}. Formamide (Merck) of analytical grade had a conductivity of the order of 6×10^{-4} Ω^{-1} cm^{-1} whereas the lowest value reported in the literature is 6.2×10^{-7} Ω^{-1} cm^{-1} [8]. This ionic contamination was found to be due to the presence of ammonium formate and to traces of formic acid, arising from the partial hydrolysis of formamide in the presence of atmospheric moisture. The ammonium formate cannot be eliminated by a simple vacuum distillation, owing to its decomposition to ammonia and formic acid, and therefore more elaborate purification procedures are required. The method of Verkoek[9] involves the neutralization of the remaining formic acid by sodium hydroxide and the subsequent separation of the formamide from the sodium formate by vacuum distillation. In order to avoid the presence of water produced by the reaction of the formic acid with NaOH, the use of sodamide ($NaNH_2$) as neutralizing agent was recommended[10]. The so-formed ammonia is easily pumped off before the distillation. The formamide was purified using the following procedure: small amounts of sodamide were added dropwise under nitrogen to formamide at 80°–90°C in order to neutralize its acidity, using bromothymol blue as indicator. The ammonia formed was pumped off; the procedure was repeated four or five times, until the medium remained neutral, and the formamide was distilled. The neutralization procedure is repeated twice and the final distillation yields formamide with a conductivity of the order of 2×10^{-5} Ω^{-1} cm^{-1}. Only a fractional crystallization in a dry atmosphere could reach a better degree of purity and a conductivity of the order of $1\text{–}2 \times 10^{-6}$ Ω^{-1} cm^{-1}. The residual content of ammonium formate was estimated by conductiometry as described below.

Viscometry

The viscosity of the solutions in formamide was measured at 25°C with a Desreux–Bisschoff dilution viscometer having a flow time of 180 s for the pure solvent.

Electro-optics

The value of the electric birefringence and of the field-free relaxation times at room temperature have been measured at 550 nm with a previously described instrument[11,12]. The procedures allowing calculation of the average values of the birefringence at saturation $\overline{\Delta n_s}$, the electric polarizability $\overline{\Delta\alpha}$ and the Kerr constant $K_B = \overline{\Delta\alpha}\ \overline{\Delta n_s}/15\,kT$ have been discussed in detail in ref. 6. The field strength dependences of the electric birefringence have been analysed with the aid of the orientation function valid for a pure induced dipole moment mechanism. The mean relaxation time $\bar{\tau}$ was computed from the area under the exponential birefringence decay curve.

Conductimetry

The conductance measurements were performed with the aid of a Kohlrausch bridge working at a frequency of 10^3 Hz and a Philips cell (PW 9512/01) whose constant ($K = 1.376$ cm) was determined at 25°C with KCl standard solutions. The electrodes were black platinized in order to reduce polarization effects.

RESULTS AND DISCUSSION

Preliminary observations

Various solubility tests indicated that sodium polystyrene sulphonate was soluble at room temperature in formamide, *N*-methylformamide and formic acid, but insoluble in other polar solvents such as sulpholane, hexamethylphosphortriamide, dimethylsulphoxide, dimethylformamide and nitromethane, even after heating for several hours at 60°C.

The field strength dependences of the electric birefringence of various sodium and potassium polystyrene sulfonate samples have been recorded at a constant concentration of 0.6 g/l, using nonpurified formamide of specific conductivity equal to 6×10^{-4} Ω^{-1} cm^{-1}. Peculiar shaped Δn vs. E^2 curves have been observed, characterized by a change of sign of the steady-state birefringence which is, for some samples, negative at low electric fields and positive at high electric fields (*Figure 1c*). The electric birefringence of the PSSNa samples in water have always been found to be negative, showing saturation at high field strength, with the most accentuated being found at the lower the polymer concentration. The recorded signals displayed sharp peaks in the rise and decay phases of the transient signals (*Figure 1a, b*), similar to those previously described in the case of solutions of poly-*N*-butyl-4-vinylpyridinium bromide in dimethylsulphoxide[13]. This type of transient arises from the solvent positive birefringence contribution which involves extremely rapid rise and decay transitory states. *Figure 2* shows Δn vs. E^2 dependences of formamide, *N*-methylformamide and *N,N'*-dimethylformamide as compared with that of nitrobenzene; the latter is often chosen as a reference solvent for the birefringence calibration owing to its very large permanent dipole moment and optical anisotropy values. *Table 1* collects some physical parameters of these solvents at 25°C[14,15], namely density, refractive index, viscosity, dielectric constant, specific conductivity, dipole moment, Kerr constant (measured in the present work) and compares them with the physical parameters of water. It can be seen

that the Kerr constants of formamide and *N*-methylformamide are much larger than those of water, dimethylsulphoxide (1.8×10^{-9} kV^{-2} cm^2) and nitromethane (0.4×10^{-9} kV^{-2} cm^2)[13]. We also noted that the abilities of formamide and water to act as electron acceptors with respect to a charged entity do not differ markedly; the acceptor numbers, as defined by Gutman on an experimental basis[16], are 40 for formamide and 55 for water, while dimethylformamide has a much lower value, of about 16. On the contrary, the degree of auto-association by hydrogen bonding[17,18], is certainly much larger for formamide than for water, and would be responsible for its larger viscosity. The optical polarizabilities of various *N*-alkylamides have been recently determined by Beevers from the measurement of the molecular Kerr constant and of the permanent dipole moment in dioxane, benzene and water[19]. It has been shown that the experimental Kerr constants in dioxane can be linearly correlated with the theoretical values calculated from the polarizability tensors associated with the single bonds. No data are presented in order to explain, in terms of the associated structure at the liquid state, the very large Kerr constants observed for the pure amides[19]. A large positive birefringence contribution of the solvent is however capable of explaining the anomalous shape of the Δn vs. E^2 curves (*Figure 1a*).

Some other preliminary experiments indicated that the reduced viscosity η_{sp}/C of different NaPSS samples in

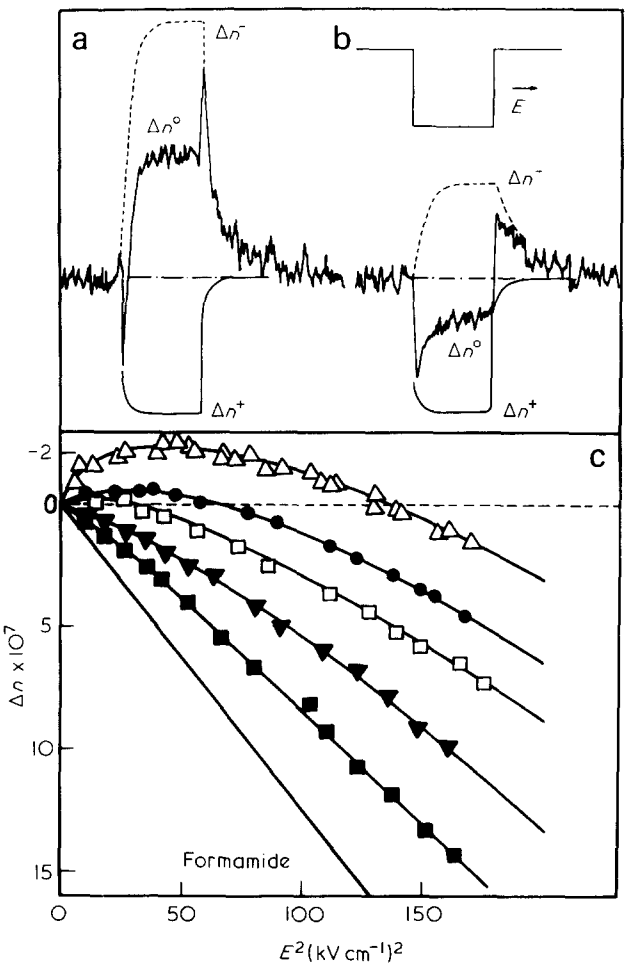

Figure 1 Typical electro-optical transients recorded at low (4 kV cm^{-1}, a) and high (11 kV cm^{-1}, b) electric field on a solution of PSSNa sample D in unpurified formamide (c=0.6 $g.l^{-1}$); (c) field strength dependences of the eledtric birefringence of various sodium [D(●), C(▼), A(■)] and potassium [K(△), H(□)] polystyrene sulphonates at c=0.6 $g.l^{-1}$ in unpurified formamide, and of purified formamide (———)

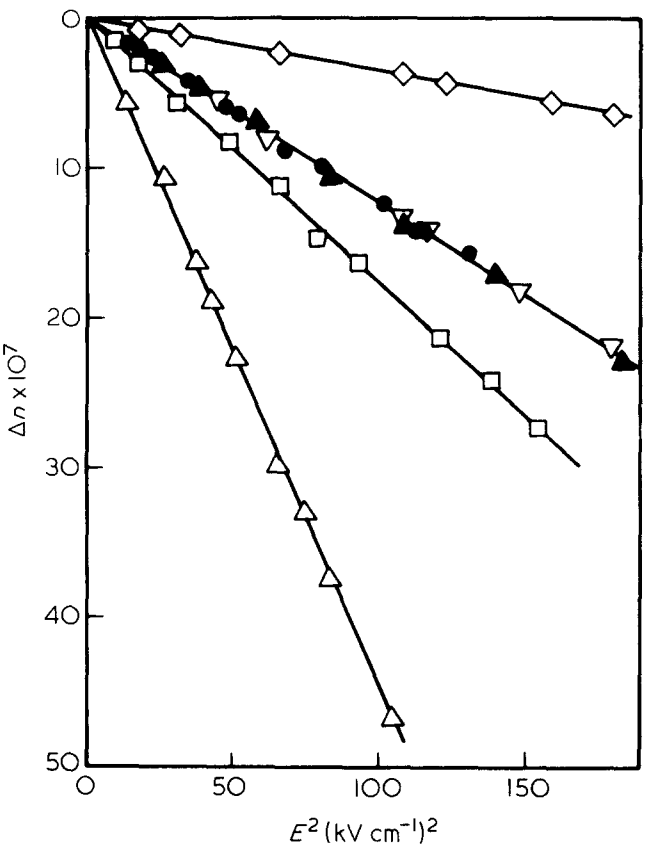

Figure 2 Kerr law behaviour of the positive electric birefringence of some pure organic solvents: dimethylformamide (◇), nitrobenzene (□), N-methylformamide (△) and formamide containing different amounts of ammonium formate: 7×10^{-4} (●), 1.4×10^{-3} (▲) and 2×10^{-2} (▽) mol l^{-1}

Table 1 Physical constants of alkylamides and water at 25°C (ref. 14): density, refractive index at 589 nm, viscosity, dielectric constant, specific conductivity, dipole moment and Kerr constant at 550 nm

Solvents	d	n^D	$\eta \times 10^2$ (Poise	ϵ	κ (Ω^{-1} cm^{-1})	μ (Debye) in benzene	$K_B{}^b \times 10^9$ (kV^{-2} cm^2)
Formamide	1.12918	1.44682	3.302	109.5[a]	2×10^{-7}	3.37 (30°C)	12.4
N-methylformamide	0.99880	1.4300	1.650	182.4	8×10^{-7}	3.86	44.3
N,N'-dimethylformamide	0.94397	1.42817	0.802	36.7	6×10^{-8}	3.86	3.5
Water	0.99705	1.33250	0.8902	78.4	5.9×10^{-8}	–	0.18

[a] Ref. 15
[b] This work

formamide did not exhibit the classical polyelectrolytic behaviour observed in pure water, but showed a decrease of η_{sp}/C as the concentration decreased. The polystyrene sulphonate would thus behave as a weakly charged and rather less extended polyion in formamide. This appears rather inconsistent with the large dielectric constant of the formamide ($\varepsilon = 109.5$) as compared with that of water ($\varepsilon = 78.4$). Only the effect of additional ionic strength could be responsible for such behaviour and this could arise from the presence of small amounts of ammonium formate, completely dissociated in this medium having a high dielectric constant. In a study devoted to the viscometric behaviour of heparin in glycerol and formamide, Garg and Stivala showed that this mucopolysaccharide did not display the expected polyelectrolytic behaviour in the latter solvent[21]. The authors stated that the specific conductance of their formamide would indicate the presence of an ionic strength equivalent to 0.02 M KCl, and hence sufficient to markedly reduce, by a shielding effect, the repulsion between the charged groups of the polyion. It thus appears essential to determine quantitatively the amounts of ammonium formamide in the purified and crude formamide solvents.

Conductimetric behaviour of ammonium formate in formamide

In order to obtain the equivalent conductance at zero concentration, Λ_0, the equivalent conductance values Λ_c have been treated in terms of the classical Falkenhagen procedure[21] on the basis of the relationship:

$$\Lambda_c = \Lambda_0 - (A\Lambda_0 + B)\frac{\sqrt{C}}{1 + B'a\sqrt{C}} \quad (1)$$

in which a represents the mean ionic diameter.

For 1,1-valent electrolytes, the constants A, B, and B' are respectively equal to[21]:

$$A = 8.205 \times 10^5 (\varepsilon T)^{-3/2} = 0.141 \quad (2)$$

$$B = 82.5 \times \eta^{-1} (\varepsilon T)^{-1/2} = 13.89 \quad (3)$$

$$B' = 50.89 (\varepsilon T)^{-1/2} = 0.2796 \quad (4)$$

where ε and η are the dielectric constant and viscosity values given in *Table 1* for formamide at 25°C. The product $B'a$ has been put equal to 1.275, corresponding to a product $B'a$ equal to 1.5 in pure water and to a mean ionic diameter of 4.65 Å. The conductiometric behaviour of ammonium formate in water is not described in the present paper. Equation (1) can thus be expressed as:

$$\Lambda_c = \Lambda_0 - (0.141\Lambda_0 + 13.89)\frac{\sqrt{C}}{1 + 1.175\sqrt{C}} \quad (5)$$

Using a purified formamide sample (conductivity = 3.706×10^{-5} Ω^{-1} cm^{-1}) and concentration of ammonium formate ranging from 0.022 to 0.010 equivalents l^{-1}, we obtained, with the aid of relation (5), a Λ_0 value equal to 29.6 ± 0.2 Ω^{-1} equivalents^{-1} cm^2. The concentration dependence of the equivalent conductance of ammonium formate in formamide can thus be expressed as:

$$\Lambda_c = 29.6 - \frac{18.064\sqrt{C}}{1 + 1.275\sqrt{C}} \quad (6)$$

Otherwise, Λ_c is also equal to:

$$\Lambda_c = \left(\frac{1}{R} - \frac{1}{R_0}\right)\frac{1000}{KC} \quad (7)$$

where R and R_0 define the resistance of the cell filled with the solution and the pure formamide (K = 1.376 cm) respectively. Using the conductivity value of the literature, or 6.2×10^{-7} Ω^{-1} cm^{-1} ($R_0 = 1.17 \times 10^6$ Ω), and equalizing equations (6) and (7), the residual amount of ammonium formate can thus be calculated from the relationship:

$$0.0271\, C^{3/2} + 0.0407C - \left(\frac{1}{R} - \frac{1}{R_0}\right)(1 + 1.275\sqrt{C}) = 0 \quad (8)$$

The specific conductivity values and the ammonium formate content of the different purified fractions of formamide, as well as of the crude formamide, are given in *Table 2*.

Viscosity and electric birefringence relaxation times

The concentration dependence of the reduced viscosity η_{sp}/C has been studied for four PSSNa samples. At high ammonium formate content (2×10^{-2} M; *Figure 3a*), the viscosity always decreased with decreasing concentration. Although the concentration dependence was not linear, the reduced viscosity values could be grossly extrapolated to zero concentration, yielding intrinsic voscisity values (η) of the order of (0.45 ± 0.05), (0.60 ± 0.05), (1.30 ± 0.10), (2.20 ± 0.10) and (5.10 ± 0.10) dl g^{-1} for samples B, C, D, E and F respectively. These values yield a Kuhn–Mark–Houwink coefficient close to 0.9 (if we except the large value of sample F); a similar coefficient is obtained if the reduced viscosity at $C = 0.5$ g l^{-1} is considered instead of the intrinsic viscosity. We also noticed that the viscosity was practically the same in formamide with similar contents (0.02 M) of sodium chloride and of ammonium formate, so that the nature of the added salt does not seem to influence the viscometric behaviour of PSSNa in formamide. The coefficient of 0.9 is slightly larger than that determined by Takahashi *et al.*[7] in NaCl 0.02 M (namely 0.78). Quite different shapes for the η_{sp}/C vs. C dependences were observed in formamide + ammonium formate 1.4×10^{-3} M

Table 2 Values of the resistance of the cell, of the specific conductivity and of the residual concentration of ammonium formate in the different formamide fractions

Solvent	R (Ω)	κ (Ω^{-1} cm^{-1})	C (equivalents, l^{-1})
FA-1	34.200	2.106×10^{-5}	7.02×10^{-4}
FA-2	24.300	2.965×10^{-5}	1.00×10^{-3}
FA-3	19.610	3.706×10^{-5}	1.26×10^{-3}
FA-4	17.070	4.258×10^{-5}	1.45×10^{-3}
FA-0 (crude formamide)	1.200	60.6×10^{-5}	2.21×10^{-2}

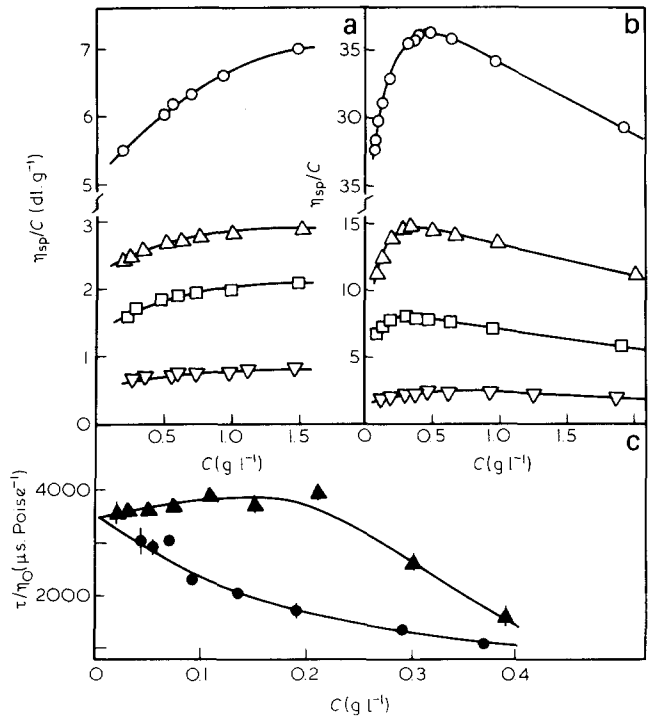

Figure 3 Concentration dependences of the reduced viscosity in formamide + 2×10^{-2} M (a) and 1.4×10^{-3} M (b) ammonium formate for samples C (▽), D (□), E (△) and F (○); (c) variations of the ratio of the relaxation time of the birefringence to the viscosity of the solvent with concentration for sample D in formamide + 7×10^{-4} ammonium formate (●) and water + 6×10^{-4} M NaCl (▲)

(*Figure 3b*). The viscosity first increased owing to the expansion of the polyion and reached a maximum at a concentration of 0.4–0.5 g l^{-1}. This kind of curve, frequently observed for polyelectrolytes at low ionic strength, makes any attempt at extrapolating to zero concentration meaningless.

As the conformation of polyelectrolyte at intermediate and high ionic strengths (10^{-3} to 1 M) can be identified as a wormlike chain, it seems useful to determine, from the $[\eta]$ vs. $\bar{M}_n$ dependence, the persistence length defining the degree of rigidity of the chain. Making use of a computed fitting procedure based on the Yamakawa–Fujii treatment[22] and described in detail in ref. 23, we obtained for PSSNa in formamide + ammonium formate 2×10^{-2} M, a persistence length of 80 Å and a diameter of 1.8 Å. As a comparison, the same calculation procedure applied to the viscosity–molecular weight data given by Takahashi *et al.*[7] for fully charged PSSNa in 2×10^{-2} M NaCl yielded persistence length and diameter values of 74 and 8.4 Å, respectively[23]. Both calculations were performed by taking a monomer length equal to the theoretical length of a vinylic unit (2.5 Å) and monomer molecular weights equal to 206 for the samples of Takahashi and 191 for our samples, the degrees of sulphonation being equal to 1 and 0.85 (average value), respectively. It ensues that the rigidity of the PSSNa is quite similar in both media (water or formamide) at the same ionic strength (0.02 M).

As shown in *Figure 3b*, the use of the viscometric experiments to study the conformational behaviour of polyelectrolytes failed at very low ionic strengths. On the contrary, the relaxation time of the electric birefringence can be easily measured in these conditions and relaxation experiments have been performed at low electric fields on PSSNa sample D ($\bar{M}_n = 2.04\times10^5$) in formamide + 7×10^{-4} M ammonium formate ($E = 3.5$ kV cm^{-1}) and in water + 6×10^{-4} M NaCl ($E = 6.7$ kV cm^{-1}).

The relaxation times observed are entirely related to the rotational motion of the macromolecules, with additional motions of chain segments. The appearance of the relaxation of the induced dipole occurs on a much faster scale (< 1 μs). Taking into account the viscosities of the two solvents, which differ by a factor of about 4 (*Table 1*), it appeared that the τ/η_0 values tended towards a similar value at zero concentration (*Figure 3c*). However, we have at present no explanation for the discrepancy by a factor of about 2 between the τ/η_0 values in the intermediate concentration range, near 0.2 g l^{-1}. Taking a τ_0/η_0 value equal to 3500 μs. Poise^{-1} and an axial ratio p roughly estimated to 300, the relationship valid for rigid rods:

$$L_0^3 = 18kT\tau_0(\ln 2p - 0.8)/\Pi\eta_0 \qquad (8)$$

yield a chain length of 1660 Å at infinite dilution. This value is consistent with the chain lengths determined in water for polyelectrolytes of similar structure and molecular weight, for instance the polyvinylpyridinium salts[24,25]. In the range of very low ionic strength, the degrees of extension of the PSSNa is the same in formamide and water; however, no conclusion can be drawn about the degree of ridigity in these conditions, since we have not studied the molecular weight dependence of the relaxation time.

Electric polarizability and optical anisotropy

The field strength dependences of the electric birefringence have been measured at various concentrations for sample D in formamide + 7×10^{-4} and 2×10^{-2} M ammonium formate and for sample F in formamide + 1.4×10^{-3} M ammonium formate. As shown in *Figure 4*, after correction for the positive birefringence of pure formamide, the Δn vs. E^2 curves resembled those observed

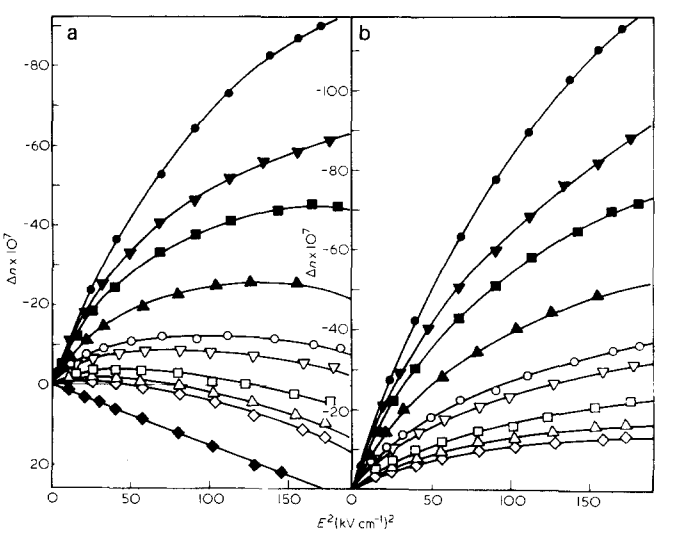

Figure 4 (a) Field strength dependences of the measured electric birefringence of formamide + 7×10^{-4} M ammonium formate (◆) and of solutions of sample D in this solvent at various concentrations: 0.623 (●); 0.368 (▼); 0.290 (■); 0.190 (▲); 0.133 (○); 0.0912 (▽); 0.0705 (□); 0.0555 (△) and 0.0439 (◇) g l^{-1}; (b) similar curves after correction for the birefringence contribution of the solvent

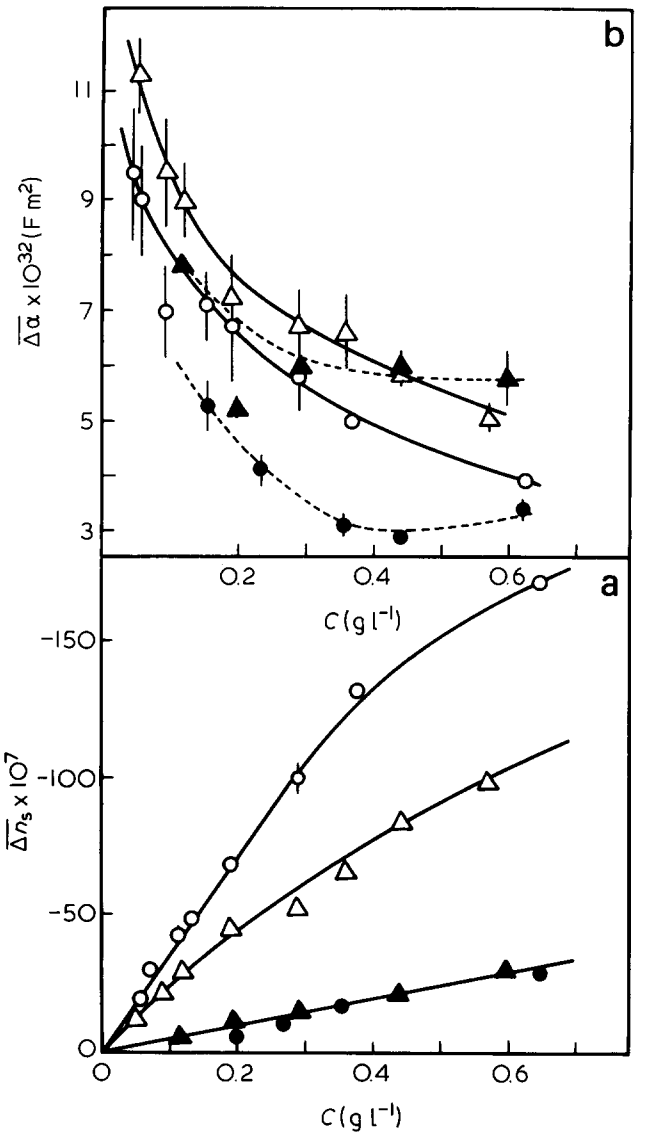

Figure 5 Variations of the birefrigence at saturation (a) and of the average electric polarizability (b) with concentration for samples D (○) in formamide + 7×10^{-4} M and F in formamide + 1.4×10^{-3} M ammonium formate (△), and for samples D (●) and F (▲) in formamide + 2×10^{-2} M ammonium formate

in water, exhibiting a pronounced saturation effect at high fields, as the concentration decreased. Some experiments using the bipolar pulse method confirmed that the orientation of the PSSNa can be attributed to a pure induced dipole moment orientation mechanism. In agreement with other reports[3,4,6], the Kerr constant of PSSNa in solvents of high dielectric permittivity is negative. This is due to the negative sign of the intrinsic optical anisotropy arising from the orthogonal orientation of the aromatic rings with respect to the long axis of the particle. This behaviour is general and is observed with most natural and synthetic macromolecules having flat aromatic side chains.

The average electric polarizability values, determined as described in ref. 6, increased with decreasing concentration (*Figure 5a*) and were extrapolated to zero concentration with a plot of $(\overline{\Delta\alpha})^{-1}$ vs. c. The $\overline{\Delta\alpha_0}$ values, equal to $(11.0 \pm 1.5) \times 10^{-32}$ F m^2 and $(17 \pm 2) \times 10^{-32}$ F m^2 for samples D and F respectively, markedly depart from the $\overline{\Delta\alpha_0}$ values for the same samples in water, namely (138 ± 17) and $(95 \pm 7) \times 10^{-32}$ F m^2, respectively[6]. We previously observed that, in pure water, the electric polarizability increased with a power of 2.6 ± 0.2 for the molecular weight in the low molecular weight range ($M < 2 \times 10^5$), but remained more or less constant, or even slightly decreased in the high molecular weight range ($M > 2 \times 10^5$)[6]. The latter effect, also detected with polyvinylpyridinium salts[25] was tentatively explained by a polarization of the counterionic atmosphere along rigid subunits of the polyion under the action of the external electric field. It seems reasonable to assume that a similar polarization mechanism occurs in formamide, the smaller $\overline{\Delta\alpha_0}$ values arising from the effect of the ionic strength which reduces the length of the subunits and hence the magnitude of the induced dipole moments.

If we now examine the variations of the optical term, i.e. the birefringence at saturation, we see (*Figure 5b*) that the optical anisotropy is larger for sample D at 7×10^{-4} M than for sample F at 1.4×10^{-3} M, but was markedly decreased in 2×10^{-2} M ammonium formate. Taking into account the refractive index of the solvent $n_0 = 1.447$ and partial specific volume $\bar{v}$ given in *Table 3*, the experimental optical anisotropy factor $(g_a - g_b)_{meas}$ can be calculated from the relationship:

$$(g_a - g_b)_{meas} = \frac{n_0 \, \Delta n_s}{2\Pi c \bar{v}} \tag{9}$$

and compared with the results obtained in water[6].

It should be recalled that the measured anisotropy may be considered as the sum of two terms of opposite signs: the negative intrinsic anisotropy of the polymer $(g_a - g_b)_i$ and the positive form anisotropy $(g_a - g_b)_f$. The latter's contribution has its origin in the difference in the refractive indices between the polymer, n_p, and the solvent, n_0, which can be estimated using the following approximate relationship[12,13].

$$(g_a - g_b)_f = \frac{(n_p^2 - n_0^2)^2}{4\Pi(n_p^2 + n_0^2)} \tag{10}$$

From the refractive index increment and the partial specific volume of the PSSNa in various media: $dn/dc = \bar{v}(n_p - n_0)$, the refractive index of the polymer has been estimated to be of the order of 1.60–1.65 (*Table 3*). Hence, the refractive index of formamide is closer to that of the polymer, resulting in contributions from the positive form anisotropy being smaller than those found in aqueous media (*Table 3*).

The validity of the theoretical treatments allowing the calculation of the form anisotropy has often been questioned and most workers are aware of possible overestimations of the form contributions. It is not intended here to discuss the validity of those theories and we shall limit ourselves to comparing the intrinsic optical anisotropies of sample D in water and in formamide + 7×10^{-4} M ammonium formate.

The only slightly smaller value observed in the latter solvent would be due to the effect of the added ionic strength. *Table 3* also shows that the measured and intrinsic optical anisotropy factor decreases with increasing content of ammonium formate. Moreover, we see that the contribution of the measured anisotropy is preponderant over that of the form anisotropy in

Table 3 Partial specific volume, refractive index increment, refractive index of the polymer and optical anisotropy factors of PSSNa samples D and F in water and formamide + ammonium formate

Sample	Solvent	$\bar{v}$ ($cm^3 . g^{-1}$)	dn/dc ($cm^3 . g^{-1}$)	$(g_a - g_b)_{meas} \times 10^3$	n_p	$(g_a - g_b)_f \times 10^3$	$(g_a - g_b)_i \times 10^3$	$(\alpha_a^0 - \alpha_b^0) \times 10^{-40}$ F m^2	$\alpha^0 \times DP^b \times 10^{-40}$ F m^2
F[a]	Water	0.58	0.179	−10.7	1.64	14.9	−25.6	−20 980	82 800
D[a]	Water	0.565	0.180	−10.3	1.65	15.8	−26.1	− 5 560	20 800
F	Formamide + formate 1.4×10^{-3}	0.59	0.120	− 9.5	1.65	6.5	−16.0	−13 340	63 200
D	Formamide + formate 7×10^{-4}	0.52	0.109	−15.7	1.65	6.5	−22.2	− 4 350	15 850
D	Formamide + formate 2×10^{-2}	0.65	0.095	− 1.8	1.60	3.3	− 5.1	− 1 250	15 850

[a] Ref. 6
[b] $\overline{DP}$ = 1093 and 4360 for samples D and F, respectively

formamide media. These results confirm our previous opinion that the form of anisotropy must be taken into account in the interpretation of the optical anisotropy results, even if the theories of this form anisotropy require further improvements.

The last step of our investigations was to determine experimentally the optical polarizability $(\alpha_{\parallel} - \alpha_{\perp})$ of the benzene sulphonate chromophoric group responsible for the electro-optical effects of PSSNa. A semiempirical estimation of this parameter could be performed with molecular orbital theories such as the Hückel method or the self-consistent-field theory, using a procedure analogous to that used by Takashima in the calculation of the π-electron polarizability of adenine and uracil bases of DNA[26]. An approximated value of the average electric polarizability α^0 can be obtained from the measurements of the refractive index and the density of solutions of the monomeric model compound sodium paratoluenesulphonate. Assuming the additivity of the molar refractions R of the solute and the solvent, α^0 can be estimated with the aid of the classical Lorenz–Lorentz equation:

$$R_M = \frac{(n^2-1)M}{(n^2+2)d} = \frac{N_A \alpha^0}{3\varepsilon_0} \qquad (11)$$

where M is the molecular weight, N_A Avogadro's number and $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1} the permittivity of a vacuum. Using the density and refractive index values ($\lambda = 589$ nm) measured at 25°C, we determined a α^0 value with 14.5×10^{-40} F m^2 in formamide + 7×10^{-4} M ammonium formate. Such values are consistent with those previously obtained for the 4-ethyl-1-methyl pyridinium bromide: $\alpha^0 = 14.5 \times 10^{-40}$ F m^2 in water and 21×10^{-40} F m^2 in nitromethane[27]. We are now able to compare the α^0 values with the excess of optical polarizability of the polymer particle $(\alpha_a^0 - \alpha_b^0)$ determined with the aid of the following relationship:

$$(\alpha_a^0 - \alpha_b^0) = 4\Pi\varepsilon_0 (g_a - g_b) M / N_A \qquad (12)$$

Table 3 shows that the $(\alpha_a^0 - \alpha_b^0)$ values in water and in formamide of low formate content differ by a factor of 3.5–4 from the $\alpha^0 DP$ values, i.e. the optical polarizability of the chromophoric group multiplied by the degree of polymerization. The discrepancy reaches a factor of about 12 in formamide + 2×10^{-2} M ammonium formate in which the PSSNa adopts a rather coiled conformation. In this medium, the optical polarizability of the particles would correspond to three times the calculated optical polarizability of a persistent segment, or $\pm 1400 \times 10^{-40}$ F m^2 (80 Å or 32 monomer units). Two factors are able to explain the discrepancy observed; first, the conformation of the polyion, even in water, is not fully stretched, which results in a tilting of the benzene sulphonate group with respect to the main axis of the polyion. The tilting is expected to increase with increasing ionic strength, the conformation of the polyion becoming more and more coiled. As a confirmation, Matsuda and Yamaoka[28] determined, from electric dichroism measurements, average angles between the transition moments of the phenylene side groups and the orientation axis of PSSNa equal to 60° at 224.5 nm and 57° at 262 nm. Secondly, the α^0 value of the sodium paratoluenesulphonate, identified as the optical polarizability of the

chromophoric group of PSSNa, is an average value and a rough estimation of the $(\alpha_{\parallel} - \alpha_{\perp})$ value, i.e. the excess of optical polarizability defined in respect to axes parallel and transverse to the long axis of the polyion.

CONCLUSIONS

We have shown that the apparently anomalous viscometric and electro–optical behaviour of sodium polystyrene sulphonate in formamide can be attributed to an ionic strength effect resulting from the presence of variable amounts of ammonium formate, even in commercial formamide of very high purity (analytical grade). The latter, produced by hydrolysis of formamide in the presence of atmospheric moisture, can reach values as large as 2×10^{-2} M and hence is able to counterbalance, by a screening effect, the repulsion between charged sites, so that the polyelectrolytic character disappears. Appropriate purification allows reduction of the ammonium formate content to values of the order of 10^{-3}–10^{-4} M, provided that the solvent is kept in dark conditions under dry nitrogen. From a study of the conductiometric behaviour of ammonium formate in formamide, we have determined, with good accuracy, the residual amount of this salt in purified fractions of formamide.

Some preliminary conductiometric experiments, not reported here, have proved that the PSSNa behaves as a strong polyelectrolyte in water as well as in formamide + ammonium formate 7×10^{-4} M, the conductivity being five times smaller in the latter solvent. Moreover, at the same molar concentration, the ratios of the conductivity of pTSNa to that of PSSNa are of the same order of magnitude, i.e. 2.3 in water and 2.6 in formamide.

At very low salt contents (0.7 to 1.4×10^{-3} M), the PSSNa displays, as in aqueous media of low ionic strength, the so-called polyelectrolytic effect, i.e. the sharp increase in viscosity and electric polarizability with dilution. From electric birefringence experiments, we also showed that the degrees of extension of PSSNa in water and formamide of similar ionic strength (6–7×10^{-4} M) are the same. At higher ionic strength (2×10^{-2} M), it has been possible to calculate from the viscosity results a persistence length value of the order of 80 Å, practically the same as in 2×10^{-2} M NaCl (74 Å).

It should also be noted that the optical anisotropy factor for sample D, which adopts similar conformations in water ($\bar{\tau}_0 = 48$ μs, $L_0 = 1920$ Å) and in formamide + 7×10^{-4} M ammonium formate ($\bar{\tau}_0 = 115$ μs, $L_0 = 1660$ Å), was about 1.5 times greater in the former solvent. After correction for the form anisotropy contribution, the intrinsic optical anisotropy factors are of the same order of magnitude in the two media, the value in formamide being 15 percent smaller as a result of the ionic strength effect. As a more general implication of this work, one has to be aware of the fact that any physico–chemical study performed in formamide or formamide/water media can be markedly influenced by a strong ionic strength effect of the ammonium formate arising from hydrolysis of the formamide.

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