Polyelectrolyte behaviour of acrylonitrile methallylsulphonate copolymers in dimethylformamide

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The properties in organic solvent (DMF) of two ionic copolymers are investigated and compared to those of polyelectrolytes in aqueous solutions. First, the viscometric behaviour is disccussed: it is demonstrated that $[\eta]$ varies linearly with $C_T^{-1/2}$, where C_T is the ionic concentration of the solution. At infinite salt concentration we obtain data in agreement with unperturbed dimensions. Using isoionic dilution, we deduce ϕ_p, the osmotic coefficient. From osmometry, the dependence of ϕ_p on the concentration is obtained and compared to the theoretical value. In the presence of neutral salt, the osmotic pressure is determined as a function of salt and polymer concentrations. The results are interpreted in terms of a Donnan equilibrium.

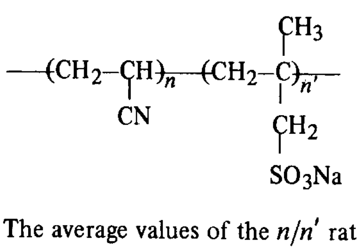
INTRODUCTION

Many reports of polyelectrolyte properties in aqueous solutions have recently been published[1-4]. In organic solvents, specific behaviour has been observed even on uncharged polymers; for instance, we have noted an increase in the specific viscosity when the concentration is lowered[5,6].

In this paper, the viscometric and osmometric data obtained from dimethylformamide (DMF) solutions of sulphonated copolymers are given and discussed. The experimental results are compared with the usual properties of polyelectrolytes in aqueous solutions. The influences of the charge density, the concentration of the polymer and the ionic concentration after addition of a neutral monovalent salt, are investigated.

EXPERIMENTAL

The polymers used, which are manufactured by Rhône–Poulenc, are two copolymers (AN 600 and AN 1200) whose chemical structure is as follows:



$$-(CH_2-\underset{CN}{CH})_n-(CH_2-\underset{\substack{CH_2\\SO_3Na}}{\overset{CH_3}{C}})_{n'}- \qquad n \gg n'$$

The average values of the n/n' ratio are 28.5 and 12.7 corresponding to a capacity Z of 0.6×10^{-3} and 1.2×10^{-3} eq/g, respectively. These copolymers have also been characterized by their weight-average molecular weight determined from g.p.c. experiments[7]; the values are

$$\bar{M}_{W(AN\ 600)} = 250\,000 \text{ and } \bar{M}_{W(AN\ 1200)} = 170\,000$$

The solvent used is freshly distilled DMF to which $NaNO_3$ is added in order to control the ionic concentration. The viscosities are determined with an Ubbelohde capillary viscometer thermostatically controlled at 25.000° ± 0.005°C and adapted to a FICA Viscomat automatic apparatus.

The osmotic coefficient of the copolymers is obtained in pure DMF using Sartorius membranes (SM 11539) with porosity below 5 nm, placed in a Melabs CSM_2 osmometer at 25°C. A Knauer vapour phase osmometer thermostatically controlled at 90°C is used to determine the activity coefficient of $NaNO_3$ (ϕ_s) and the osmotic coefficient (ϕ_p) of the AN in DMF with dibenzoyl as reference solute.

Viscometric behaviour

Concentration dependence. If we study the variation of the specific viscosities as a function of polymer concentration in salt-free DMF as solvent, we observe the classical increase when diluted as pointed out in *Figures 1* and *2*.

The Fuoss representation gives by extrapolation to zero concentration: 2960 and 4610 ml/g for AN 600 and AN 1200, respectively. As previously discussed[8], these values have no meaning from a hydrodynamic point of view. Nevertheless, the linear representation C/η_{sp} $(C^{0.5})$ is similar to the one we could obtain with an aqueous solution of polyelectrolyte.

In order to deduce an intrinsic viscosity $[\eta]$ from a linear extrapolation to $C = 0$ of $\eta_{sp/C}$ (C) at a given ionic strength we use the technique of isoionic dilution. As proposed by Pals and Hermans[9], this linear variation is only obtained if neutral salt is added to the solvent so as to maintain a constant concentration taking into account that of the free counterions. Thus with monovalent small electrolytes, the total ionic concentration C_T remains constant for all dilutions if the following conditions are maintained:

$$C_T = \phi_P C_P + C_s \tag{1}$$

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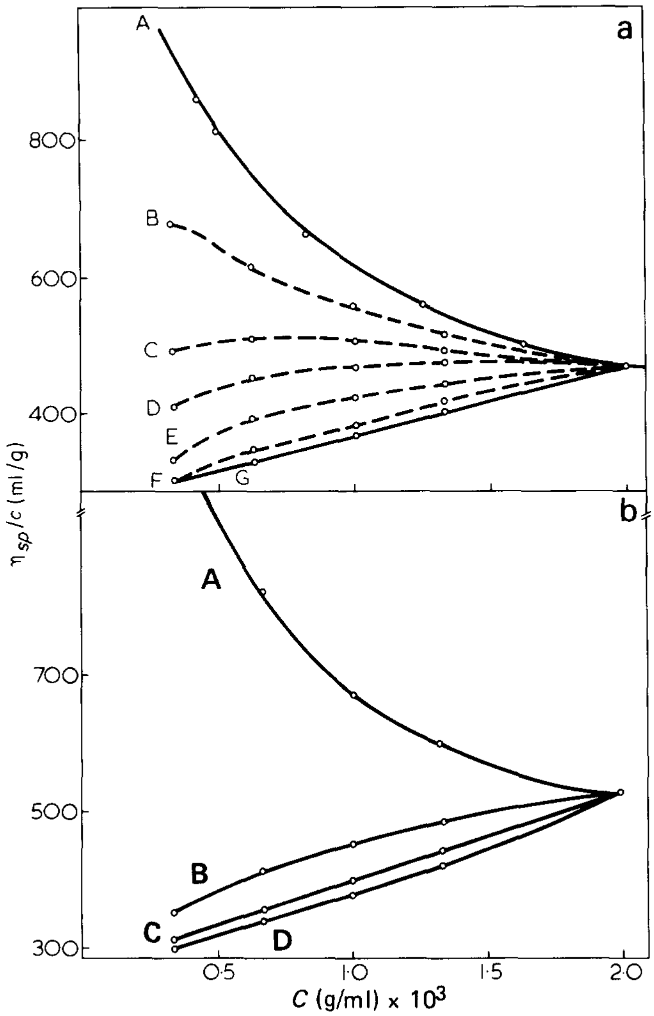

Figure 1 Viscometric determination of the osmotic coefficient: (a) AN 600: A (pure DMF), and B, C, D, E, F, G for ϕ_p = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, respectively; (b) AN 1200: A (pure DMF) and B, C, D for ϕ_p = 0.6, 0.8, 1.0

where ϕ_p, the fraction of free counterions is assumed to be equal to the osmotic coefficient of the copolymers and C_p its concentration expressed in eq/l; C_s is the ionic concentration of salt in the initial solution and C_T that of the electrolyte used as solvent for the dilution.

So, in pure DMF, $C_s = 0$ and the salt concentration C_T for dilution will be equal to $\phi_p C_p$. On the contrary, this technique can also be useful to find the value for ϕ_p when it is unknown. In this case, the salt concentration C_T is changed stepwise, giving a different value each time for ϕ_p, in order to obtain a linear plot. An example of such a determination is shown in *Figure 1*. We obtain $\phi_p = 1$ and 0.8 for AN_{600} and AN_{1200}, respectively; the linear dependence implies that ϕ_p is fairly constant in the narrow range of concentrations investigated.

Ionic strength dependence. We have tested the variation of $[\eta]$ as a function of the salt concentration. When $C_s <$ 5×10^{-2} eq/l, the isoionic dilution is used; when $c_s > 5 \times 10^{-2}$ eq/l, $\phi_p C_p$ becomes negligible with regard to C_s and the polymer is directly dissolved in the same solvent as for dilution (*Figure 2*). The concentration dependence is generally expressed in terms of the relation:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

in which k' is the Huggins constant and $[\eta]$ the intrinsic viscosity characterizing the polymer in a given solvent.

In *Table 1*, we give the data obtained for both copolymers. The values of $[\eta]$ are compared with a g.p.c. determination measured by means of a multidetector as recently discussed[7]; the values obtained for the Huggins constant show clearly the influence of the solvent ionic strength.

In *Figure 3*, we have plotted the variation of $[\eta]$ as a function of $C_T^{-1/2}$. As previously proposed for aqueous solutions[10,11], a linear behaviour is obtained according to the following equation:

$$[\eta] = [\eta]_\infty + kC_T^{-1/2} \qquad (2)$$

The slope k is connected to the charge density and increases with it. The values of $[\eta]_\infty$ corresponding to the extrapolation to infinite salt concentration are:

131 ml/g for AN_{600}

110 ml/g for AN_{1200}

They verify a dependence $[\eta] \sim M^{1/2}$, which means to a first approximation, that the infinite ionic strength nearly corresponds to the θ-conditions. The K values of the Mark–Houwink relationship $[\eta] = KM^a$ for both polymers are found equal to 0.27 and 0.26, respectively, assuming $a = 1/2$.

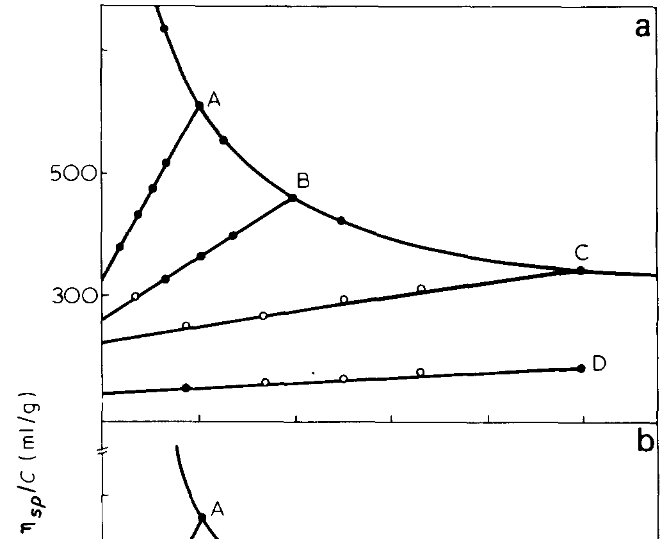

Figure 2 Ionic strength dependence of the reduced viscosity: (a) AN 600, A, B, C, D for $C_T = 6 \times 10^{-4}$, 12×10^{-4}, 30×10^{-4}, 1.0×10^{-1} eq/l, respectively; (b) AN 1200, A, B, C, D, E, F, for C_T = 9.84×10^{-4}, 1.95×10^{-3}, 3.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 1.0×10^{-1} eq/l, respectively

Table 1 Variation of the viscosity parameters with salt concentration (DMF/$NaNO_3$)

AN 600					AN 1200				
C_s (mol/l)	$[\eta]$ g.p.c. (ml/g)	$[\eta]$ (ml/g)	k' Huggins	α_η	C_s (mol/l)	$[\eta]$ g.p.c. (ml/g)	$[\eta]$ (ml/g)	k' Huggins	α_η
6×10^{-4}	–	348	2.01	1.39	6.96×10^{-4}	–	384	3.47	1.52
1.2×10^{-3}	–	267	1.44	1.27	9.8×10^{-4}	–	349	2.58	1.47
3.0×10^{-3}	–	233	0.44	1.21	1.38×10^{-3}	–	333	1.62	1.45
5×10^{-3}	203	198	–	1.15	1.95×10^{-3}	–	287	1.33	1.38
1.5×10^{-2}	166	172	–	1.09	2.30×10^{-3}	–	246	1.02	1.31
5×10^{-2}	149	152	0.38	1.05	5×10^{-3}	223	220	0.61	1.26
1×10^{-1}	–	149	0.36	1.04	1.0×10^{-2}	–	179	0.48	1.17
2×10^{-1}	134	140[a]	–	1.02	1.5×10^{-2}	165	170	–	1.16
					5×10^{-2}	138	142	0.44	1.09
					1×10^{-1}	–	131	0.40	1.06
					2×10^{-1}	127	127[a]	–	1.05
					5×10^{-1}	–	123	0.37	1.04
$\|\eta\|_{C_s \to \infty}$ = 131 ml/g			$\|\eta\|_{C \to 0}$ = 2960 ml/g (Fuoss)		$\|\eta\|_{C_s \to \infty}$ = 110 ml/g			$\|\eta\|_{C \to 0}$ = 4610 ml/g (Fuoss)	

[a] Values from the curve $[\eta] = f(C_T)^{-1/2}$

They can be compared with that for the polyacrylonitrile in DMF at 25°C, equal to $K_\theta = 0.2$ using the unperturbed conditions relation $[\eta]_\theta = K_\theta M^{1/2}$ [12]. In fact, the copolymers have a composition close to polyacrylonitrile; from the statistics of polymer chains with restricted rotation, taking into account the average weight per monomol, we deduced a steric factor $\sigma = 2.2$; 2.51 and 2.55 for polyacrylonitrile, AN_{600} and AN_{1200}, respectively.

In addition, we have calculated an expansion coefficient α_η deduced from:

$$\alpha_\eta^3 = [\eta]/[\eta]_\infty \tag{3}$$

This expresses the modification of the dimensions when the screening ionic effect is sufficiently high to neglect the first electroviscous effects; the values demonstrate the effect of the charge density; nevertheless, α remains small due to the low capacity of both polymers.

Osmotic behaviour

Theoretical approach. If we consider a semipermeable membrane separating a solution of polyelectrolyte from the solvent, on either side of the membrane we have the following situations:

Concentrations (mol/l) before equilibrium		Concentrations (mol/l) after equilibrium	
$2\,m_s$	$2\,m_s$	$2(m_s + x)$	$2(m_s - x)$
	m_p		m_p
	Nm_p		Nm_p

where: m_s is the initial concentration (mol/l) of the considered monovalent salt, m_p corresponds to the polymer concentration (mol/l), N is the average number of charges carried by a polymer molecule and x represents the salt transferred from one compartment to the other at equilibrium.

The activity of the diffusible salt is the same on either side of the membrane and after equilibrium, we have:

$$[(m_s - x) + \phi_p m_p N]\ [(m_s - x)] = [(m_s + x)]^2 \tag{4}$$

in the assumption of ideality with ϕ_p the osmotic coefficient of the polymer, considered independent of m_s. Then:

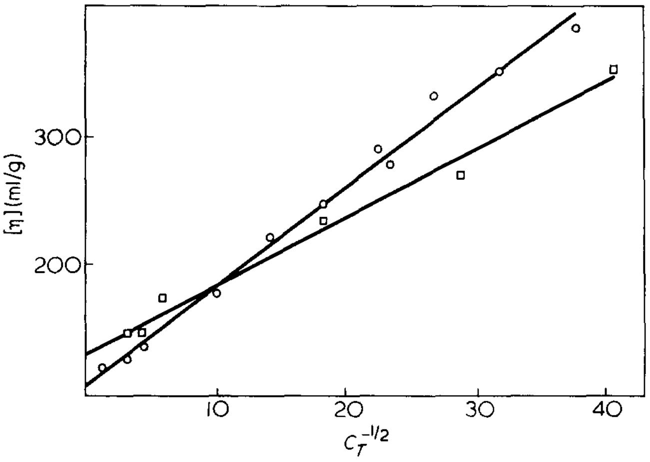

Figure 3 Variation of the intrinsic viscosity with ionic concentration □, AN 600; ○ AN 1200

$$x = \frac{m_s}{\dfrac{4m_s}{Nm_p\phi_p} + 1} \tag{5}$$

The difference of pressure between both compartments can be determined from:

$$\Delta\pi = RT[m_p + 2\phi_s(m_s - x) + \phi_s\phi_p Nm_p - 2\phi_s(m_s + x)] \tag{6}$$

where ϕ_s is the osmotic coefficient of the salt. The equation can be reduced to:

$$\Delta\pi = RT[m_p + \phi_s\phi_p Nm_p - 4x\phi_s] \tag{6a}$$

If the osmotic measurements are made in a salt-free solvent, m_s and x are both equal to zero and equation (6a) becomes:

$$\Delta\pi = RT[m_p + \phi_s\phi_p Nm_p] \tag{7}$$

Owing to the fact that $\phi_s\phi_p Nm_p \gg m_p$, we deduce:

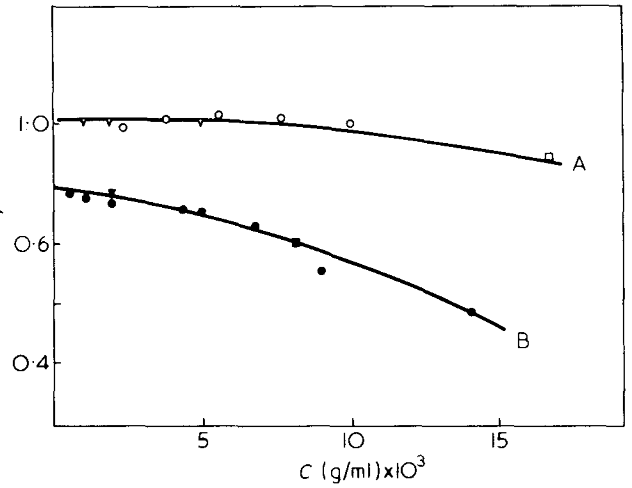

Figure 4 Dependence of ϕ_p with the polymer concentration: A, for AN 600 by: viscometry (△) osmometry (○), vapour phase osmometry (□); B, for AN 1200 by: viscometry (▲), osmometry (●), vapour pression osmometry (■)

$$\phi_p = \frac{\Delta\pi \text{ experimental}}{\Delta\pi \text{ calculated}}$$

$$= \frac{\Delta\pi}{RT}\,\frac{1}{\phi_s N m_p} \qquad (8)$$

When osmotic determination is performed in the presence of a simple electrolyte, the equation (6a) becomes:

$$\Delta\pi = RT\left[m_p + \phi_s\phi_p N m_p - 4\frac{\phi_s m_s}{\dfrac{4m_s}{Nm_p\phi_p} + 1}\right] \qquad (9)$$

and

$$\frac{\Delta\pi}{C} \equiv RT\left[\frac{1}{\bar{M}_n} + \frac{\phi_p\phi_s\, 10^3}{m_0\left(\dfrac{4m_s m_o}{C\phi_p} + 1\right)}\right] \qquad (10)$$

where C is the concentration of the polymer (g/ml), ($\Delta\pi/RT$) expressed in cgs units, $\bar{M}_n$ the number-average molecular weight and m_0 the molecular weight of the repeating unit. Now, for both copolymers studied here, we always have conditions such that $4\, m_s m_o/C\phi_p \gg 1$, then equation (10) becomes:

$$\frac{\Delta\pi}{C} = RT\left[\frac{1}{\bar{M}_n} + \frac{\phi_s\phi_p^2\, 10^3}{4m_s m_o^2}C\right] \qquad (11)$$

From the extrapolation of $\Delta\pi/C$ to $C = 0$, we can deduce the value of $\bar{M}_n$. Equation (11) can be used to interpret the variation of $\Delta\pi/C$ with the polymer concentration and with the ionic strength if we take into account the values of ϕ_p determined in the absence of salt.

Salt free solutions. The osmotic pressure has been determined in pure DMF as a function of the polymer concentration. From equation (8) in which $\phi_s = 0.5$ (as has been measured by vapour phase osmometry with $NaNO_3$ in pure DMF) we deduce the corresponding values of ϕ_p. The results are plotted in *Figure 4* which also shows the values obtained from viscometry and vapour osmometry. The different determinations are in good agreement and confirm the hypothesis previously made concerning the viscometric determination of the osmotic coefficient.

The values of ϕ_p can be discussed using the theoretical patterns proposed for linear polyelectrolytes in dilute solutions. From the chemical structure of both polymers we can calculate the charge parameter under stretch conformation $\lambda = \gamma e^2/DhkT$ with D the dielectric constant ($D = 37$), kT the Boltzman term, e the elemental charge and γ/h the linear charge density, thus $\lambda_{(\text{AN } 600)} = 0.19$ and $\lambda_{(\text{AN } 1200)} = 0.39$.

From Manning theory[13,14], defined for infinite dilution, $\phi = 1 - 1/2\lambda$ when $\lambda < 1$. The values corresponding to both polymers are:

$$\phi_M^{(\text{AN } 600)} = 0.91 \text{ and } \phi_M^{(\text{AN } 1200)} = 0.81$$

The Oosawa model for linear polyelectrolytes[2] can be used to discuss the concentration dependence by means of equation (12):

$$\ln\left(\frac{1-\phi}{\phi}\right) = \ln\left(\frac{\rho}{1-\rho}\right) + \phi\lambda\ln\left(\frac{1}{\rho}\right) \qquad (12)$$

in which $\rho = a^2/R^2$, with R the radius of the cellular volume directly connected with the concentration and 'a' the radius of the volume containing the bound counterions chosen equal to 10 Å. The values we obtain are listed in *Table 2*, where they are compared with the experimental ones. For the lowest concentrations (1 g/l), the two theories give values that reflect fairly well the experimental results, especially Manning's theory, but they cannot predict the concentration dependence. In fact, the Oosawa model shows a decrease of ϕ with the concentration; nevertheless, the experimental decrease observed on AN 1200 is higher, probably due to the high concentration of the solution for which the theory is not valid. Furthermore, as soon as the charge parameter becomes much lower than 1, no theoretical approach can be used to describe rigorously the experimental values[15].

Influence of the salt concentration. The study of the variation of $\Delta\pi/C$ as a function of C, as is pointed out in equation (11) permits us to deduce $\bar{M}_n$ at infinite dilution: $\bar{M}_n$ (AN 600) = 37 000 and $\bar{M}_n$ (AN 1 200) = 35 000. In *Figure 5*, the curves obtained for two values of m_s are given. The slopes vary with C and C_s. This behaviour can be attributed to a Donnan equilibrium established in the cell. In addition, a second virial coefficient A_2 due to volume exclusion must be introduced. Then, if C is expressed in g/ml:

$$\left(\frac{1}{RT}\right)\frac{\Delta\pi}{C} = \frac{1}{\bar{M}_n} + \frac{\phi_s\phi_p^2}{4m_s m_o^2}10^3 C + A_2 C + A_3 C^2 + \ldots \quad (13)$$

Table 2 Comparison between experimental and calculated values of the osmotic coefficient

AN 600 $C \times 10^3$ (g/ml)		a = 10Å		AN 1200 $C \times 10^3$ (g/ml)		a = 10Å	
	R (Å)	ϕ_{exp}	ϕ_{cal}		R (Å)	ϕ_{exp}	ϕ_{cal}
1	104	1.0	0.98	1	108	0.80	0.95
3	60	1.0	0.95	3	62	0.74	0.91
6	43	1.0	0.91	6	44	0.65	0.87
9	35	1.0	0.88	9	36	0.56	0.84
12	30	0.98	0.85	12	31	0.48	0.81

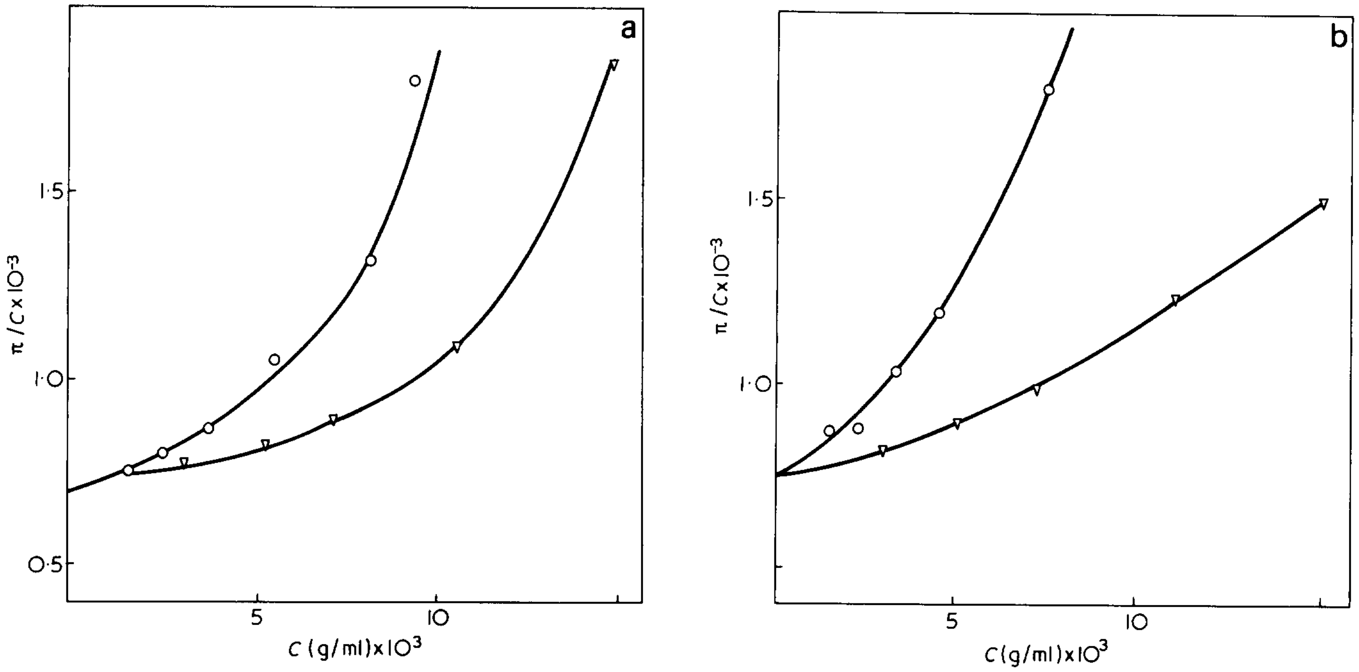

Figure 5 Polymer and salt concentration dependence on the reduced osmotic pressure: 0.01 M (○), 0.05 M (▽). π/c is expressed in (cm of liquid) x ml/g. (a), AN 600; (b) AN 1200

Table 3 Comparison between experimental and calculated values of the Donnan term and the contribution due to the exclusion volume

	AN 600		AN 1200		AN 600	AN 1200
	$\frac{10^3 C\phi_s\phi_p^2}{4m_s m_0^2}$ (mol/g)		$\frac{10^3 C\phi_s\phi_p^2}{4m_s m_0^2}$ (mol/g)		$\frac{4V}{M_W} C$ (mol/g)	
	$m_s = 0.05$		$m_s = 0.01$			
$C \times 10^3$ (g/ml)	exp $\times 10^6$	cal $\times 10^6$	exp $\times 10^6$	cal $\times 10^6$	cal $\times 10^6$	
2	2	4	5	20	0.03	0.05
4	7	9	14	34	0.06	0.09
6	15	13	29	42	0.10	0.13
8	24	17	46	51	0.13	0.19

When m_s is low, the experimental values corresponding to the increase of $\Delta\pi/C$ are in good agreement with those calculated from the Donnan term. In *Table 3*, they are compared to the contribution due to the excluded volume, we deduce from $(4v/\bar{M}_w)C$ with a specific volume $v = 1$ cm^3/g as previously discussed by Tanford[16]; the latter term is negligible with regard to the first.

CONCLUSION

In this work, the polyelectrolyte behaviour of two sulphonated copolymers (AN) dissolved in DMF with charge parameters 0.19 and 0.39 has been investigated.

The reduced viscosity has been discussed as a function of the dilution with pure solvent or by isoionic dilution. By means of the latter technique we determined the osmotic coefficients of the two AN copolymers. Furthermore, the dependence of the intrinsic viscosity on the salt concentration can be expressed as $[\eta] = [\eta]_\infty + kC_T^{-1/2}$ in which k is connected to the charge density. The values of $[\eta]_\infty$ obtained an infinite salt concentration correspond to a first approximation to the intrinsic viscosity under θ conditions.

Using osmometry, the osmotic coefficients have been studied as a function of the charge density. The results are interpreted in terms of Manning's and Oosawa's models. In salt solutions, the osmotic pressure is determined as a function of the polymer concentration for two concentrations of neutral salt. It is proposed that the slope of the curves be interpreted in terms of a Donnan equilibrium established in the cell.

The results indicate that, for two polymers with low charge parameters studied here, the behaviour in DMF solution may be assumed to be similar to the behaviour of polyelectrolytes in aqueous solution.

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