Poly(sulphopropylbetaines): 2. Dilute solution properties

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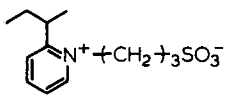
Solution properties of a series of aromatic ($5\times10^3<\bar{M}_w<2.5\times10^5$) and aliphatic ($10^6<\bar{M}_w<1.2\times10^7$) poly(sulphopropylbetaines) have been investigated by examining three complementary phenomena: (a) solubility in organic protic solvents; (b) water solubility promoted by various (cloud point titrations), with special emphasis on the influence of the anion polarizability and a comparison between Na^+ and Ca^{++}; (c) hydrodynamic and morphological properties in aqueous NaCl solutions at 25°C, as derived from the Mark–Houwink–Sakurada relations. Chain expansion is a slightly increasing function of the NaCl concentration ($\leqslant 1$ M) but it remains, however, relatively low, even for high molecular weights ($\alpha_\eta<1.15$). With respect to the polymeric amino precursors, the zwitterionic group $-\overset{|}{\underset{|}{N}}{}^{+}\!-\!(CH_2)_3SO_3^-$ enhances chain rigidity (steric factor σ), as a result of its steric hindrance and specific dipolar interactions between neighbouring units.

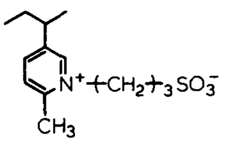
Keywords Aliphatic and aromatic poly(sulphopropylbetaines); solubility properties; Mark–Houwink–Sakurada relations; unperturbed dimensions and chain rigidity; chain expansion in aqueous NaCl solutions

INTRODUCTION

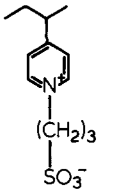
In Part 1[1] the synthesis and the characterization of a series of high molecular weight aromatic and aliphatic poly(sulphopropylbetaines) were described as summarized:



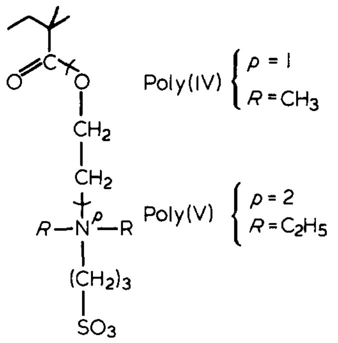
Poly(I)



Poly(II)



Poly(III)



polyzwitterions are examined with special emphasis on three complementary phenomena: (a) solubility in organic protic solvents; (b) water solubility promoted by various salts; (c) hydrodynamic and morphological properties in aqueous NaCl solutions at 25°C, as derived from the Mark–Houwink–Sakurada relations. Critical confrontation of these studies with some pioneering but limited data on poly(2-vinylpyridinium sulphobutylbetaine)[2] and with more recent results on poly(vinylimidazolium sulphopropylbetaine)[3] may allow a better

In this investigation the dilute solution properties of these understanding of the specific properties of these homologous polyzwitterions, as a well-defined series in the field of polyampholytes[4].

EXPERIMENTAL

Polymers and salts

Poly(sulphopropylbetaines) (poly(I)–poly(V)) were prepared by free radical polymerization of the corresponding monomers, as described previously[1], and poly(2-vinylpyridinium sulphobutylbetaine) was obtained similarly[2].

Aromatic and aliphatic poly(amine N-oxides) were derived from the parent poly(amines) by oxidation according to a literature procedure[5]: oxidation at 75–80°C of a 10% wt/vol solution of the polymeric precursor in glacial acetic acid by aqueous hydrogen peroxide (30%) for 24 h, using a stoichiometric ratio: $[H_2O_2]/[\text{amine}]=2.1$. The original purification step was improved as follows: after rotary evaporation of the solvent, the residue was dissolved in water, and acetic acid was removed by three successive elutions on a strongly basic ion-exchange resin, Merck-III. The polymer was recovered by freeze drying: element analyses were in reasonably good agreement with quantitative oxidation taking into account the high hygroscopicity of the samples, and potentiometric measurements show that the residual acidity was always lower than 0.7 wt% (CO_2H). Unfortunately, as mentioned by Loucheux *et al.*[6], simultaneous degradation does occur to a relatively high extent, as illustrated by the following calculated and experimental $\bar{M}_w$ values: poly(2-vinylpyridine N-oxide) (P2VPO): $\bar{M}_w\times10^{-5}=0.85$ (calc.), 0.56 (exp.); poly(2-

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methyl, 5-vinylpyridine N-oxide) (P2M5VPO): $\bar{M}_w \times 10^{-5} = 1.15$ (calc.), 1.01 (exp.); poly(4-vinylpyridine N-oxide) (P4VPO): $\bar{M}_w \times 10^{-5} = 8.33$ (calc.), 0.86 (exp.); poly(*N*,*N*-dimethylaminoethylmethacrylate N-oxide) (PDMAEMAO): $\bar{M}_w \times 10^{-5} = 1.31$ (calc.), 0.28 (exp.). The various salts, of best reagent grade, were used without further purification.

Fractionation

Polymer fractionation was carried out by precipitation, using water–methanol as the solvent–non solvent system. The coacervation of the successive fractions from the initial 1% polymer solution was monitored by progressive increase of the non-solvent volume fraction (γ) and simultaneous lowering of temperature within the range 40–20°C. Fractionation of poly(I) ($\bar{M}_w \approx 10^5$) was relatively straightforward, yielding fractions of moderate polydispersity $\bar{M}_w/\bar{M}_n$ of ≈ 1.2–1.3, as established by gel permeation chromatography (g.p.c.). For high molecular weight poly (V) ($\bar{M}_w > 10^6$), however, fractionation was difficult in spite of refractionation of the larger fractions, showing low efficiency and selectivity ($\bar{M}_w/\bar{M}_n \approx 1.6$) as shown, for example, by the following data: $\gamma = 0.446$, $T = 25°\text{C}$: $\bar{M}_w = 3.9 \times 10^6$; $\gamma = 0.556$, $T = 21°\text{C}$: $\bar{M}_w = 4.0 \times 10^6$; $\gamma = 0.460$, $T = 23°\text{C}$; $\bar{M}_w = 7.4 \times 10^6$.

Solubility measurements and cloud point titrations in aqueous salt solutions

Solubility of the various polymers in organic solvents at room temperature was established for the 3% wt/vol solution, after preheating at 80°C for 2 h. The critical minimum salt concentration (CSC) required to promote water solubility at 25°C was measured by titration of 1% wt/vol polymer solution at sufficiently high salt concentration with pure water: the accuracy of the CSC values obtained by visual determination of the first cloud point was approximately $\pm 2\%$.

Physical measurements

The contribution of the polyzwitterions to the ionic strength of the aqueous salt solutions may be reasonably neglected: thus, dialysis of isoionic dilutions were omitted. The lack of any significant deviation of the experimental data from their expected rectilinear dependence *versus* concentration for light scattering and viscosity measurements may be considered as an *a posteriori* justification of the simple dilution method. Whenever necessary, the pH values were monitored by addition of calculated amounts of HCl or NaOH, avoiding buffer solutions. Molecular weights were measured by light scattering at 25°C as previously described[1], using the following values of the refractive index increments: $dn/dc = 0.197$ and 0.144, ml g^{-1} for poly(I) ($\lambda = 6320$ Å) and poly(V) ($\lambda = 5460$ Å), respectively, in aqueous 0.1 M NaCl; dn/dc ($\lambda = 6320$ Å) $= 0.220$, 0.262, 0.241 and 0.119 ml g^{-1} for P2VPO (1 M H_2O–NaCl), P2M5VPO (CH_3OH), P4VPO (0.1 M H_2O–NaCl) and PDMAEMAO (0.1 M H_2O–NaCl), respectively. For the high molecular weight fractions of poly(V) ($\bar{M}_w > 10^6$), the Zimm plots did not show any curvature of the $P^{-1}(\theta)$ function: poly(V) dilute solutions were thus safely considered free from eventual aggregates. Viscometric measurements were carried out at 25°C on an automatic Fica device: in all cases the experimental data gave a good fit of the Huggins equation $\eta sp/c = [\eta] + k'[\eta]^2 C$. The reproducibility of $[\eta]$ and $\bar{M}_w$ determinations was not better than ± 3 and $\pm 6\%$, respectively, chiefly because of the high hygroscopicity of the samples[1]. The partial specific volumes of the polymers, $\bar{v}$, were measured at 25°C on a digital densiometer, Anton Paar KG model DMA-02: $\bar{v} = 0.673$, 0.672 and 0.656 ml g^{-1} for poly(I) in 0.01, 0.1 and 1 M aqueous NaCl, respectively; $\bar{v} = 0.740$ ml g^{-1} for poly(V) in 0.05 M aqueous NaCl. Gel permeation chromatography (g.p.c.) was carried out at room temperature on a laboratory built apparatus fitted either with Sephacryl S-200 or with Sepharose CL-2B (Pharmacia) gels for the low ($\bar{M}_w < 2 \times 10^5$) and the high ($\bar{M}_w > 10^6$) molecular weight ranges, respectively. Sephacryl S-200: elution solvent, 0.1 M aqueous NaCl; calibration, polyethyleneglycol standards; $\sigma^2/a^2 = 0.41$. Sepharose CL-2B: elution solvent, 0.5 M aqueous NaCl; calibration, sulphonated polystyrene and polyethyleneoxide standards; $\sigma^2/a^2 = 0.46$. Because of the relatively low efficiency of these columns, as shown by the relatively high σ^2/a^2 values, g.p.c. measurements were used only for an estimation of the fraction polydispersity indexes $\bar{M}_w/\bar{M}_n$.

RESULTS AND DISCUSSION

Solubility properties of the poly(sulphopropylbetaines) poly(I)–poly(V)

Solubility in organic solvents. The results of solubility tests are given in *Table 1*, together with some polarity parameters of the various solvents: the Hildebrand solubility parameter δ[7,8] (cohesive energy density of the medium), the dipole moment μ and the dielectric constant ε[9,10], and finally the Dimroth–Reichardt empirical E_T parameter[11] which combines polarity effects (ε, μ) and hydrogen-bond donating power of the solvent[12].

The few experimental data do not allow a quantitative interpretation of the solubility properties, for example within the framework of the three component solubility parameter concept[7,8], but they may be tentatively rationalized as follows:

(1) The polymers are insoluble in aprotic solvents, even in the highly dipolar ones ($\mu > 3.8$ D, $\varepsilon > 30$) such as tertiary amides (DMF, DMAC, NMP, HMPA), sulphoxides (DMSO), sulphones (sulpholane) or cyclic carbonates (propylene carbonate).

(2) As a general trend, solubility is restricted to protic solvents of high E_T values, $E_T > 55$ kcal mol^{-1}: formamide, polyhydric or halogenated alcohols, strong carboxylic acids. The intrinsic viscosities of poly(I), which may be considered as a quantitative measure of the thermodynamic affinity of the solvents for the chain, indicate that fluorinated alcohols are the best solvents in spite of their relatively low dipole moments and dielectric constants. This feature emphasizes the significance of the hydrogen-bond donating power of the medium which is the strongest for these very weakly self-associated alcohols: TFE and HFIP are actually the best hydrogen-bond donors in terms of E_T[11] as well as in the α-scale recently developed by Taft *et al.*[12]. Hydrogen-bond solvation of the sulphonate anion may thus appear more efficient than dipolar interactions.

(3) The weight fraction of the common zwitterionic structure is the main solubility factor for all polymers, but small structural variations may induce significant solubility differences, especially for water (see later). In the aromatic series, the most symmetric poly(III) is also the

Table 1 Solubility of poly(sulphopropylbetaines) at room temperature

Solvent	δ (cal cm^{-3})$^{0.5}$	μ (D)	ϵ	E_T (kcal mol^{-1})	$[\eta]_I$ (dl g^{-1}) (25°C)	I[a]	II	III	IV	V
Water	23.4	1.82	78.4	63.1	0.091[b]	+	–	–	–	+
Formamide	19.2	3.37	111.0	56.6	0.146	+	+	–	+	+
N-methylformamide	16.1	3.86	182.4	54.1		–	+	–	–	+
N-methylacetamide	14.6	4.39	191.3	52.0		–	+	–	–	–
Glycol	14.6	2.28	37.7	56.3		+	+	–	–	+
Diethyleneglycol	12.1	2.31	31.7	53.8		+	+	–	–	+
Triethyleneglycol	10.7	5.58	23.69	53.5		–	–	–	–	±
1,2-propanediol	12.6	2.25	32.0	54.1		–	±	–	–	–
1,3-propanediol	–	2.50	35.0	54.9		–	–	–	–	+
Glycerol	16.5	2.68	42.5	57.0		+	±	–	–	±
Trichloroethanol	–	2.04	–	56.6		+	+	+	+	+
Trifluoroethanol	11.7	2.03	27.0	59.5	0.261	+	+	+	+	+
Hexafluoroisopropanol	9.34	2.05	–	69.3	0.231	+	+	+	+	+
Formic acid	12.1	1.82	58.5	–	0.204	+	+	–	+	+
Acetic acid	10.1	1.68	6.15	51.2		–	–	–	–	–
Dichloroacetic acid	11.0	–	8.2	–	0.194	+	+	+	+	+

[a] $\bar{M}_w = 8.45 \times 10^4$
[b] pH = 5.3
+ Soluble
– Insoluble
± Swelled

least soluble, while poly(V) is the most soluble of all the tested samples.

(4) Finally the solubility of the polyzwitterions poly(I)–poly(V) in protic solvents may be opposed to the total insolubility of the homologues poly(vinylimidazolium sulphopropylbetaine) observed by Salamone *et al.*[13].

Water solubility. Poly(I) and poly(V) are water soluble at $T \geqslant 20°C$, a very unusual property for poly(sulphobetaines), only shared by poly(2-vinylpyridinium sulphobutylbetaine)[2]. However, salt addition has been shown previously to promote water solubility of these polyzwitterions[2,3], a very specific property in sharp contrast with the polyelectrolyte behaviour. The critical salt concentration (CSC) necessary to dissolve poly(IV) was determined at 25°C by cloud point titrations (see Experimental). The respective influence of the cation and the anion nature on the CSC values are shown in *Table 2*.

Table 2 Critical salt concentrations for aqueous solutions of poly(IV) at 25°C

Chlorides		Sodium salts	
cation	(mol l^{-1})	anion	(mol l^{-1})
H^+	0.066	OH^-[a]	>5
Li^+	0.088	F^-[b]	
Na^+	0.054	Cl^-	0.054
K^+	0.061	Br^-	0.020
NH_4^+	0.062	I^-	0.0038
$N(CH_3)_4^+$	0.047	SCN^-	0.0028
Mg^{++}	0.050	ClO_4^-	0.0011
Ba^{++}	0.060	$(C_6H_5)_4B^-$	<0.0005
Ca^{++}	0.062		
Tetraalkylammonium bromides			
$N^+(CH_3)_4$	0.0145		
$N^+(C_2H_5)_4$	0.0135		
$N^+(C_3H_7)_4$	0.0125		
$N^+(C_4H_9)_4$	0.0115		

[a] Partial hydrolysis of the ester function
[b] Not soluble in saturated NaF solution (≈1 M)

For a common anion, Cl^-, the CSC values remain in a relatively narrow range of ≈0.047–0.088 M, perhaps because all the tested cations belong to 'hard acids'[14]. The sequence of increasing solubility power (decreasing order of CSC values):

$$Li^+ < H^+ < Ca^{++},\quad NH_4^+ \leqslant K^+ \leqslant Ba^{++} < Na^+ < Mg^{++} < N^+(CH_3)_4$$

is not the same as that observed by Salamone *et al.*[3] for poly(vinylimidazolium sulphopropylbetaine):

$$NH_4^+(0.52\,\text{M}) < Li^+ < K^+ \leqslant Na^+ < Ca^{++} < Mg^{++} \leqslant Ba^{++}(0.24\,\text{M})$$

and it does not agree with the binding affinity of the various cations for polysulphonates[15,16]:

Increasing order of binding

$$\left\{\begin{array}{l} {}^+N(CH_3)_4 < Li^4,\ H^+ < Na^+ < K^+ \\ Mg^{++} < Ba^{++} \end{array}\right.$$

The tetramethylammonium cation is the more efficient to promote water solubility for poly(IV). Moreover, the experimental sequence:

$$N^+(CH_3)_4 < N^+(C_2H_5)_4 < N^+(C_3H_7)_4 < N^+(C_4H_9)_4$$

observed for tetraalkylammonium bromides is in good agreement with the cation binding selectivity of sulphonic resins[16], but the very low magnitude of the observed effects indicates that the hydrophobic contribution to polyzwitterion solvation is negligible.

For a common cation, Na^+, the CSC values are very sensitive to the anion structure, and cover a range of approximately two orders of magnitude. The sequence of increasing solubilizing power:

$$OH^-, F^- \ll Cl^- < Br^- < I^- < SCN^- < ClO_4^- < {}^-B(C_6H_5)_4$$

is reasonably consistent with that observed previously for poly(4-vinyl-pyridinium sulphobutylpyridine)[2] and for poly(vinylimidazolium sulphopropylbetaine)[3]: CSC = 0.37 and 0.03 M for NaCl and $NaClO_4$, respectively, in the latter case. The similar behaviour of aliphatic and aromatic polyzwitterions suggests that the polarizability or the 'softness' of the quaternary ammonium cation is of minor importance. This sequence of anion binding affinity is also in good agreement with that observed for aliphatic poly(ionenes)[17], and it is closely parallel to the well-known Hofmeister 'lyotropic series'[18], increasing polarizability or 'softness'[14] of the anion.

Finally, urea in relatively moderate concentration of ≈ 2.5 M also promotes water solubility for poly(IV); both hydrogen bonding solvation of the sulphonate anion and 'breaking' of the water structure may contribute to such a solubilization, as in the well-known case of protein denaturation[19].

Salt effects on the intrinsic viscosities of poly(I) and poly(V) aqueous solutions

The effects of salt on the intrinsic viscosities (25°C) of aqueous solutions of poly(I), poly(V) and poly(2-vinylpyridinium sulphobutylbetaine) are shown in *Figure 1* for NaCl and $CaCl_2$ as representative mono- and divalent species.

At a constant molarity, Na^+ leads to significantly higher chain expansion only for poly(I), especially within the lower salt concentration range (< 0.5 M). The effects of Na^+ and Ca^{++} are much less differentiated for the other polymers, although Ca^{++} has been shown more efficient for poly(vinylimidazolium sulphopropylbetaine)[3].

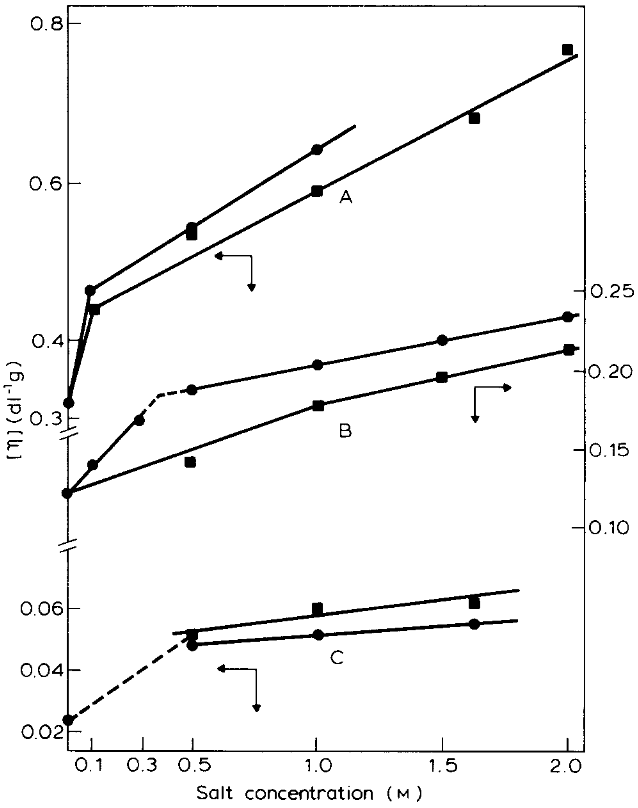

Figure 1 Influence of NaCl and $CaCl_2$ on intrinsic viscosities of A, poly(I); B, poly(V); and C, poly(2-vinylpyridinesulphobutylbetaine) in H_2O at 25°C. $\bar{M}_w$[poly(V)] = 1.05×10^6, $\bar{M}_w$[poly(I)] = 8.2×10^4, $\bar{M}_w$[poly(2-vinylpyridinesulphobutylbetaine)] = 1.73×10^4. ●, NaCl; ■, $CaCl_2$

As observed previously[3], the effects of salt are much higher in the lower concentration range: the $[\eta]$ variations may be tentatively described by two consecutive increasing rectilinear functions of salt concentration. For poly(I) and poly(V), NaCl, for example, would be ≈ 6 and 4 times more efficient at concentrations less than 0.3 and 0.1 M, respectively, as measured approximately by $d[\eta]/d[NaCl]$. According to Salamone *et al.*[3] these two modes of increasing chain expansion could be attributed, respectively, to site and atmospheric binding of the anion by the polyzwitterion, the first and stronger interactions leading to the more marked effects. This apparently reasonable assumption for such a complex phenomenon[15,16] would have to be established by direct experimentation.

For poly(I) and poly(V), increasing chain expansion is still observed within the high salt concentration range, and no asymptotic behaviour is evident even for 2 M solutions. This is not the case, however, for poly(2-vinylpyridinium sulphobutylbetaine), but the possible influence of the slightly more hydrophobic zwitterion cannot be ascertained as the low molecular weight of this sample ($\bar{M}_w = 1.73 \times 10^4$) may be the major factor influencing such behaviour.

The intrinsic viscosities of poly(I) are almost pH independent (monitored by HCl or NaOH): $[\eta]$ $dl\,g^{-1} = 0.0946$, 0.0912, 0.0855 and 0.0912 for pH = 3.0, 5.3, 8.0 and 10.0, respectively. These non-monotonous, very weak fluctuations may be due to the corresponding weak variations of the ionic strength of the medium and the nature itself of the pH regulating reagents (see previously); they are, moreover, in good agreement with the inability of the zwitterion to be protonated in an acid medium[1]. This expected behaviour is in sharp contrast with that of poly(4-vinylpyridinium sulphobutylbetaine) in a 0.42 M NaCl aqueous solution which shows steadily and markedly decreasing specific viscosities with increasing pH values[2].

Increasing chain expansion with increasing salt content, especially in the presence of a divalent cation such as Ca^{++}, indicates the fundamental difference between polyzwitterions and polyelectrolytes. However, this specific property may not be unique as similar behaviour may be actually found for some apparently different polymer–solvent systems. As a more general concept, it may be assumed that whenever strong intra- or inter-chain interactions inhibit solubility, whatever their nature, (dipolar, hydrogen-bond etc.), addition of salts able to disrupt the physical network may promote solubility and further chain expansion: this is found, for example, with LiCl or $CaCl_2$ in dipolar aprotic solvents for aromatic polyamides[20] (hydrogen bonding), with concentrated aqueous solutions of $ZnCl_2$[21,22] or NaSCN[23] for polyacrylonitrile (dipolar and hydrogen bonding interactions disrupted by salt complexation on the nitrile group), or with a moderately concentrated aqueous solution of NaSCN for poly(glycinamide)[24].

It was thus of interest to establish whether there are other very dipolar water-soluble polymers which could eventually reproduce the polysulphobetaine behaviour. Because of their ready availability poly(amine N-oxides) were examined, which show a very dipolar function ($\mu > 4D$) of strong zwitterionic character[25] ($-\overset{\diagup}{\underset{|}{N}}{}^{+}-O^{-}$ is the major mesomeric form) and of high chelating power towards a variety of metal cations[26]. For the three poly(vinylpyridine N-oxides) and for poly(dimethylaminoethylmethacrylate N-oxide) intrinsic viscosities were measured as a function of salt concentration at a constant pH value selected to minimize the $[\eta]$ fluctuations *versus* pH[27] and to avoid N-oxide protonation. The results are shown in *Table 3*. For poly(pyridine N-oxides) the variations of intrinsic viscosity with salt concentration within the range 0–2 M are not monotonous, and fluctuations around their average values remain weak, <8% in most cases, for Na^+ as well as for Ca^{++}. For the more ionic poly (aliphatic amine N-oxide), which is the most expanded taking into account its lowest molecular weight, intrinsic viscosity seems to be a steadily decreasing function of the electrolyte concentration. The inaccuracy of the $[\eta]$ measurements (see Experimental) precludes any quantitative interpretation of the data, but the lack of any well-defined chain expansion with increasing salt concentration is well ascertained. Moreover, the results are not consistent with the relatively sharp decrease of η_{sp} (of ≈30%) recently observed for the system P2VPO–$CaCl_2$ when the salt concentration is increased up to 0.24 M[28]. The very weak sensitivity of poly(amine N-oxides) towards salt effects may be tentatively accounted for by the thermodynamic quality of pure water for these chains being too good: the amine N-oxide function is actually one of the best hydrogen-bond acceptors[29].

Mark–Houwink–Sakurada relations for aqueous solutions of poly(I) and poly(V)

Light scattering and intrinsic viscosity measurements were carried out on fractionated samples ($\bar{M}_w/\bar{M}_n \approx 1.25$, 1.60 for poly(I) and poly(V), respectively) for three NaCl concentrations. The experimental data in *Table 4* lead to the MHS relations $[\eta]=K\bar{M}_w^a$ outlined in *Table 5*.

For the high molecular weight poly(V) fractions in 0.1 M aqueous NaCl, the dependence of the radius of gyration on molecular weight is well described by the relation:

$$(\bar{S}_z^2)^{1/2}, \text{Å} = 0.122 \times \bar{M}_w^{0.57}, \quad R(6) = 0.9986$$

Table 3 Variations of the intrinsic viscosities of poly(amino-N-oxides) in aqueous solutions at 25°C as a function of salt concentration

Polymer	Salt conc. (M)	$[\eta]$ NaCl (dl g^{-1})	$[\eta]$ $CaCl_2$ (dl g^{-1})
P2VPO	0.0	0.218	0.218
$\bar{M}_w = 5.6 \times 10^4$	0.1	0.192	0.196
pH = 7.0 ± 0.5 (NaCl)	0.2	–	0.202
pH = 6.8 ± 0.2 ($CaCl_2$)	0.5	0.192	0.195
	1.0	0.197	0.217
	2.0	0.191	0.226
P2Me5VPO	0.0	0.405	0.405
$\bar{M}_w = 1.01 \times 10^5$	0.5	0.470	–
pH = 7.1 ± 0.2 (NaCl)	1.0	0.451	0.426
pH = 7.0 ± 0.3 ($CaCl_2$)	1.5	0.479	–
	2.0	0.416	0.441
P4VPO	0.0	0.428	0.428
$\bar{M}_w = 8.6 \times 10^4$	0.5	0.389	0.457
pH = 8.6 ± 0.3 (NaCl)	1.0	0.406	0.465
pH = 9.0 ± 0.3 ($CaCl_2$)	2.0	0.380	0.413
PDMAEMAO	0.0	0.480	0.480
$\bar{M}_w = 2.85 \times 10^4$	1.0	0.458	0.418
pH = 7.00 ± 0.03 (NaCl and $CaCl_2$)	2.0	0.392	0.404

Within the non-free draining limit, Kurata and Yamakawa[30] have correlated the viscosity α_η and the geometric α expansion coefficients of flexible coils through the semi-empirical equation:

$$\alpha_\eta^3 = \alpha^{2.43}, \text{ with } \alpha_\eta^3 = [\eta]/[\eta]_\theta, \ \alpha = (\bar{S}_z^2)^{1/2}/(\bar{S}_z^2)_\theta^{1/2}$$

which essentially holds for thermodynamically poor solvents. This allows a direct comparison of the exponents a and b of the previous power laws, $[\eta] \propto \bar{M}_w^a$ and $(\bar{S}_z^2)^{1/2} \propto \bar{M}_w^b$, which are expected to obey the following relation:

$$a - 0.5 = 2.43(b - 0.5)$$

The values obtained for the system poly(V)–0.1 M aqueous NaCl, $a = 0.637 \pm 0.012$ and $b = 0.575 \pm 0.015$, are in reasonably good agreement with this semi-empirical equation; this feature may be considered as a strong argument for the self-consistency of the light scattering and viscosity measurements.

The second virial coefficients are systematically very low and even negative in some cases, and the inaccuracy of their values precludes establishment of any reliable molecular weight dependence. They indicate, however, that aqueous NaCl solutions up to 1 M are actually very poor solvents for the polyzwitterions.

Polyzwitterion unperturbed dimensions and polymer–solvent interactions

Within the general framework of the so-called two-parameter theories, a number of semi-empirical equations[31] may be established from the $[\eta]-\bar{M}_w$ data obtained in good solvents allowing calculation of:

(a) the unperturbed dimensions of the chain, K_θ, which reflect short range interactions;

(b) the long-range interactions related to polymer–solvent interactions (B parameter) which promote the excluded volume effect.

In spite of the theoretical drawbacks, this approach is used for the purpose of comparison by selecting the following two complementary equations:

$$[\eta]\bar{M}_w^{-1/2} = K_\theta + 0.346\phi_0 B\bar{M}_w^{1/2}, \quad 1 < \alpha_\eta^3 < 1.6 \tag{1}$$

$$[\eta]^{1/2}\bar{M}_w^{-1/4} = K_\theta^{1/2}(1 + 0.42\phi_0 B\bar{M}_w[\eta]^{-1}), \quad 1.8 < \alpha_\eta^3 < 4 \tag{2}$$

$K_\theta = \phi_0\left(\frac{\bar{r}_0^2}{M}\right)^{3/2}$ where $\bar{r}_0$ is the unperturbed root mean square end-to-end distance

$\phi_0 = 2.7 \times 10^{21}$ ($[\eta]$ in dl g^{-1}) Flory constant corrected value for polydispersity indexes $\bar{M}_w/\bar{M}_n \approx 1.3$

The Burchard–Stockmayer–Fixman equation[32] as amended by Yamakawa[33] (equation (1)) holds for medium molecular weight range and low chain expansion, whereas the Berry equation[34] (equation (2)) is still valid for very high molecular weights in a wide expansion range.

Because of the scattering of experimental points, the previously calculated MHS relations were used to derive the expected rectilinear variations: this is actually possible only for a given molecular weight range as often observed, and this restriction leads to some ambiguity for the K_θ and B values: see *Figures 2–5*.

Table 4 $[\eta]$, $(\overline{S_z^2})^{1/2}$ and $\bar{M}_w$ data for poly(I) and poly(V) in NaCl aqueous solutions at 25°C

		[NaCl] (mol l^{-1})			
		0.01	0.1		1.0
	$M_w \times 10^{-4}$	$[\eta]$, (dl g)	$[\eta]$, (dl g^{-1})	$(\overline{S_z^2})^{1/2} \times 10^{-3}$ (Å)	$[\eta]$, (dl g^{-1})
poly(I)	21.4	–	0.218	a	–
	16.4	0.199	–	a	0.316
	11.8	0.163	–	a	–
	10.8	–	0.157	a	0.213
	7.93	0.132	–	a	0.206
	6.85	–	–	a	0.164
	4.94	0.104	0.105	a	0.123
	3.93	0.087	–	a	0.105
	2.23	–	0.060	a	–
	1.02	–	0.035	a	0.055
	0.570	–	0.024	a	–
		[NaCl] (mol l^{-1})			
	$M_w \times 10^{-6}$	0.05	0.1		1.0
poly(V)	11.8	2.17	2.43	1.43	3.13
	9.47	–	–	1.20	–
	7.38	1.75	1.89	1.10	2.62
	4.08	–	–	0.800	–
	2.07	0.755	0.801	0.500	1.08
	1.09	0.511	0.545	0.360	0.723

[a] $(\overline{S_z^2})^{1/2} < 200$ Å

Table 5 MHS parameters for poly(I) and poly(V) in aqueous NaCl solutions at 25°C

	[NaCl] (mol l^{-1})	K (dl g^{-1})	a	$R(n)^a$
Poly(I)	0.01	2.38×10^{-4}	0.56	0.9887 (5)
$5 \times 10^3 < \bar{M}_w < 2.5 \times 10^5$	0.1	1.26×10^{-4}	0.61	0.9976 (6)
	1.0	1.51×10^{-4}	0.63	0.9860 (7)
Poly(V)	0.05	9.23×10^{-5}	0.62	0.9990 (4)
$10^6 < \bar{M}_w < 1.2 \times 10^7$	0.1	7.70×10^{-5}	0.64	0.9996 (4)
	1.0	1.10×10^{-4}	0.63	0.9976 (4)

[a] Correlation coefficient for n experimental points

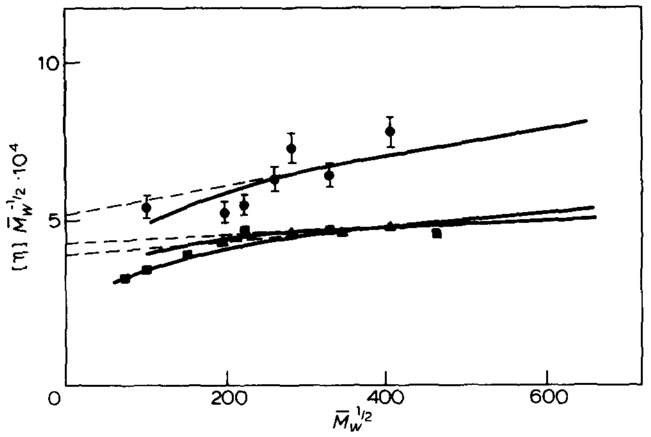

Figure 2 B-S-F plot of $[\eta]$–$\bar{M}_w$ data for poly(I) in NaCl aqueous solutions at 25°C. ▲, 0.01 M; ■, 0.1 M; ●, 1.0 M

None of the other equations, such as Bodhanecky–Cowie relation[35], allows better linearization of the experimental points. The various structural parameters, such as the steric factor σ, the characteristic ratio C_∞ and the length of the statistical element b, were calculated in the usual manner[31,36] and are given in *Table 6*.

$$\sigma = \left(\frac{\bar{r}_0^2}{\bar{r}_{0,f}^2}\right)^{1/2} \text{ with } \left(\frac{\bar{r}_{0,f}^2}{M}\right)^{1/2} = \frac{3.08}{M_0^{1/2}}$$

$$C_\infty = \lim_{n\to\infty}\left(\frac{\bar{r}_0^2}{nl^2}\right) = \left(\frac{K_\theta}{\phi_0}\right)^{2/3} \cdot \frac{M_0}{2l^2}$$

$$b = \left(\frac{K_\theta}{\phi_0}\right)^{1/3} . M_0^{1/2} \qquad M_0 \begin{cases} (\mathrm{I}) = 227.3 \\ (\mathrm{II}) = 241.3 \\ (\mathrm{III}) = 227.3 \\ (\mathrm{IV}) = 279.3 \\ (\mathrm{V}) = 351.4 \end{cases} \quad l = 1.54 \text{ Å}$$

where M_0 is the molecular weight of a monomeric unit, n the number of backbone bonds and l the corresponding bond length. $(\bar{r}_{0,f}^2)^{1/2}$ is the unperturbed root mean square end-to-end distance for a freely rotating chain.

Unperturbed dimensions and chain rigidity

The slight but probably significant increase of K_θ, b and C_∞ values observed for 1 M aqueous NaCl may be related to the fact that unperturbed dimensions may actually be solvent dependent, as established previously for polar systems involving specific solvent–solute interactions or self-associated solvents[37]. With respect to poly(2-vinylpyridine) $K_\theta = 5.4$ and 7.6×10^{-4} dl g^{-1}, $\sigma = 1.98$ and 2.16 for aprotic and protic solvents respectively[37], poly(I) shows an enhanced rigidity of ≈30%, $\sigma \simeq 2.7$, which may reflect the higher steric hindrance of the 2-pyridinium zwitterion: this effect is notably more important than in the various methyl ring substituted polystyrenes where σ is increased by only ≈10% with respect to polystyrene[38].

When compared to poly(*N*-vinylimidazole)[39], $C_\infty \approx 12$ in 0.1 M aqueous NaSCN, the sulphopropylbetaine derivative studied by Salamone *et al.*[3] in good solvents, seems slightly less rigid, $C_\infty \approx 10$, but this difference is hardly significant taking into account all the assumptions and the accuracy of the extrapolation methods. Steric hindrance provided by charged ammonium groups is not directly comparable within the two series of poly(2-vinylpyridine) and poly(*N*-vinylimidazole) because of their different positions with respect to the chain backbone. However, quaternization of poly(*N*-vinylimidazole) by the bulky benzylchloride[39] increases the chain rigidity significantly, as reflected by the high value of ≈18 for C_∞.

Poly(V) is characterized by a very high steric factor, σ, of ≈3.3. Long chain poly(*n*-alkylmethacrylates) up to poly(laurylmethacrylate)[40] actually show relatively high flexibility ($\sigma \approx 2.5$), whereas poly(cetylmethacrylate), studied in a good solvent, n-heptane, has been claimed to be much more rigid[41], $\sigma \approx 3.5$. Such a sharp loss of flexibility with increasing the chain length of the alkyl moiety from $n = 12$ to $n = 16$ is surprising as the length of the lateral linear chain is not a good measure of its steric hindrance, and as there is no clear reason for a conformational transition for $n > 12$. Thus, the polyzwitterion precursor is probably relatively flexible and the relatively high rigidity for poly(V) may be tentatively attributed to specific dipolar interactions between vicinal zwitterions: in addition to steric hindrance, such interactions may contribute to the restriction of internal free rotation.

As noted previously, the calculation of unperturbed dimensions K_θ relies upon extrapolation procedures

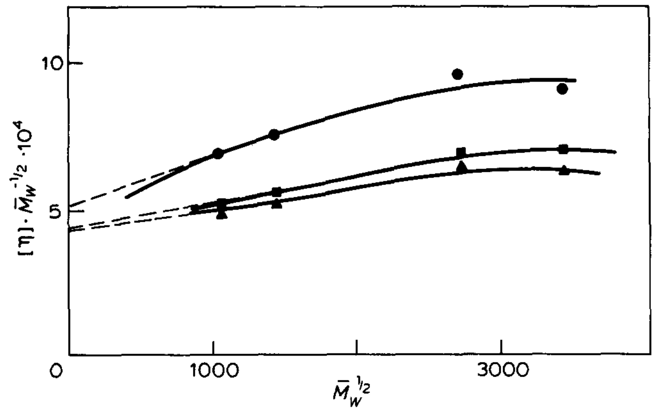

Figure 3 B-S-F plot of $[\eta]$–$\bar{M}_w$ data for poly(V) in NaCl aqueous solutions at 25°C. ▲, 0.05 M; ■, 0.1 M; ●, 1.0 M

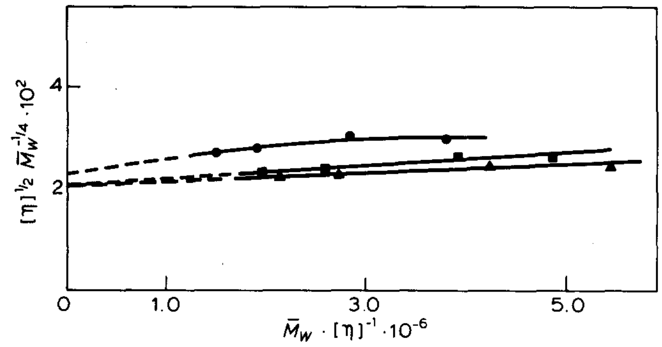

Figure 4 Berry plot of the $[\eta]$–$\bar{M}_w$ data for poly(V) in NaCl aqueous solutions at 25°C. ▲, 0.05 M; ■, 0.1 M; ●, 1.0 M

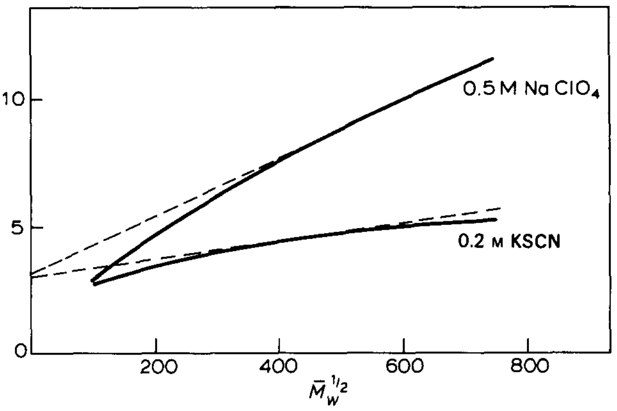

Figure 5 Berry plot of the $[\eta]$–$\bar{M}_w$ data for poly(vinylimidazolium sulphopropylbetaine), (PVISB), in aqueous salt solutions at 25–30°C[3]. A, 0.5 M NaClO$_4$; B, 0.2 M KSCN

Table 6 Structural and polymer–solvent interaction parameters of poly(sulphopropylbetaines)

Polymer	(mol l^{-1})		$K_\theta \times 10^4$ (dl g$^{-3/2}$ mol$^{1/2}$)		α_η[b]	$B \times 10^{28}$ (dl g^{-2} mol^2)	σ	C_∞	b (Å)
				[a]					
Poly(I)	NaCl	0.01	4.30	4.62	1.04	1.48	2.65	14.0	8.17
		0.10	4.03	4.28	1.06	2.33	2.59	13.4	7.99
		1.00	5.22	6.31	1.11	4.29	2.89	16.7	8.89
PVISB	KSCN	0.2	2.85		1.18	4.01	2.24	9.95	6.90
	NaClO$_4$	0.5	3.09		1.42	12.4	2.30	10.5	7.08
Poly(V)	NaCl	0.05[c]	4.32	3.72	1.09	0.744	3.30	21.6	10.17
		0.10[c]	4.19	3.74	1.13	1.05	3.27	21.2	10.07
		1.00[c]	6.11	5.27	1.10	1.16	3.70	27.3	11.42

[a] Calculated values according to ref 42

[b] α_η values were calculated for $\bar{M}_w = 1.6 \times 10^5$, 2.5×10^5 and 3.24×10^6 for poly(I), PVISB and poly(V), respectively

[c] $K_\theta \times 10^4$ (dl g$^{-3/2}$ mol$^{1/2}$) = 4.08, 4.02 and 5.60 for 0.05, 0.1 and 1.0 M H$_2$O–NaCl, respectively, as derived from Berry equation

which may lead to ambiguous values. To ascertain these important parameters, a different analysis of the $[\eta]-\bar{M}_w$ data recently developed by Munk *et al.*[42] (a Monte-Carlo technique of modelling polymer coils by a random non-intersecting walk on a lattice) was used:

$$K_\theta=[K(\phi l^3)^{1-\gamma}]^{1/2-\gamma}F(\gamma)$$

$$\gamma=2(a+1)/3, \text{ with } [\eta]=K\bar{M}_w^a$$

The volume factor $F(\gamma)$ is easily derived from the MHS exponent a and the analytical expression given in the original publication[42]. The structural parameter l is given by $l=L_0/M_0$, where L_0 is the contribution of a monomer unit of molar mass M_0 to the contour length. In a first approach the conformational and geometrical characteristics of poly(I) and poly(V) may be assumed to be similar to that of polystyrene[42] and poly(methylmethacrylate), respectively: these estimated values, $l(\text{poly(I)})\approx 1.12\times10^{-2}$ and $l(\text{poly(V)})\approx 7.08\times10^{-3}$ Å g^{-1} (as derived from the data of Flory *et al.*[43] in the latter case), lead to K_θ values which are not in reasonably good agreement with the previous ones, as shown in *Table 6*. hey may be $\approx$15% higher or lower for poly(I) and poly(V), respectively. The discrepancy is indeed not surprising taking into account all the necessary assumptions and the accuracy of the method. The study of an appropriate θ medium (NaCl < 0.01 M or T < 20°C), clearly would be more decisive.

Long range interaction and coil expansion

As expected, the values of the polymer–solvent interaction parameter B are a slightly increasing function of NaCl concentration, but they remain always low (see *Table 6*), leading to Flory χ interaction parameters of 0.49–0.50, as derived from the equation:

$$0.5-\chi=0.5\mathcal{N}_A V_1 B/\bar{v}^2$$

where $\mathcal{N}_A$ is the Avogadro's number, V_1 the molar volume of the solvent and $\bar{v}$ the partial specific volume of the polymer. NaCl aqueous solutions ($\leqslant$1 M) are very poor solvents for both poly(I) and poly(V), being close to a θ medium. In *Table 6*, the hydrodynamic expansion coefficients, $\alpha_\eta=([\eta]/K_\theta\bar{M}_w^{1/2})^{1/3}$, are calculated for molecular weights representative of the range under study. Even for a poly(V) sample of very high molecular weight of 3.24×10^6, α_η remains <1.15 with $\alpha<1.19$. The exponent a of the MHS relations may appear relatively high for such poor solvents, but this apparent discrepancy may be accounted for within the framework of the blob theory in its original or amended form[44].

Poly(vinylimidazoliumsulphopropylbetaine), however, is reasonably well solvated in 0.2 M aqueous KSCN and even more so in 0.5 M $NaClO_4$ solutions: for a molecular weight of 2.5×10^5, Salamone's data[3] lead to α_η values of $\approx$1.18 and 1.42 for these two solvents, respectively. This increased chain expansion with respect to poly(I) or poly(V)–NaCl aqueous systems merely reflects the stronger polyzwitterion interactions with the highly polarizable anions SCN^- and ClO_4^-.

CONCLUSIONS

The zwitterion functions $-\overset{|}{\underset{|}{N}}{}^{+}-(CH_2)_3-SO_3^-$ imparts to aliphatic and aromatic poly(sulphopropylbetaines) a number of specific properties which clearly differentiate these polyampholytes from the usual polyelectrolytes:

(1) Solubility in organic solvents is strictly limited to protic solvents of very high hydrogen-bond donating power.

(2) Water solubility, observed only in the two exceptional cases of poly(I) and poly(V), may be promoted by electrolytes which disrupt the intra- and inter-molecular ionic or dipolar 'network'. The higher the polarizability of the anion, the higher its efficiency for polyzwitterion solvation.

(3) Both mono- and divalent species, such as NaCl and $CaCl_2$, enhance significantly chain expansion which remains, however, low, even for concentrated salt solutions. The respective contribution of eventual site and atmospheric binding, however, cannot be ascertained.

(4) With respect to tertiary amine polymeric precursors, the increased rigidity observed on the sulphopropyl derivatives may reflect trivial steric effects but, more probably, specific dipolar intramolecular interactions between the lateral zwitterions.

(5) The characteristic behaviour of poly(sulphopropylbetaines) in aqueous salt solution does not deviate significantly from that of random coils of moderate flexibility in a thermodynamically very poor solvent.

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