Poly(ammonium sulfopropylbetaine)s: 5. Interactions in dilute aqueous solution with low molecular weight salts or zwitterions and with poly(electrolyte)s

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Interactions in dilute aqueous solution at 25°C between atactic poly[diethyl-(2-methacryloyloxyethoxy-2-ethyl)-1-(3-sulfopropyl)ammonium betaine] (lateral group $-N^+-(CH_2)_3-SO_3^-$ with dipole moment $\mu = 22.7$ D) and a series of low and high molecular weight dipolar or ionic species were studied by viscometry and fluorescence. For constant additive concentrations (<1.5 M), the salt $CH_3SO_3^-$, $N^+(C_2H_5)_4$ is more efficient than the homologous zwitterions such as $(C_2H_5)_3N^+-(CH_2)_3-SO_3^-$ ($\mu = 22.7$ D) or $(C_2H_5)_3N^+-(CH_2)_2-N(COCH_3)-(CH_2)_3-SO_3^-$ ($\mu = 28.9$ D) for promoting the poly(zwitterion) chain expansion. Progressive increase of the concentration of the salt $C_2H_5-NH_3^+$, NO_3^- results first in a moderate poly(zwitterion) chain expansion followed by an asymptotic behaviour over a very broad concentration range from 0.75 up to 11 M (pure liquid salt). At low concentration (<0.04 M) where the ammonium salts $(CH_3)_4N^+$, X^- ($X^- = Cl^-$, Br^-) behave as inert additives, the corresponding poly(methacryloyloxyethyltrimethylammonium) halides interact with the poly(zwitterion) chain and lead to water-soluble interpolymer complexes of no definite stoichiometry and of very high viscosity: this binding is more efficient with Br^- than with Cl^-. The lack of any significant modification of the fluorescence emission wavelength and quantum yield ($\Delta\Phi \sim 10\%$) in the same dansyl labelled poly(electrolyte) ($X^- = Cl^-$) shows that stacking of the two polymers over rather long blocks is very unlikely. However, poly(zwitterion)–poly(sodium acrylate) interactions lead to a hypsochromic shift of the emission wavelength of ~ 15 nm.

(Keywords: poly(zwitterion); poly(ammonium sulfopropylbetaine); interactions in aqueous solution; salts; zwitterions; poly(electrolyte)s; interpolymer complexes; viscometry; fluorescence)

INTRODUCTION

Since their emergence more than 30 years ago[1,2] and after a long period of relative oversight, stable zwitterionic polymers have recently received a lot of attention and can now be considered as a well identified class of highly dipolar polymeric materials showing a wide spectrum of unique and specific properties[3]. More especially, poly(ammonium sulfoalkylbetaine)s (zwitterionic lateral group $\gtrless N^+-(CH_2)_p-SO_3^-$, $p = 2$–4) display in dilute aqueous solution a very typical 'anti-polyelectrolyte' behaviour: the coil expansion of the linear chains[4–8] and the swelling of crosslinked polymers[9,10] are increasing functions of the ionic strength of the solution. Strong intramolecular dipolar interactions between the lateral zwitterionic groups (for $p = 3$, dipolar moment $\mu = 20.7$ and 27.7 D, as derived from molecular mechanics calculations for the curled and the extended conformations, respectively[11], *versus* 22.7 D, as derived from dielectric measurements in aqueous solution[12]) result in a rather collapsed coil in pure aqueous solution (most of the poly(ammonium sulfobetaine)s are indeed water insoluble at room temperature[1,4–8]) and competitive ion dipole interactions in the presence of added electrolyte disrupt this labile intramolecular physical network allowing the chain to expand. The anionic species plays the major role in this 'salting in' process and the higher its polarizability or its softness the higher its efficiency[3–7]: the well-known Hoffmeister series is generally obeyed[3]. A quantitative approach of these specific interactions has been recently performed through the study of the binding equilibrium of a series of sensitive anionic probes (optical and fluorescent dyes, chemical reporter) on a zwitterionic chain[13].

Within the general framework of the poly(zwitterion) properties in aqueous solution this paper addresses two complementary topics. (1) Interactions with low molecular weight co-solutes: what is the asymptotic behaviour of the zwitterionic random coil in concentrated salt solution and to what extent can highly dipolar species such as zwitterions be compared with the homologous electrolytes for promoting chain expansion? (2) Interactions with poly(electrolyte) co-solutes: besides 'salting in' effects as with their low molecular weight analogues, can specific poly(zwitterion)–poly(electrolyte)

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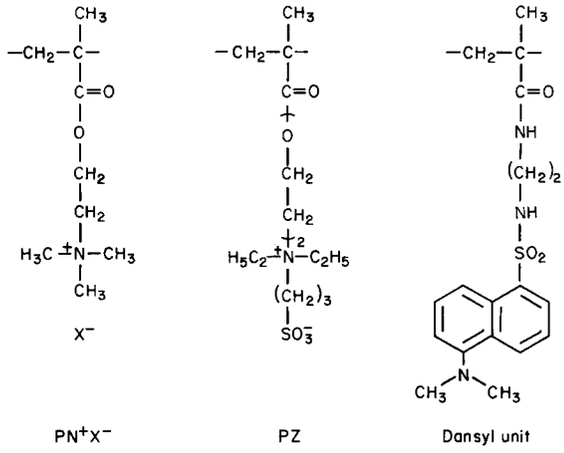
interactions result in more or less soluble and stable complexes, as in the well-known case of ionic or hydrogen bond stabilized interpolymer complexes[14–18]?

Because of its fair solubility in pure water at 25°C (a very rare case) poly[diethyl-(2-methacryloyloxyethoxy-2-ethyl)-1-(3-sulfopropyl) ammonium betaine] was selected as a model poly(zwitterion).

The poly(zwitterion)/co-solute interactions in aqueous solution were analysed at two different levels: (1) by viscosity measurements, as a global method reflecting the variations of chain expansion of the poly(zwitterion) in the presence of low molecular weight species; and (2) by viscosity and fluorescence measurements in the case of poly(electrolyte) additives, the latter technique involving dansyl labelled poly(methacryloyloxyethyltrimethylammonium chloride) and poly(sodium acrylate) (molar fraction of fluorescent chromophore $\leqslant 1 \times 10^{-2}$). Because of the high sensitivity of its fluorescence characteristics (emission wavelength and quantum yield) towards small changes in the local polarity of its microenvironment[19–21], the dansyl probe has been repeatedly involved as an efficient reporter of short-range interactions and binding phenomena between macromolecular chains in aqueous solution: see hydrogen-bonded polymer complexes for instance[22–24].

In this paper the following abbreviations will refer to the various polymers: PAA and PA^-Na^+ for poly(acrylic acid) and its sodium salt, respectively; PN^+X^- ($X^- = Cl^-$, Br^-, ClO_4^-) for poly(methacryloyloxyethyltrimethylammonium) salts; PZ for zwitterionic polymers; and P* for the dansyl labelled polymers.



EXPERIMENTAL

Tetraalkylammonium salts, zwitterions, monomers and reagents

Tetramethylammonium salts (chloride, bromide and perchlorate), acrylic and methacrylic acids, methacryloyloxyethyltrimethylammonium chloride (Atochem 80% aqueous solution), dansyl chloride and *N,N'*-carbonyl-diimidazole of the best reagent grade available (purity > 98% in all cases) were used as received. Aqueous solutions of tetraethylammonium methanesulfonate of known concentrations were obtained by stoichiometric neutralization of previously titrated tetraethylammonium hydroxide and methanesulfonic acid solutions. Ethylammonium nitrate was prepared according to the literature[25]: the liquid salt ($T_m = 14$°C), dried at 70°C under 1.3 Pa, has a residual water content of ~500 ppm (Karl-Fischer titration). Triethylammonium sulfopropylbetaine and *N*-(3-sulfopropyl)-*N*-[(2-triethylammonium) ethyl acetamide] were obtained by nucleophilic ring-opening of 1,3-propanesultone and 2-methyl-1,3-oxazolidinium propanesulfonate[26], respectively, by triethylamine: the detailed procedures are given elsewhere[12]. Diethyl-(2-methacryloylethoxy-2-ethyl)-1-(3-sulfopropyl)ammonium betaine (zwitterionic monomer Z) was prepared as previously described[27].

Fluorescence probes

The polyelectrolytes were labelled with the fluorescent dansyl group by copolymerization of a specially synthesized dansylated monomer. Because of the lack of any detailed procedure in the literature[22,28,29] an improved synthesis of the dansyl substituted methacrylamide is given below. In the final step of the condensation of methacrylic acid and *N*-dansylethylene diamine, *N*-methacryloylimidazole directly formed *in situ*, according to the Staab procedure[30], has proved to be more efficient than methacryloylchloride.

[*1-Dimethylamino-5-(2-aminoethyl)sulfonamido-naphthalene*] (*NDED*). Dansyl chloride (3.24 g, 12 mmol) dissolved in acetone (120 ml) was added dropwise over 1 h under argon to freshly distilled ethylenediamine (3.14 ml, 47 mmol), kept under stirring at 0–5°C. After stirring for a further hour at room temperature ethylenediamine chlorhydrate was filtered off and the solvent rotary evaporated. The remaining oil was dissolved in $CHCl_3$ and washed successively with a 5% aqueous solution of $NaHCO_3$ and pure water. After evaporation, the dried brown oil was passed through a chromatography column filled with Silicagel Merck 60, using as eluting solvents first $CHCl_3$, then C_2H_5OH. Evaporation of the alcoholic eluate gives pale yellow crystals: yield 70%, $T_m = 149$–150°C (lit.[28]: 140–151°C). Analysis calculated for $C_{14}H_{19}O_2N_3S$ ($M = 293.39$): C, 57.31%; H, 6.53%; O, 10.91%; N, 14.32%; S, 10.93%. Found: C, 57.42%; H, 6.54%; O, 11.19%; N, 14.19%; S, 11.08%. U.v.: $\lambda_{max} = 328$ nm in H_2O (lit.[23,29]: 328 nm); 336 nm in CH_3OH. I.r. ($CHCl_3$): 3373 cm^{-1} ($\underline{NH_2}$ asym. str.), 3305 cm^{-1} ($\underline{NH_2}$ sym. str.), 1320 cm^{-1} ($\underline{SO_2}$–NH asym. str.), 1444 cm^{-1} ($\underline{SO_2}$–NH sym. str.). ^1H n.m.r. ($CDCl_3$): $\delta = 8.59$–7.17 (m, 6 H, CH arom.), 2.84–2.52 (m, 4 H, N–CH_2–CH_2), 2.90 (s, 6 H, NCH_3).

[*1-Dimethylamino-5-(2-aminoethyl)sulfonamido-naphthalene*] *methacrylamide*. An equimolecular mixture (7.0 mmol) of methacrylic acid (0.59 ml) and *N,N'*-carbonyldiimidazole (1.14 g) in anhydrous tetrahydrofuran (THF) (10 ml) was stirred at room temperature until no more CO_2 was evolved (~1 h). NDED (2.05 g, 7.0 mmol) in THF (20 ml) was then added dropwise during 1.30 h. Then THF was rotary evaporated at room temperature and replaced by $CHCl_3$. This solution was washed four times with water, dried over $MgSO_4$ and concentrated, then passed through a Silicagel Merck 60 chromatography column using as elution solvents first $CHCl_3$, then C_2H_5OH. The alcoholic eluate was passed a second time through the column and yielded, after evaporation, light yellow crystals (19%) (part of the monomer polymerizes during the purification process), $T_m = 114$–115°C (lit.: 136–136.5°C[23] or 104–105°C[24]). Analysis calculated for $C_{18}H_{23}O_3$ NS ($M = 361.47$): C, 59.44%; H, 6.34%; O, 13.28%; N, 11.36%; S, 8.87%. Found: C, 59.44%; H, 6.34%; O, 13.55%; N, 11.61%; S, 9.08%. U.v.: $\lambda_{max} = 328$ and 336 nm in H_2O and C_2H_5OH, respectively. I.r. ($CHCl_3$): 3378 cm^{-1} (CO–$\underline{NH}$), 3296 cm^{-1} (SO_2–$\underline{NH}$),

1660 cm^{-1} (>C=O), 1618 cm^{-1} (>C=C<), 1522 cm^{-1} (>CO–NH), 1405 cm^{-1} (=CH_2 def.), 1319 cm^{-1} (SO_2–NH asym. str.), 1144 cm^{-1} (SO_2–NH sym. str.), 973+894 cm^{-1} (=CH_2 wag.). ^1H n.m.r. ($CDCl_3$): δ=8.69–7.25 (m, 6 H, CH arom.), 6.33 (s, 1 H, CO–NH), 5.65 and 5.31 (2 s, 2 H, CH_2=), 3.29 and 3.12 (2 q, 4 H, CH_2–N), 2.98 (s, 6 H, N–CH_3), 1.90 (s, 3 H, CH_3–C=).

Polymers and dansyl labelled polymers

The polymers were obtained by free radical polymerization of the corresponding monomers in homogeneous solution at 60°C: acrylic acid in methanol in the presence of azobisisobutyronitrile, methacryloyloxyethyltrimethylammonium chloride and the zwitterionic monomer[27] in water in the presence of 4,4'-azobiscyanovaleric acid. The labelled P*AA and P*N^+Cl^- were obtained in an analogous way using a 0.01 molar fraction of the dansylmethacrylamide with respect to total monomers. The concentration of the fluorescent probe in the chain was determined by u.v. spectrometry in aqueous solution: ε=4290 l mol^{-1} cm^{-1} at λ_{max}=327 nm for NDED as a model compound at pH=7.1.

Preparation of PN^+Br^- and $PN^+ClO_4^-$ from PN^+Cl^- by ion exchange

The PN^+Br^- was obtained according to a procedure briefly outlined in the literature[31]. An aqueous solution of PN^+Cl^- (2.4×10^{-2} M) and NaOH (0.2 M) was exhaustively dialysed against distilled water through a Spectrapor membrane of molecular weight cut-off 3400, until no more precipitation occurred upon addition of $AgNO_3$ in the water compartment. The procedure was repeated once. The polymer solution was then acidified with an excess of HBr ([HBr]/[polymer]=1.5) and exhaustively dialysed in the same conditions as in the previous step. The PN^+Br^- was recovered by lyophilization and dried at 60°C under 1.3 Pa (yield 66%). Analysis calculated for $C_9H_{18}O_2NBr$, 1.0 H_2O: C, 40.01%; H, 7.46%; O, 17.77%; N, 5.19%; Br, 29.58%. Found: C, 40.54%; H, 7.60%; O, 18.34%; N, 5.05%; Br, 28.37%. DP_w experimental (light scattering)=3.34×10^3 as compared with $DP_w=3.63\times10^3$ for the PN^+Cl^- precursor.

$PN^+ClO_4^-$ was obtained by ion exchange with $NaClO_4$ according to the following procedure. Addition of a 10-fold excess of $NaClO_4$ to a 0.5 M aqueous solution of PN^+Cl^- results in the precipitation of $PN^+ClO_4^-$. After filtration, the sparingly soluble polymer was redissolved in a large amount of water and treated again with an excess of $NaClO_4$, as in the previous step. The precipitated polymer was filtered, and dried at 40°C under 1.3 Pa. It was further purified by two successive precipitations upon cooling hot saturated aqueous solution and finally dried as in the previous step (yield 51%). Analysis calculated for $C_9H_{18}O_6NCl$, 0.83 H_2O: C, 37.71%; H, 6.91%; O, 38.12% N, 4.89%; Cl, 12.37%. Found: C, 37.92%; H, 6.58%; O, 38.11%; N, 4.77%; Cl, 12.62%.

Physical measurements

Weight average molecular weights of the various polymers were derived from light scattering experiments (Fica device, λ=632 nm); refractive index increments dn/dc=0.090 ml g^{-1} for PAA in dioxane, 0.160 ml g^{-1} and 0.144 ml g^{-1} for PN^+Cl^-[32] and PZ[5], respectively, in 0.1 M aqueous NaCl at room temperature.

Viscosity measurements were performed at 25°C on aqueous solutions previously annealed overnight at room temperature using an automatic Ubbelohde type dilution device. For high viscosities obtained in the presence of poly(electrolyte)s the lack of any significant shear rate effects was checked using capillaries of various diameters (0.4–0.7 mm). For the derivation of the intrinsic viscosities of the poly(zwitterion)s in the various systems, no significant deviation from the Huggins equation could be observed, in contrast to some reports on 'alternating' poly(zwitterion)s derived from 'ion-pair comonomers'[33].

Plots of pH=f (ionization degree α) for an aqueous solution of poly(acrylic acid) (PAA) in the concentration range 0.2×10^{-3}–4×10^{-2} M were derived in the usual way[34] from potentiometric titration performed on a Mettler DL-21 automatic device fitted with a glass electrode (NaOH as titrant, nitrogen atmosphere, 20±1°C).

The fluorescence spectra of the aqueous solutions of the dansyl labelled poly(electrolyte)s were recorded on a Hitachi F-4010 spectrofluorimeter which gives directly corrected emission spectra up to 600 nm, using dye concentration in the range 1×10^{-4}–2×10^{-4} M. At the excitation wavelength 312–330 nm (corresponding to the pH dependent maximum of the absorptions) the optical densities of the solutions were always <1. The accuracy on the maximum emission wavelength is ~±1 nm, and that relative to the quantum yield (normalized to constant absorption) not better than ±10%. No significant difference could be observed between solutions after preparation or after overnight ageing at room temperature.

I.r. spectra ($CHCl_3$ solutions) and ^1H n.m.r. spectra ($CDCl_3$ solutions) were recorded on Perkin Elmer 983 and Bruker 200 MHz spectrometers, respectively; chemical shifts (δ, ppm) were measured with respect to the solvent signal ($CHCl_3$) fixed at 7.27 ppm.

RESULTS AND DISCUSSION

Interactions between poly(zwitterion) and low molecular weight polar species in dilute aqueous solution

Comparison of the influence of electrolytes and zwitterions on the chain expansion of a poly(zwitterion) in aqueous solution was performed using four species:

1 H_5C_2–NH_3^+, NO_3^-

2 $(H_5C_2)_4N^+$, $CH_3SO_3^-$

3 $(H_5C_2)_3N^+$–$(CH_2)_3$–SO_3^- μ=22.7 D

4 $(H_5C_2)_3N^+$–$(CH_2)_2$–N(–C(=O)–CH_3)–$(CH_2)_3$–SO_3^- μ=28.9 D

Ethylammonium nitrate (**1**, T_m=11°C) allows different media to be studied over the whole composition range from pure water to the pure liquid salt (11 M). The two ammonium sulfobetaines (**3** and **4**) of different dipole moment are good counterparts of the tetraethylammonium methanesulfonate (**2**), because of the identical structure of the charged sites.

The variations of the intrinsic viscosity of the high molecular weight poly(zwitterion) ($M_w=5.67\times10^6$) with the additive concentration plotted in *Figure 1* enables the low molecular weight species to be ordered with

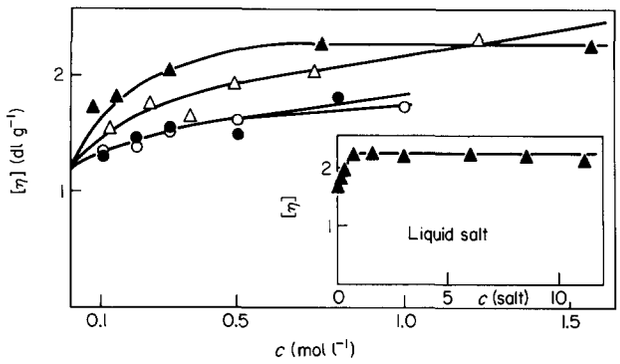


Figure 1 Variations of the intrinsic viscosity of the poly(zwitterion) PZ in aqueous solution at 25°C in the presence of a series of additives at various concentrations: (○) $(C_2H_5)_3N^+(CH_2)_3$–SO_3^-; (●) $(C_2H_5)_3N^+$–$(CH_2)_2$–$N(COCH_3)$–$(CH_2)_3$–SO_3^-; (△) $(C_2H_5)_4N^+$, $CH_3SO_3^-$; (▲) $C_2H_5NH_3^+$, NO_3^- (liquid salt)

respect to increasing efficiency for promoting chain expansion according to:

$$1 > 2 > 4 \geqslant 3$$

Critical analysis of the experimental data may suggest the following comments:

For a concentration <1 M, the general behaviour of the ammonium salts **1** and **2** is in good agreement with that expected from the literature: the initial sharp increase of the poly(zwitterion) chain expansion at salt concentrations <0.25 M (corresponding to a Debye screening length χ^{-1} of ~ 6.1 Å) is followed by a strongly reduced increase for higher values. According to Salamone *et al.*[4] these two regimes may be ascribed, respectively, to specific sites and 'atmospheric' binding of the ions by the poly(zwitterion), the more polarizable and softer nitrate anion being the more efficient in both cases. However, while no asymptotic behaviour is reached for the sulfonate at a concentration of 1.2 M, for the nitrate chain expansion remains practically constant over a broad concentration range from 0.75 ($\chi^{-1} = 3.5$ Å) up to 11 M (pure liquid salt): this characteristic behaviour suggests some kind of rather rapid 'saturation' of the poly(zwitterion)–ion specific interactions resulting in a 'complexed' chain which does not show any more sensitivity towards the surrounding solvent medium with respect to excluded volume effects. It has to be stressed that chain expansion remains indeed low in the pure liquid salt, as typified by a viscometric expansion coefficient α_η of only 1.31 for a very long chain of $DP_w = 1.61 \times 10^4$ ($\alpha_\eta = [\eta]/[\eta]_\theta$ with $K_\theta = 4.15 \times 10^{-4}$ dl g$^{3/2}$ mol$^{1/2}$)[5]. Moreover, this completely ionized medium does not lead to the maximum chain expansion, as could be naively expected: for a shorter chain of $DP_w = 1.24 \times 10^4$, α_η reaches already a higher value of 1.43 in a 0.04 M tetramethylammonium perchlorate solution for instance (see further).

Addition of the ammonium sulfobetaines significantly increases the dielectric permittivity of water: $\varepsilon = 136$ and 151 for 1 M aqueous solutions of **3** and **4**, respectively (dielectric measurements between 10^7 Hz and 10^8 Hz as detailed elsewhere[12]). This enhancement of the overall solvent polarity may account for its better solvation power towards the zwitterionic chain with respect to pure water: $\alpha_\eta = 1.22$ at a concentration of 1 M, the efficiencies of the zwitterions **3** and **4** being nearly identical in spite of a higher dipole moment for the latter. However, the homologous salt **2** promotes significantly higher chain expansion over the whole concentration range: $\alpha_\eta = 1.30$ for 1 M solution ($\chi^{-1} = 3$ Å) for instance. This characteristic difference may likely arise from specific ion–dipole interactions which are stronger and extend to longer range than the dipole–dipole interactions.

Interactions between the poly(zwitterion) PZ ($M_w = 4.3 \times 10^6$) and the cationic poly(electrolyte) PN^+Cl^- ($M_w = 7.54 \times 10^5$) in dilute aqueous solution

In a preliminary approach, viscometric measurements were performed at 25°C on the two polymers separately and on their equimolar mixture by successive dilution. The experimental data plotted in *Figure 2* allow the direct comparison of the reduced viscosity $(\eta_{red})_i$ at a concentration c of a given chain i either in pure water (binary systems) or in the presence of its polymeric partner j at the same c (ternary systems) calculated according to:

$$(\eta_{red})_i = \left(\frac{\eta_{sp}}{c}\right)_i = \frac{1}{c}\frac{t_m - t_{j,c}}{t_{j,c}}$$

with $t_{j,c} = t_0\,[(\eta_{sp})_{j,c} + 1]$ for the binary system water and polymer j at concentration c, where t_0, $t_{j,c}$ and t_m are, respectively, the flow times of water, of the polymer j binary solution at concentration c, and of the ternary solution of the equimolar mixture of polymer i and j at the same concentration c.

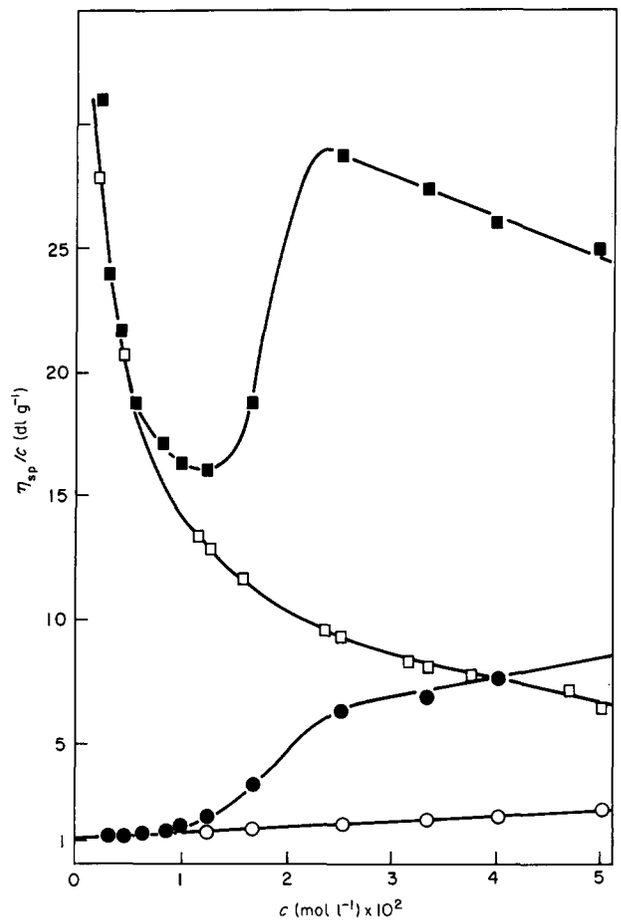


Figure 2 Variations of the reduced viscosity of the poly(zwitterion) PZ (○, ●) and of the poly(electrolyte) PN^+Cl^- (□, ■) with concentration in various aqueous systems at 25°C (see text). The open and solid symbols refer to binary and ternary systems (equimolar mixtures of PZ and PN^+Cl^-) respectively

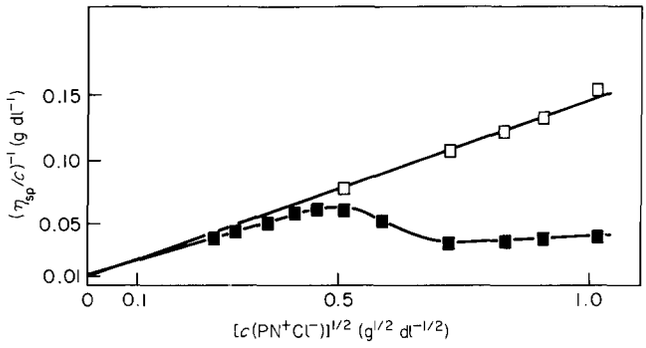


Figure 3 Fuoss plot of the reduced viscosity of the poly(electrolyte) PN^+Cl^- with concentration in various aqueous systems at 25°C. Symbols as in *Figure 2*

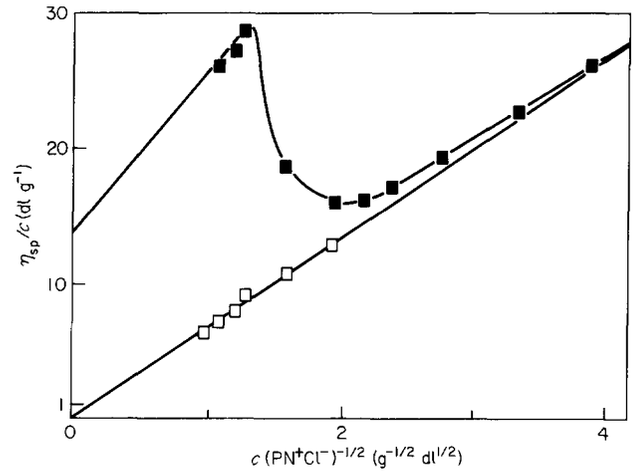


Figure 4 Yuan–Dougherty–Stivala plot of the reduced viscosity of the poly(electrolyte) PN^+Cl^- with concentration in various aqueous systems at 25°C. Symbols as in *Figure 2*

In other words, for every molar concentration c, $(\eta_{red})_i$ is the calculated reduced viscosity of the polymer i in a 'solvent' [or relative viscosity $(\eta_{sp})_{j,c}$] which is an aqueous solution of the polymer j in an equimolar amount.

As expected, PN^+Cl^- in water shows the strong increase in η_{red} at low concentration characteristic of poly(electrolyte)s, see *Figure 2*. The experimental data may be linearized according to the Fuoss[35,36] or the Yuan–Dougherty–Stivala[37] equations (see *Figures 3* and *4*):

$$\text{Fuoss} \qquad \frac{\eta_{sp}}{c} = \frac{A}{1+Bc^{1/2}}$$

$$\text{Yuan–Dougherty–Stivala} \qquad \frac{\eta_{sp}}{c} = [\eta]_\infty + k\frac{[\eta]_\infty}{c^{1/2}}$$

where $[\eta]_\infty$ refers to the hypothetic idealized intrinsic viscosity of the same chain in the absence of any electrostatic interaction (no more charged sites on the chain).

The variations of the η_{red} data for the PZ and PN^+Cl^- derived from measurements performed in the ternary system discriminate three concentration ranges (*Figures 2–4*). First, at concentrations <0.01 M, every polymer behaves as in the corresponding binary system: there is no intermolecular interaction between the two chains at such low concentrations and the thermodynamic quality of the binary solvent water and polymer i with respect to polymer j is identical to that of pure water and vice versa. For concentrations $> \sim 0.02$ M, the η_{red} variations for PZ and PN^+Cl^- show the same trends as those observed in the corresponding binary systems (see the linear variations of the Huggins plot for PZ and of the F and YDS ones for PN^+Cl^-), but the absolute values are dramatically enhanced: at a concentration of 0.03 M for instance, the η_{red} values are increased by a factor of about 4 and 3 for PZ and PN^+Cl^-, respectively. The transition observed between these two regimes within the concentration range 0.01–0.025 M is characterized by a sharp increase in the η_{red} variations for both polymers. These typical behaviours suggest that specific ion–dipole interactions progressively occur between the two chains resulting in new species of definitely higher hydrodynamic volumes.

Another way to confirm poly(zwitterion)–poly(cation) interactions is to consider the gain in specific viscosity of the ternary solution with respect to that calculated assuming simple additivity of the contributions of the two species at any concentration according to[38]:

$$g = \eta_{sp}/(\eta_{sp,i} + \eta_{sp,j})$$

Each line in *Figure 5* shows the g variations for a series of ternary systems of constant poly(electrolyte) concentration and variable stoichiometric ratio $r = [PZ]/[PN^+Cl^-]$. For $[PN^+Cl^-] < 0.01$ M the viscosity enhancement of the ternary system with respect to the ideal mixture (no chain interactions→simple additivity) already occurs and slightly increases with the ratio r, but it remains rather low, less than a factor 3 even for a relatively high r value of 4. For $[PN^+Cl^-] > 0.01$ M however, g is a very strongly increasing function of r, and reaches one order of magnitude for an equimolar system at $c \sim 0.04$ M ($r = 1$).

The inflection point occurring for the stoichiometric ratio $r = 1$ may have a genuine physical meaning which cannot be elucidated at present. In any case, all these data clearly point out that ion–dipole interactions between the chains result in a non-stoichiometric poly(electrolyte)–poly(zwitterion) water soluble complex of higher hydrodynamic dimensions. This general behaviour is quite reminiscent of a number of hydrogen bonded poly(acid)–poly(base) complexes, such as PAA–poly(vinyl pyrrolidone) or poly(oxyethylene) for instance[22–24,38].

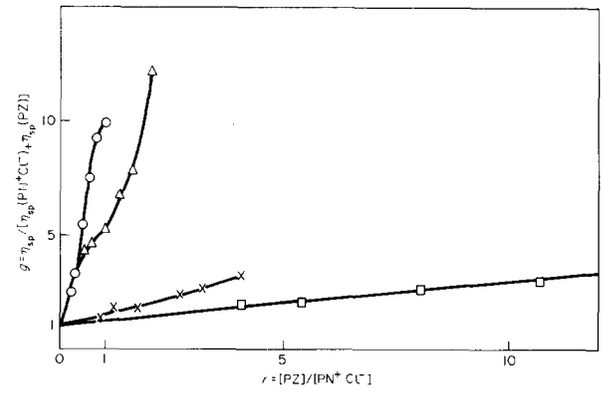


Figure 5 Variations of the gain in specific viscosity of ternary aqueous solutions of mixtures of PZ and PN^+Cl^- at 25°C with the stoichiometric ratio $r = [PZ]/[PN^+Cl^-]$ for various PN^+Cl^- concentrations. $[PN^+Cl^-] \times 10^2$ (mol l^{-1}): (○) 3.85; (△) 1.93; (×) 0.963; (□) 0.241

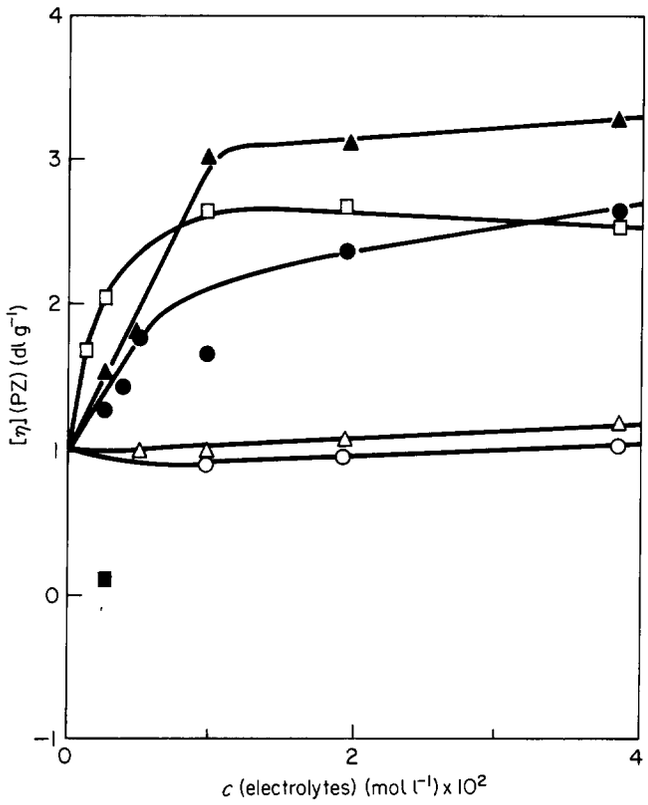


Figure 6 Variations of the intrinsic viscosity of the poly(zwitterion) PZ in aqueous solution at 25°C in the presence of $(CH_3)_4N^+X^-$ salts (open symbols) and of the homologous poly(electrolyte) PN^+X^- (solid symbols). X^-: (○, ●) Cl^-; (△, ▲) Br^-; (□, ■) ClO_4^-

Comparison of electrolytes and cationic poly(electrolyte)s PN^+X^-–poly(zwitterion) interactions in dilute aqueous solution

Such a comparison may be performed through the study of the variations of the apparent intrinsic viscosity of the poly(zwitterion) as a function of the concentration of the added electrolyte or poly(electrolyte). Such an analysis of ternary systems using a solution of constant concentration in polymer *j* as a solvent for polymer *i* has been extensively used for a long time for the analysis of polymer–polymer interactions in dilute solution[39] (compatibility problems for uncharged chains for instance). Intrinsic viscosities of the poly(zwitterion) PZ ($M_w = 4.35 \times 10^6$) were measured within the concentration range 0.3–1.3 g dl^{-1} ($c^* \sim [\eta]^{-1} \sim 1$ g dl^{-1}) keeping the additive concentration at low values between 0.0012 M and 0.038 M corresponding to a Debye screening length χ^{-1} in the range 88–16 Å for the electrolyte and in the range 208–37 Å for the poly(electrolyte)s (χ^{-1} calculated in the latter case taking into account only the fraction of osmotically free counterions[40]). The experimental results plotted in *Figure 6* clearly show three main characteristic features:

1. Tetramethylammonium chloride and bromide have nearly no influence on the poly(zwitterion) chain expansion, while the perchlorate has a definite and positive effect: the intrinsic viscosity first rapidly increases for a salt concentration $< \sim 0.008$ M ($\chi^{-1} \sim 34$ Å) before reaching an asymptotic value corresponding to an expansion coefficient α_η of ~ 1.45. Direct comparison with analogous zwitterionic systems is unfortunately impossible since literature data essentially deal with a significantly higher salt concentration[4–8] (0.1 M), but the efficiency observed in the only case of the more polarizable perchlorate anion is consistent with the general trends in 'salting in' effects[3].
2. In sharp contrast to the low molecular weight salts, the high molecular weight poly(electrolyte)s PN^+X^- ($DP_w \sim 3500$), with chloride or bromide as the counterions, promote a two-step enhancement of the intrinsic viscosity $[\eta]_{PZ}$ characterized by an initial sharp increase for a concentration $< \sim 0.01$ M ($\chi^{-1} = 72$ Å) followed by a strongly reduced effect. As expected the polymeric bromide is more efficient than the corresponding chloride, and becomes rapidly more efficient even than $(CH_3)_4N^+ClO_4^-$: compare, for instance, the 0.03 M solutions where $\alpha_\eta = 1.54$ and 1.45 for the poly(electrolyte) and the tetramethylammonium salt, respectively.
3. The polymeric perchlorate shows a quite different behaviour. A concentration as low as 0.0022 M is high enough to decrease the poly(zwitterion) intrinsic viscosity to a very low value corresponding apparently to a strongly collapsed chain ($\alpha_\eta = 0.12$); at a concentration of ~ 0.01 M the solution appears slightly opalescent and does not allow any reliable viscosity measurement or separation of insoluble aggregates by centrifugation at 10^4 rev min^{-1}. Finally, for a 0.02 M perchlorate concentration, the ternary solution is no longer homogeneous at 25°C, and reversible solubility–insolubility occurs at an upper critical solution temperature of $\sim 45 \pm 3$°C.

All these three characteristic features clearly confirm that the hydrodynamic behaviour of the zwitterionic chain in the presence of poly(electrolyte) cannot be rationalized in terms of non-specific free ion–dipole electrostatic interactions, i.e. by an increase of the overall thermodynamic quality of the solvent towards the zwitterionic chain. Counterion condensation along the chain (Manning theory) implies less free and efficient anions in the poly(electrolyte) solution with respect to the low molecular weight salt solution at identical concentrations and thus would result in a lower chain expansion of the zwitterionic chain, a prediction completely denied by the experimental results. It appears that more specific and short range poly(electrolyte)–poly(zwitterion) interactions may occur even in dilute solution resulting in a rather loose and soluble interpolymer complex. The viscosity measurements no longer reflect the zwitterionic chain expansion alone, and probably include the contribution of the hydrodynamic volume of the 'complex'. The perchlorate poly(electrolyte) is drastically less water soluble than its chloride precursor (see Experimental), but one cannot completely exclude in this case more tightly bound polymer chain in the complex (more interacting units or longer interaction blocks) resulting in a drastically decreased solvation and possible microphase separation.

The PN^+Cl^-–poly(zwitterion) interactions may be analysed at a very short distance using the fluorescence of the labelled poly(electrolyte) ($M_w = 7.17 \times 10^5$, 1.1×10^{-2} molar fraction of dansyl units). Representative experimental results given in *Table 1* essentially show two main features:

1. The covalent bonding of the chromophore in the poly(electrolyte) chain results in a simultaneous hypsochromic shift of ~ 15 nm and a broadening of

Table 1 Absorption (λ_{max}) and emission (λ_{max}, relative quantum yield Φ) characteristics of the free dansyl probe NDED or of the dansyl labelled poly(electrolyte)s (ionization degree α) in various aqueous systems

Fluorescent species	Solvent	[Polymer][a] (mol l^{-1}) × 10^2	[Dansyl unit] (mol l^{-1}) × 10^4	pH	α	Absorption λ_{max} (nm)	Fluorescence λ_{max} (nm)	Fluorescence Φ (× 10^2)
NDED	H_2O	–	2.2	7.1	–	327	585	3.2
NDED	NaOH[b] H_2O	–	2.1	11.9	–	313	581	2.8
PZ + NDED	NaOH[b] H_2O	2.3	1.1		–	313	574	2.7
PA^-Na^+ + NDED	H_2O	2.3	1.1	9.0	0.96	324	581	2.7
PN^+Cl^- + NDED	H_2O	1.0	1.1	6.5	1.00	326	586	2.4
$P^*N^+Cl^-$	H_2O	4.0	4.4	3.7	1.00	330	569	5.2
$P^*N^+Cl^-$ + PZ	H_2O	4.0	4.4	3.7	1.00	330	569	5.1
P*AA	H_2O	4.0	2.0	3.4	0	330	575	4.4
P*AA	Methanol	2.3	1.1	–	–	338	543	16.5
$P^*A^-Na^+$	H_2O	2.3	1.1	10.8	1.00	315	574	3.0
$P^*A^-Na^+$ + PZ	H_2O	2.3	1.1	10.9	1.00	314	575	2.7
$P^*A^-Na^+$	H_2O	4.0	2.0	9.2	0.97	321	584	2.7
$P^*A^-Na^+$ + PZ	H_2O	4.0	2.0	8.5	0.90	326	564	3.6
$P^*A^-Na^+$	H_2O	4.0	2.0	6.4	0.44	328	586	2.7
$P^*A^-Na^+$ + PZ	H_2O	4.0	2.0	6.3	0.41	328	576	2.6

[a] In ternary systems the molar ratio of polymers = 1
[b] $c = 2.5 \times 10^{-2}$ mol l^{-1}

the emission band with an increase of ~70% of the fluorescence quantum yield with respect to the free probe NDED in pure water. These effects may be ascribed to partial dehydration of the dansyl moiety and to a decrease of the overall local polarity of its microenvironment[21] in spite of the presence of neighbouring ionic units in the polymer chain.

2. The presence of stoichiometric amounts of poly(zwitterion) in the concentration range 0.01–0.04 M, where the previous viscosity measurements show unambiguously polymer–polymer interactions, does not change significantly the fluorescence of the labelled chain. This merely means either that the probability of finding zwitterionic units in the solvation sphere of the dansyl chromophore is too low, or, if this is not the case, that the partial substitution of some water molecules by zwitterionic units in this solvation sphere has nearly no influence on the probe fluorescence (predominance of the intramolecular solvation effects). The first hypothesis may appear more realistic, and suggests that interpolymer complexation involving strong stacking of the two chains over rather long blocks is unlikely: the 'loose' structure of the interpolymer complex is consistent with its high water solubility and its viscometric behaviour, as previously observed.

Interactions between the poly(zwitterion) PZ ($M_w = 4.35 \times 10^6$) and the anionic poly(electrolyte) PA^-Na^+ ($M_w = 8.52 \times 10^4$) in dilute aqueous solution

The detailed study of this system is beyond the scope of this work, and only the results of some preliminary experiments will be discussed below.

Potentiometric titration of PAA aqueous solutions in the concentration range 0.2×10^{-2}–4.0×10^{-2} M. The presence of stoichiometric amounts of the poly(zwitterion) PZ in the titrated PAA solution does not afford any significant change in the pH = f (ionization degree α) curves calculated in the usual way[34].

Viscometric measurements. Because the use of buffer solutions has to be avoided in order to eliminate any foreign effects due to low molecular weight salts, viscosity measurements of the poly(zwitterion) in the presence of variable amounts of PA^-Na^+ (pH in the range 8.8–10.2 for $\alpha = 1$, depending on PA^- concentration) were not reliable enough. Small pH drifts which may occur upon viscometric dilution or on ageing solutions result in a significant decrease in α for a given experiment and thus completely bias the experimental data. In any case, the increase of the viscosity of the ternary solution with respect to that calculated assuming simple additivity of the two polymer contributions (ideal mixture) appears greater with partly ionized PAA ($\alpha < 1$). This very specific behaviour suggests potential strong poly(acid)–poly(zwitterion) interactions through hydrogen bonding between the donor carboxylic acid units and either the oxyethylene spacer or more likely the sulfonate anionic moiety of the zwitterionic ones as acceptor. The poly(acid)–poly(zwitterion) system may thus appear as a new example of the much studied hydrogen bonded poly(acid)–poly(base) complexes[14–16] and is definitely worth studying further.

Fluorescence measurements. The experimental data given in *Table 1* afford semiquantitative information on three complementary topics.

First, potential binding of the free NDED probe by the water soluble chain is actually observed only in the case of the poly(zwitterion), as shown by the small hypsochromic shift of ~7 nm of the emission wavelength maximum (weak decrease of the overall local polarity around the probe), but not in the case of PA^-Na^+ which behaves as the other poly(electrolyte) PN^+Cl^-.

Second, the covalent binding of the chromophore in the PAA chain ($M_w = 6.6 \times 10^4$, 5×10^{-3} molar fraction of dansyl units) results in a small hypsochromic shift of its emission wavelength maximum of ~10 nm, but progressive ionization of the acidic units leads to a quasi-linear bathochromic shift in such a way that there

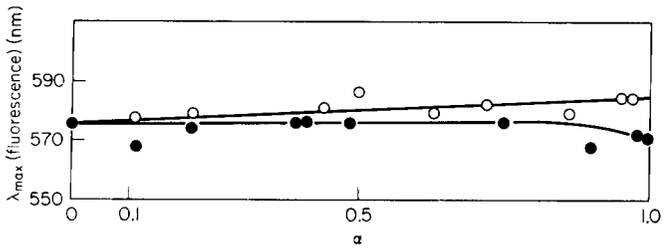


Figure 7 Variations of the maximum wavelength of fluorescence of dansyl labelled PAA* ($c = 0.04$ mol l^{-1}) with the ionization degree α in various aqueous systems at 25°C: (○) binary systems; (●) ternary systems [in the presence of an equimolar concentration of the poly(zwitterion) PZ]

is no difference between the free probe NDED and labelled $P^*A^-Na^+$ (*Figure 7*).

Finally, for ternary systems of equimolar amounts of PZ and $P^*A^-Na^+$, the concentration and the ionization degree of the poly(electrolyte) are the major factors of the observed behaviour. While no modification of the fluorescence of the labelled chain occurs at a low concentration of ~0.02 M, at a higher concentration of ~0.04 M the presence of the poly(zwitterion) results in a slight hypsochromic shift which is also an increasing function of the ionization degree α (maximum shift of ~15 nm for $\alpha = 1$), see *Figure 7*. This specific feature may be considered as unambiguous proof of poly(electrolyte)–poly(zwitterion) interactions leading to soluble 'complexes' where the overall polarity of the probe microenvironment is a decreasing function of the ionization degree. It must be stressed however, that the observed effects on the emission wavelength always remain quite weak (compare with the hypsochromic shift of 37 nm when transferring the labelled P*AA from water to methanol, for instance) and that the variations of the quantum yield of fluorescence are practically negligible taking into account the experimental accuracy of ~ ±10% (compare here again with the increase of half an order of magnitude for the same P*AA transfer from water to methanol).

CONCLUSIONS

Because of their unusually high local dipole moment μ of ~22.7 D, the poly(ammonium sulfopropylbetaine)s interact in dilute aqueous solution with a broad variety of dipolar or ionic species, and more especially with poly(electrolyte)s. With cationic poly(electrolyte)s, the existence of non-stoichiometric interpolymer complexes characterized by water solubility, drastically enhanced viscosity with respect to the ideal non-interacting mixture and the lack of any stacking of the two antagonist chains over rather long blocks may be considered as well ascertained on the basis of viscosity and fluorescence measurements. As for low molecular weight salts, the anionic counterion appears of major importance: the higher its polarizability, the higher its efficiency to promote specific short range interactions between the chains. With anionic poly(electrolyte)s, contributions of both poly(salt) and poly(acid)–poly(zwitterion) interactions depending on the ionization degree of the poly(acid) have to be taken into account according to our preliminary measurements.

In any case, the poly(zwitterion)s may thus appear as new exciting partners for poly(electrolyte)s and unionized poly(acid)s in the broad field of ionic or hydrogen bonded interpolymer complexes[14–18]. As a corollary, template effects[14,41] may be reasonably expected in aqueous radical polymerization systems involving a zwitterionic monomer or its corresponding preformed polymer associated with the antagonist ionized (or acidic) polymer or monomer, respectively.

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