Aqueous Solution Properties of Ampholytic Copolymers Prepared in Microemulsions

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ABSTRACT: The aqueous solution properties of a series of polyampholytes of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and (2-(methacryloyloxy)ethyl)trimethylammonium chloride (MADQUAT) were investigated by turbidimetry and viscometry experiments. The solution behavior in the absence and presence of salt is directly related to the copolymer composition. Neutral copolymers with balanced stoichiometry collapse into globules in pure water and adopt a Gaussian configuration at high sodium chloride contents (>1 M), due to a screening of the attractive interactions. Copolymers with a large net charge ($\simeq$60%) behave more like conventional polyelectrolytes, with a decrease in viscosity upon increasing the ionic strength. Between these two limiting cases, and depending on the salt content, the solution behavior is dominated by either the polyampholyte effect (attractions) or polyelectrolyte effect (repulsions). The results are in good qualitative agreement with a recent theory of Higgs and Joanny (*J. Chem. Phys.* **1991**, *94*, 1543). In particular, the minimum in the optical transmission observed at intermediate salt concentrations can be well accounted for by the minimum in the effective excluded volume predicted by theory.

Introduction

Water-soluble polymers of high molecular weight and more particularly polyelectrolytes are used in a large number of applications including sewage treatment, flocculation, paper manufacture, and enhanced oil recovery.[1,2] The longrange repulsive interactions associated with the presence of positive or negative charges along the polymer chains result in an increase in the hydrodynamic volume, making these materials very effective thickeners.[3] Polyelectrolytes can also interact with other charged species via strong Coulombic forces, and this property is used for the dispersion of insoluble pigments or the flocculation of solids in aqueous suspensions.

However, a major drawback for some applications is the sharp decrease in polyelectrolyte solution viscosity observed in the presence of brine. This phenomenon is more or less pronounced according to the nature of salt, but can eventually lead to polymer precipitation as, for example, in the case of polycarboxylates in the presence of divalent cations.[4] This behavior limits considerably the use of polyelectrolytes in enhanced oil recovery.

Another alternative is to use polyampholytes, which are good candidates for high-salinity media. These copolymers contain both positive and negative charges distributed along the chain.[5,6] They can be prepared from acidic and basic vinyl monomers,[7,8] from sulfobetaine monomers,[9–15] from ion-pair comonomers,[16,17] or from charged anionic and cationic monomers[18–21] mixed in varying proportions.

In the case of a polyampholyte with a balanced stoichiometry (same number of negative as positive monomers), the polymer behavior is essentially controlled by attractive electrostatic interactions. The compound is usually insoluble in water but becomes soluble upon addition of salt, which screens the interactions and weakens the attractions.[5] As a result, the solution viscosity is enhanced as the ionic strength is increased, in contrast with the polyelectrolyte behavior.

In the case of polyampholytes with an excess of charge, the overall chain conformation is the result of the competition between the polyelectrolyte effect, which tends to expand the coil, and the polyampholyte effect, which tends to collapse it. This confers these compounds a mixed character which in principle allows one to tailor their properties in aqueous solution so as to adapt them to industrial requirements.

In spite of this great potential for applications, polyampholytes have received so far little attention.[5,6] In particular, few studies have dealt with *nonstoichiometric* polyampholytes, formed by copolymerization of an anionic monomer and a cationic monomer, except for those of McCormick et al.[18–20] and Peiffer and Lundberg.[21]

The purpose of the present work was to investigate the properties in aqueous solution of polyampholytes of variable composition with special emphasis given to the effect of the net charge. The experimental results are compared with the recently developed theory of Higgs and Joanny.[22] Therefore a series of high charge density copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) with ((methacryloyloxy)ethyl)trimethylammonium chloride (MADQUAT) was synthesized by polymerization in microemulsions. This process was previously developed by one of us for various types of other water-soluble monomers (acrylamide[23] and/or sodium acrylate,[24] MADQUAT[25,26]).

The synthesis and characterization (macrostructure and microstructure) of the series of polyampholytes investigated here have been described elsewhere.[27,28] We summarize below the main characteristics of the process:

(i) The process produces clear and stable microlatex polymer particles at high solid contents ($\simeq$22%), in contrast with inverse latexes prepared in classical emulsions, which are often unstable and turbid. High rates of polymerization and quantitative yields are obtained.

(ii) The copolymers are easily stored and handled, and they have ultrahigh molecular weights (1.5×10^7) and are entrapped within small-sized water droplets dispersed in an organic phase. Such polymers would be hardly attainable by a conventional aqueous solution polymerization since a polyampholyte with a balanced stoichiometry would precipitate upon polymerization.

(iii) The copolymers are more homogeneous in composition (reactivity ratios $r_1r_2 = 1.6$) than those prepared in solution ($r_1r_2 = 0.064$). This result was accounted for by the marked differences in mechanism and microenvironment between microemulsion polymerization and other processes.[26–28]

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Table I
Polymer Characteristics

sample	composition (mol %) NaAMPS	MADQUAT	$10^{-6}M_w$
A100	100	0	8.3 ± 1.0
A80/M20	78.5	21.5	11.6 ± 1.3
A60/M40	62.2	37.8	15.4 ± 2.1
A50/M50	50.0	50.0	15.2 ± 3.5
A35/M65	32.3	67.5	11.8 ± 1.7
A20/M80	18.7	81.3	12.1 ± 1.9
M100	0	100	13.1 ± 1.5

Experimental Section

Materials. (2-(Methacryloyloxy)ethyl)trimethylammonium chloride (MADQUAT) was supplied by Norsolor-Orkem as a 75% w/w aqueous solution. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS), obtained from Cassella, was recrystallized from dry methanol prior to use. Neutralization at pH ≃ 9 was achieved by slow addition of AMPS to an aqueous sodium hydroxide solution. Water was double-distilled. Hydrophobic initiator AIBN (2,2′-azobis(isobutyronitrile)) was recrystallized in ethanol and dried under vacuum. The oil is a narrow-cut isoparaffinic mixture, Isopar M from Esso Chemie, which was filtered before use (boiling range: 207–275 °C). The emulsifier is a blend of sorbitan sesquioleate (Arlacel 83, hydrophile–lipophile balance (HLB) ≃ 3.7) and of sorbitan monooleate with 20 ethylene oxide residues (Tween 80, HLB ≃ 15), supplied by ATLAS Chemical Industries N.V.

The transparent and thermodynamically stable microemulsions were prepared with stirring by adding the aqueous solution of monomers (adjusted to pH ≃ 7) to the mixture of emulsifiers, AIBN, and Isopar M. The recipe used was the following (w/w): Isopar M, 44%; monomers, 22%; water, 22%; nonionic emulsifiers, 12%.

Polymerization Procedure. The polymerization experiments were carried out in water-jacketed reaction vessels, after bubbling purified nitrogen through the microemulsion to eliminate oxygen. The monomer feed was initiated with AIBN as the oil-soluble initiator (0.3 wt % based on monomers) by irradiation at 20 °C from a source of ultraviolet light (mercury lamp, Philips).

Total conversion to copolymer was achieved within <30 min. After polymerization, the latexes were poured into an excess of 2-propanol, and the precipitated copolymers were separated and washed several times. They were then filtered and dried under vacuum at 45 °C. To eliminate impurities (monomer, residual salt, emulsifiers, etc.) the resulting polymer powders were subsequently dissolved in 1 M NaCl aqueous solutions and dialyzed against deionized water before recovering by freeze-drying.

Copolymer Characteristics. A series of samples with variable amounts of the two monomers was prepared in microemulsions and polymerized up to complete conversion according to the recipe given above. The composition of ampholyte polymers was determined by nitrogen, sodium, chloride, and sulfur elemental analysis. An excellent agreement was observed between the copolymer compositions determined by elemental analysis and the initial monomer compositions in the feed. A more complete analysis of the data has shown that the materials after dialysis tend to self-neutralize almost completely.[27,28] In particular, it should be noted that the anionic and cationic monomers of sample with balanced stoichiometry are completely paired, with no residual sodium or chloride counterions left in the solution. The compositions of the samples and their weight-average molecular weights $\bar{M}_w$ measured by light scattering are given in Table I. The higher values found ($\bar{M}_w \geq 10^7$) are characteristic of polymers prepared in microemulsions.

Turbidimetry. The NaCl aqueous polymer solutions were slowly homogenized under gentle stirring over 48 h to prevent any shear degragation or aggregation phenomena. The experiments were conducted immediately after stirring and before the occurrence of any polymer sedimentation (for the case of stoichiometric polyampholyte). The optical transmittance of the solution was measured at 20 °C spectrophotometrically in cylindrical cells (diameter = 0.5 cm) using a helium–neon laser as a monochromatic source. Temperature control was achieved with a Peltier effect device.[29]

Viscometry. Intrinsic viscosities of dilute polymer solutions ($C < 10^{-3}$ g·cm^{-3}) were measured at 25 °C using a Contraves LS 30 low-shear rotational rheometer ($\simeq 10^{-2} <$ shear rate $(\dot{\gamma}) < 128$ s^{-1}) interfaced to a personal computer and driven by a software package supplied by the manufacturers.

Light Scattering Experiments. The molecular weights of the polymers were determined on dilute samples ($10^{-5} < C < 5 \times 10^{-5}$ g·cm^{-3}) in NaCl aqueous solutions (1 M for homopolymers and 2 M for copolymers) with an AMTEC SM 200 spectrophotometer. The optical source was a Siemens helium–neon laser operating at 632.8 nm. Molecular weight determinations as a function of the salt content in water did not exhibit any $\bar{M}_w$ variation nor any anomalous shape of the Zimm plots. This is a good indication that no aggregates are present in the solution. More details are given in refs 27 and 28.

Small-Angle Neutron Scattering (SANS). The SANS experiments were performed at the Laboratoire Léon Brillouin (LLB), Saclay, using the PACE spectrometer. The sample–detector distance was 2 m and the neutron wavelength was λ = 7.83 Å. Examinations were carried out over the q range 10^{-2}–10^{-1} Å^{-1} (scattering vector $q = (4\pi/\lambda) \sin \theta/2$, with θ the scattering angle). Classical methods of data treatment were applied: division by thickness and transmission, normalization by water, and subtraction of an incoherent background sample.[30]

The polymer solutions were contained in optical-quality quartz cells having a path length of 5 mm. The neutron scattering measurements were performed on two deuterated 0.5 and 0.6 M NaI aqueous solutions of the stoichiometric sample A50/M50. NaI was chosen for the sample dissolution because of its low critical solubilization concentration (CSC ≈ 0.36 M·L^{-1}; see Table II). Because of this high salt content, it was necessary to investigate rather concentrated solutions to obtain a signal significantly larger than the background. This led us to perform the experiments in the semidilute regime ($C = 5 \times 10^{-2}$ g·cm^{-3}).

Results

The solution properties of copolymers of MADQUAT with NaAMPS were investigated by means of two complementary techniques: turbidimetry and viscometry. Besides, preliminary experiments performed by small-angle neutron scattering (SANS) provided additional information on the chain conformation.

I. Solubility of NaAMPS–MADQUAT Copolymers in Aqueous Solution. (a) Effect of Copolymer Composition. The solubility in NaCl aqueous solutions of the series of copolymers was determined by turbidimetry experiments. Turbidimetry is a convenient method to determine phase diagram boundaries. An optical transmission T of the order of 100% obtained immediately after cessation of stirring corresponds to one phase domain whereas a reduced transmission indicates a beginning of phase separation. Depending on the polymer precipitation process, the $\% T = f(\text{salt})$ curve can be more or less sharp but of course the critical solubilization concentration (CSC) will be defined by the optimal transmission. This is illustrated by Figure 1, which gathers the solubility data obtained for homopoly-NaAMPS and NaAMPS-rich samples, whereas Figure 2 is relative to homopoly-MADQUAT and MADQUAT-rich copolymers. It is clear that the solubility properties are directly related to the sample composition. The following remarks can be drawn out:

(i) Both homopolymers exhibit a typical polyelectrolyte behavior: they are soluble in pure water and in NaCl solutions within the range investigated. However, a nonzero turbidity is observed in the case of M100, which might indicate the presence of some aggregates at this polymer concentration ($C = 10^{-2}$ g·cm^{-3}).

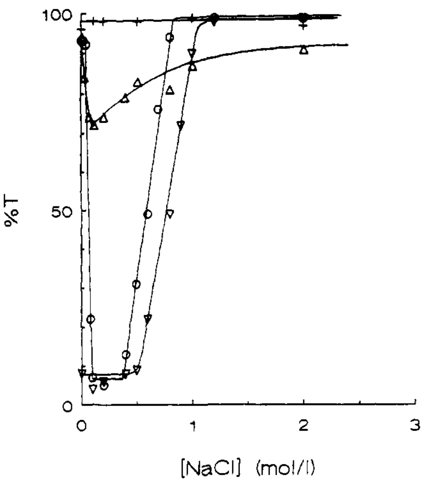

Figure 1. Optical transmission versus NaCl concentration ($C = 10^{-2}$ g·cm^{-3}, $T = 20$ °C): (+) A100; (△) A80/M20; (○) A60/M40; (▽) A50/M50.

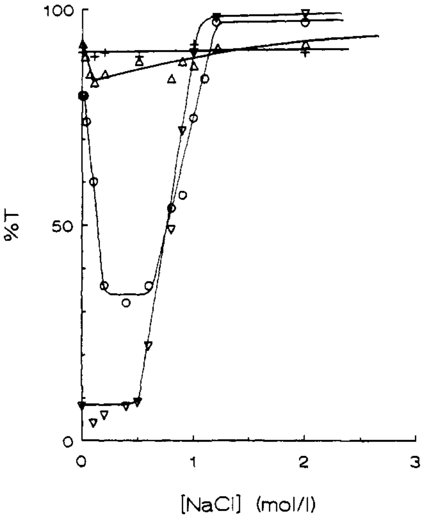

Figure 2. Optical transmission versus NaCl concentration ($C = 10^{-2}$ g·cm^{-3}, $T = 20$ °C): (+) M100; (△) A20/M80; (○) A35/M65; (▽) A50/M50.

(ii) Copolymers are all soluble in water at high salt concentrations (NaCl > 1.0 M).

(iii) Sample A50/M50 with a balanced stoichiometry is the only copolymer which is insoluble in fresh water, due to the strong electrostatic attractions between monomers of opposite signs. This sample behaves like a classical polyampholyte with overall neutrality.[9-12,17,21,31-33] The macromolecular chains are strongly collapsed. In the presence of salt, there is a screening of the electrostatic interactions and the attractive forces are smaller than in pure water. Addition of a sufficient amount of salt tends to reswell the collapsed chain, which becomes soluble. The critical solubilization concentration is obtained for $CSC_{NaCl} \simeq 1.01$ M.

(iv) Copolymers A60/M40 and A35/M65 with a net excess of charges ($\simeq$25–30%) exhibit optically clear and viscous phases in pure water, suggesting that the chains adopt a highly extended polyelectrolyte configuration. Addition of salt strongly disfavors the solubility by screening the electrostatic repulsions. The chains tend to contract and to precipitate. They eventually phase separate after a few days for a critical precipitation concentration $CPC_{NaCl} \simeq 0.04$ M.

However, the samples dissolve again upon further addition of salt (CSC $\simeq$ 0.81 for sample A60/M40; CSC $\simeq$ 1.05 for sample A35/M65). In this case, the solubilization is ensured by the screening of attractive interactions between charges of opposite signs, as in the case of a neutral polyampholyte. Therefore, the samples exhibit two critical salt concentrations.

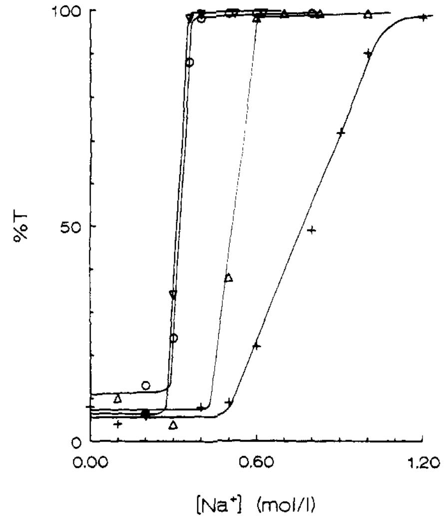

Figure 3. Effect of the nature of the anion on the solubility of sample A50/M50: (+) Cl$^-$; (△) Br$^-$; (○) I$^-$; (▽) SCN$^-$.

Table II
Effect of the Anion on the Solubility of Neutral Polyampholyte A50/M50 ($C = 10^{-2}$ g·cm^{-3})

anion	CSC_{Na^+} (mol·L^{-1})	anion	CSC_{Na^+} (mol·L^{-1})
Cl$^-$	1.01	I$^-$	0.36
Br$^-$	0.58	SCN$^-$	0.33

(v) When the net charge increases, the phenomenon described for the two above copolymers tends to disappear. Thus, samples A80/M20 and A20/M80 are soluble in fresh water and for all salt concentrations, which indicates that the polyelectrolyte effect predominates. The optical transmission variations are small with, however, a slight minimum observed at intermediate salt concentrations.

(b) Effect of the Nature of the Electrolyte. In the case of neutral polyampholyte A50/M50, it was shown by elemental analysis that after dialysis no more residual inorganic counterions were bound to the polyions.[27,28] It was then of particular interest to investigate by turbidimetry the effect of the type of electrolyte on the solubility of this sample.

The use of electrolyte solutions containing the same cation (Na^+) but different anions produces a marked increase of the copolymer solubility in water (Figure 3 and Table II) according to $Cl^- < Br^- < I^- \simeq SCN^-$.

The value of the critical solubilization concentration (CSC) is very sensitive to the anion structure since it varies by a factor of 3 from Cl^- to SCN^-. This result is quite comparable to what was reported for sulfobetaines[10-14] and can be correlated to the polarizability increase or to the softer Lewis base character[34,35] which occurs for anions from Cl^- to SCN^-.

In the case of electrolyte solutions containing the same chloride anion, the cations were shown to obey the following sequence (Figure 4 and Table III): $Li^+ < Na^+ \simeq K^+ \simeq Cs^+ < Mg^{2+} < Ca^{2+} < Ba^{2+}$.

As for polyzwitterions, a weak selectivity is observed among the various cations, which confirms the lack of affinity between sulfonate groups (soft base) and hard acids (alkali metal and alkaline-earth type cations).[11] In the case of alkali metal monovalent cations, the solubilization effectiveness does not vary from Na^+ to Cs^+. The use of divalent cations allows a better solubilization: the increase in the counterion valence leads to a more efficient

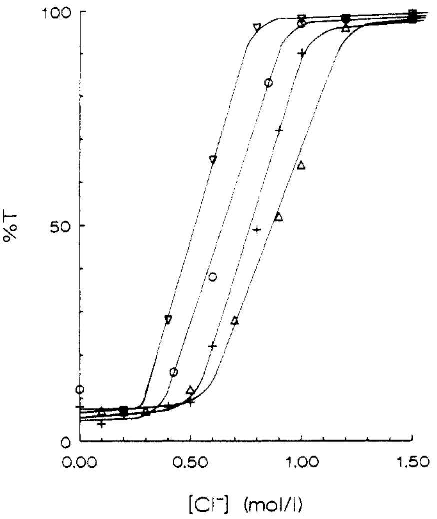

Figure 4. Effect of the nature of the cation on the solubility of sample A50/M50: (+) Na^+; (△) Li^+; (○) Mg^{2+}; (▽) Ba^{2+}.

Table III
Effect of the Cation on the Solubility of Neutral Polyampholyte A50/M50 ($C = 10^{-2}$ g·cm^{-3})[a]

cation	CSC_{Cl^-} (mol·L^{-1})	cation	CSC_{Cl^-} (mol·L^{-1})
Li^+	1.15	Mg^{2+}	0.94
Na^+	1.01	Ca^{2+}	0.83
K^+	0.97	Ba^{2+}	0.76
Cs^+	1.00		

[a] $CSC_{anion} = z(CSC_{cation})$; z = valence of the ion.

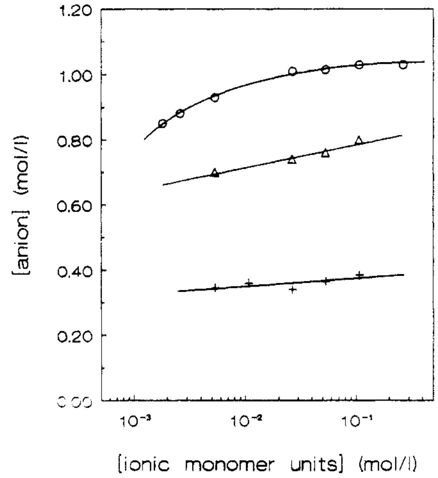

Figure 5. Solubility limit of sample A50/M50 in the presence of different electrolytes: (+) NaI; (△) $BaCl_2$; (○) NaCl.

screening of the negative charges of the polyampholyte. This result is in close agreement with those of Salamone et al.[10] but differs from those of Monroy Soto and Galin.[13] Note that the order of effectiveness slightly increases from Mg^{2+} to Ba^{2+}, conforming to other data observed for polysulfonates.[36,37]

(c) Effect of the Copolymer Concentration. The effect of copolymer concentration on the critical salt concentration (CSC) was studied for the sample A50/M50 over a two-decade range encompassing both the dilute and semidilute regimes ($5 \times 10^{-4} - 5 \times 10^{-2}$ g·cm^{-3}). Figure 5 shows the variation of the CSC with copolymer concentration for three different electrolytes. The CSC values are only slightly concentration dependent in the range investigated whatever the type of electrolyte used. Note also that the small ions are always in large excess with regard to the number of charged monomeric units to be screened.

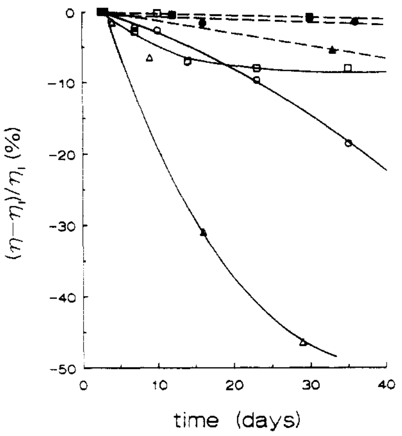

Figure 6. Relative viscosity decrease of a homopolymer solution versus time (T = 25 °C; η_i is the viscosity measured immediately after polymer solubilization: 2.0 M NaCl, (■) M100, (□) A100; 0.1 M NaCl, (●) M100, (○) A100; 0.02 M NaCl, (▲) M100, (△) A100.

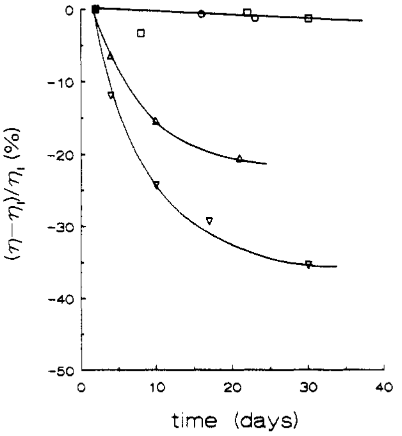

Figure 7. Relative viscosity decrease of a copolymer solution (A60/M40) versus time (T = 25 °C; η_i is as in Figure 6): (□) 2.0 M NaCl; (○) 0.75 M NaCl; (△) 0.02 M NaCl; (▽) 0.02 M NaCl (second experiment).

This almost nondependency of the CSC with copolymer concentration suggests that the interactions between polyions and counterions are characterized by nonspecific forces, with a counterion condensation of atmosphere binding type[38-41] rather than site binding.[42]

II. Viscometric Studies in the Dilute Regime. (a) Stability of the Solutions. It is well known that the viscosities of many aqueous polymer and polyelectrolyte solutions show a gradual decrease in viscosity with time.[43,44] Although still a matter of discussion, several explanations have been proposed to account for these viscosity losses: (i) progressive uncoiling of macromolecules with time, (ii) changes in conformation of polymer chains caused by the dissociation of inter- or intramolecular hydrogen bonds, and (iii) polymer degradation by microorganisms such as bacteria.

We have studied the changes in viscosity for some polymer solutions over a period of 4–5 weeks. The polymer concentrations were 10^{-3} g·cm^{-3} at high ionic strength (C_s > 0.1 M) and 5×10^{-4} g·cm^{-3} at low ionic strength (C_s < 0.05 M). Examples of plots of the relative decrease in viscosity versus time are shown in Figures 6 and 7. The aging effect for MADQUAT homopolymer and copolymer solutions at high ionic strength is rather limited. On the other hand, NaAMPS homopolymer solutions show a sharper decrease. This difference in behavior may be related to the bactericide character of the quaternary ammonium group.[45]

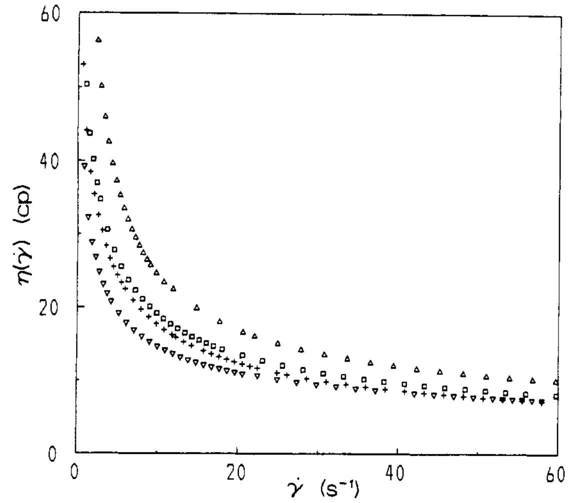

Figure 8. Viscosity of polymer solutions in pure water versus shear rate: (+) A100; (□) A20/M80; (△) A80/M20; (▽) A35/M65.

Viscosity drops are more pronounced for aqueous solutions at low ionic strength. Furthermore, the changes in viscosity solutions with time are not quite reproducible, as previously noted by Külicke for polyacrylamide.[43]

Note that the behavior of NaAMPS homopolymer differs from that observed by McCormick et al.,[46] where almost no change in viscosity with time was observed for this polymer in pure water over 30 days. The large difference in molecular weights (0.76 × 10^6 in ref 46 and 8 × 10^6 in the present study) certainly accounts for this result. It is indeed well established that the higher the molecular weight, the larger the aging effect.[43]

The effect of the nature of the electrolyte has also been investigated for both homopolymers. Again, the loss in viscosity with time is more pronounced for NaAMPS polymer solutions than for poly-MADQUAT.

In the following, the viscosity values which are given are those measured immediately after complete dissolution of the samples (≃48 h).

(b) Effect of the Ionic Strength. The solubility studies described above have shown that some samples (A60/M40 and A35/M65) exhibit two distinct solubility regions upon adding salt. Therefore the results reported below are considered separately according to the domain of ionic strength ($C_{NaCl} < 0.05$ M and $C_{NaCl} > 0.1$ M).

Low-Concentration NaCl Solutions ($C_{NaCl} < 0.05$ M). With the exception of the neutral sample A50/M50, all other samples are soluble in fresh water and for NaCl concentrations < 0.04 M. Figure 8 represents the viscosity–shear rate curves obtained for the aqueous polymer solutions in fresh water. The large viscosity drop suggests that the samples behave as electrolytes with an elongational effect of the chains during flow. In Figure 9 is reported the development of the reduced viscosity with NaCl concentration for NaAMPS-rich samples. Similar data are obtained for the corresponding MADQUAT-rich samples. The results show a sharp decrease in the reduced viscosity with increasing salt levels for both homopolymers and copolymers, also in favor of a polyelectrolyte behavior.

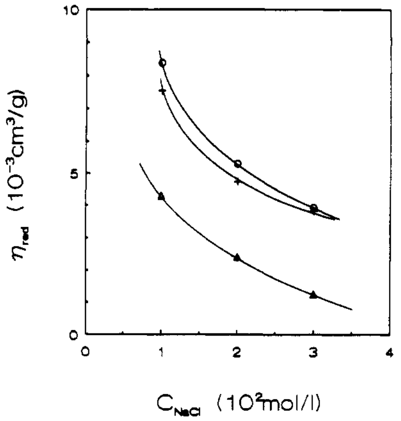

Figure 9. Reduced viscosity versus NaCl concentration ($C = 5 \times 10^{-4}$ g·cm^{-3}, $T = 25$ °C): (+) A100; (○) A80/M20; (△) A60/M40.

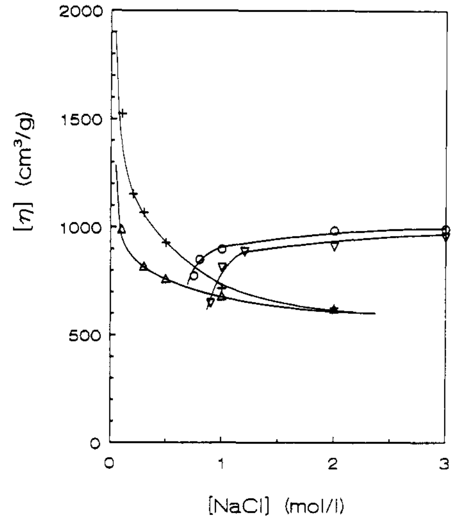

Figure 10. Intrinsic viscosity versus NaCl concentration (T = 25 °C): (+) A100; (△) A80/M20; (○) A60/M40; (▽) A50/M50.

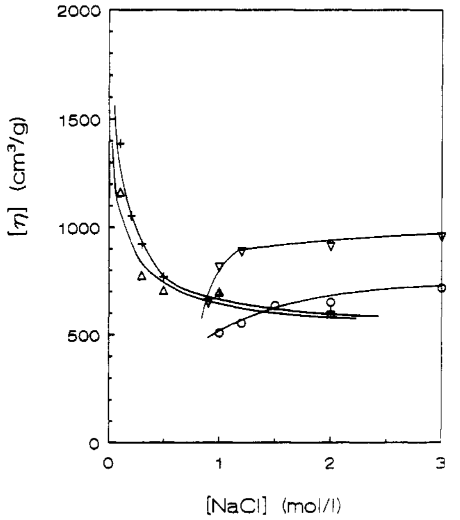

Figure 11. Intrinsic viscosity versus NaCl concentration (T = 25 °C): (+) M100; (△) A20/M80; (○) A35/M65; (▽) A50/M50.

Note that the dissolution of sample A60/M40 and to a lesser extent A35/M65 in low-salinity media has given rise to some problems. Although transparent, the solution is macroscopically inhomogeneous with a mixture of very viscous phases adjoining fluid areas, making the measurements very difficult, if not impossible, to perform. The values reported in Figure 9 were repeated several times on different samples at a given copolymer concentration ($C = 5 \times 10^{-4}$ g·cm^{-3}) until a good reproducibility was achieved.

High-Concentration NaCl Solutions ($C_{NaCl} > 0.1$ M). The effect of added sodium chloride on the zero-shear intrinsic viscosity [η] of the series of samples is reported in Figures 10 and 11. Except for the highest copolymer concentrations, the samples have a Newtonian or shear-rate-independent viscosity. The values of [η] and of the

Table IV
Intrinsic Viscosities and Huggins Coefficients for the Copolymers in NaCl Aqueous Solutions at T = 25 °C

sample	C_{NaCl} (mol·L^{-1})	[η] (g·cm^{-3})	K_h
A100	0.1	1523	0.36
	0.2	1151	0.36
	0.3	1065	0.36
	0.5	926	0.38
	1.0	717	0.52
	2.0	625	0.64
M100	0.1	1386	0.67
	0.2	1057	0.66
	0.3	922	0.67
	0.5	770	0.70
	1.0	684	0.70
	2.0	606	0.96
A80/M20	0.1	991	0.67
	0.3	819	0.60
	0.5	761	0.59
	1.0	682	0.67
	2.0	621	0.75
A20/M80	0.1	1163	0.50
	0.3	776	0.43
	0.5	707	0.37
	1.0	699	0.32
	2.0	598	0.62
A60/M40	0.75	775	0.42
	0.8	851	0.53
	1.0	899	0.44
	2.0	984	0.35
	3.0	992	0.28
	4.0	987	0.28
A35/M65	1.0	508	0.41
	1.2	554	0.62
	1.5	636	0.36
	2.0	651	0.46
	3.0	718	0.50
A50/M50	0.9	649	0.91
	1.0	815	0.56
	1.2	888	0.54
	2.0	912	0.59
	3.0	955	0.55
	4.0	963	0.58

Huggins interaction coefficient K_h are reported in Table IV.

The solution behavior of the samples is directly related to their composition and depends essentially on the overall net charge of the macromolecule.

When the net charge is large enough as is the case for homopolymers and A80/M20 and A20/M80 samples (excess of charges ≃ 60%), the chains behave like usual polyelectrolytes, with a decrease in viscosity upon increasing the ionic strength, as a result of the screening of the electrostatic repulsive interactions. Note that, as expected, the viscosity decrease is less pronounced for A80/M20 and A20/M80 samples than for the pure polyelectrolyte homopolymers.

For polyelectrolytes, the variation of the intrinsic viscosity versus salt concentration is often expressed by the general law[42,47]

$$[\eta] = a + b/C_s^{1/2} \qquad (1)$$

where a and b are numerical coefficients. The linearity of $[\eta] = f(1/C_s^{1/2})$ obtained within the experimental accuracy for the A80/M20 and A20/M80 samples over the 0.1–2 M salt concentration range (Figure 12) is in favor of a polyelectrolyte behavior.

The Huggins interaction coefficients K_h range within 0.3–0.9 for both homopolymers and the A80/M20 and A20/M80 samples. These values are characteristic of marginal Θ solvents and corroborate the almost zero values of the second virial coefficients measured by light scattering.[27,28]

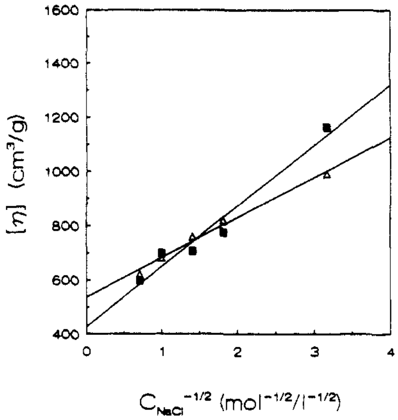

Figure 12. Intrinsic viscosity versus NaCl concentration (T = 25 °C): (△) A80/M20; (■) A20/M80.

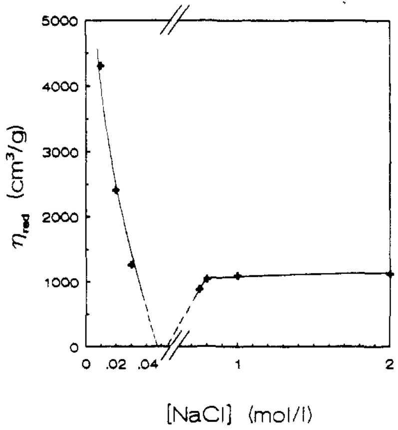

Figure 13. Reduced viscosity versus NaCl concentration for sample A60/M40 (C = 5 × 10^{-4} g·cm^{-3}, T = 25 °C).

Furthermore, the systematic increase of K_h at the highest salt level (2 M NaCl) indicates a decrease in solvent quality.

In the case of the neutral polyampholyte A50/M50, one observes a completely opposite behavior. The intrinsic viscosity increases sharply around the CSC and then levels off at higher salt contents. This viscosity increase conforms to the data obtained with other highly charged polyampholytes[8,21,32] and with polyzwitterions.[10–14] Concomitantly, the Huggins coefficient K_h strongly decreases around the CSC, reflecting a better solvent quality and remains approximately constant upon further addition of salt. These observations corroborate the solubility data. A specific ionic atmosphere is necessary to screen the attractive interactions between charges and to solubilize the polymer chain. The addition of small ions in excess does not further modify the polymer behavior.

Samples A60/M40 and A35/M65 possess an excess of net charge (≃25–30%) which is intermediate between the two preceding cases. From Figures 10 and 11 it can be seen that the viscometric behavior at high salt contents is similar to that of a globally neutral polyampholyte, contrary to what was observed below the CPC (≃0.04 M NaCl). Figure 13 represents the general behavior of sample A60/M40 with salt concentration.

(c) Effect of the Nature of the Electrolyte. This effect has been studied for both homopolymers and for the copolymer A50/M50 with balanced stoichiometry (Figures 14–16 and Table V).

In the case of the homopolymers, the variation of the intrinsic viscosity versus ionic strength depends on the type of salt investigated: the stronger the decrease in hydrodynamic volume, the more efficient the screening of polyion charges by small ions. The results obtained

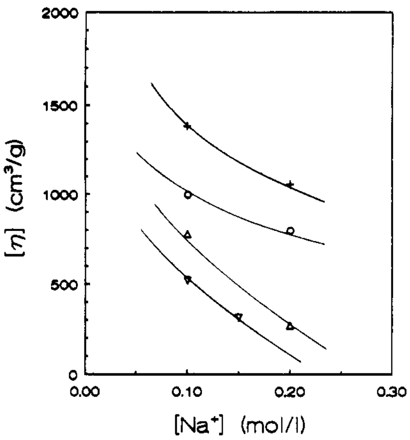

Figure 14. Effect of the anions on poly-MADQUAT intrinsic viscosity (T = 25 °C): (+) Cl^-; (○) Br^-; (△) I^-; (▽) SCN^-.

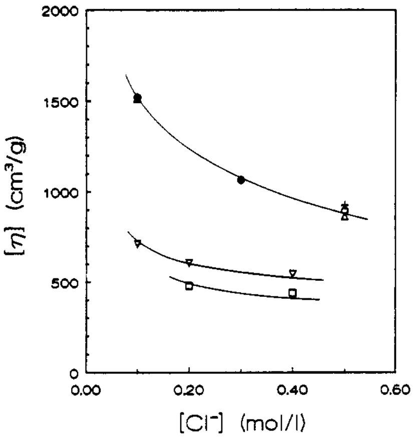

Figure 15. Effect of the cations on poly-NaAMPS intrinsic viscosity (T = 25 °C): (+) Na^+; (○) Li^+; (△) Cs^+; (▽) Mg^+; (□) Ba^{2+}.

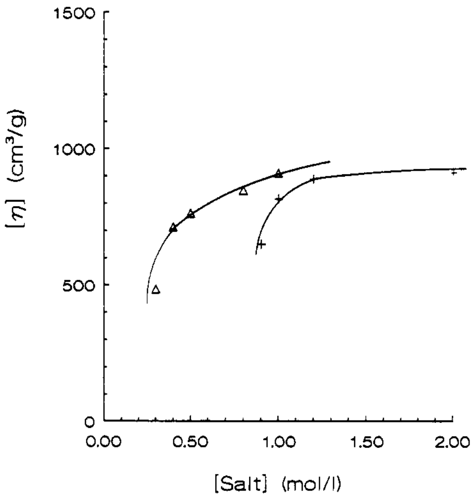

Figure 16. Effect of the nature of the electrolyte on the intrinsic viscosity of sample A50/M50: (+) NaCl; (△) NaI.

confirm the order of interaction of the anions with the quaternary ammonium groups of the polycation on one hand and of the cations with the sulfonate groups of the polyanion on the other hand.

$$Cl^- < Br^- < I^- < SCN^-$$

$$Li^+ \simeq Na^+ \simeq Cs^+ < Mg^{2+} < Ba^{2+}$$

The expansion of the poly-MADQUAT chains is very sensitive to the anion structure. This can be correlated to the polarizability increase of the anions from Cl^- to SCN^-. The selectivity is lower for the cations, confirming the lack of affinity between the sulfonate groups and the hard acids. Interestingly, the divalent cations do not induce the precipitation of the sulfonate polymer, contrary to what is often observed for polycarboxylates.[48,49]

Table V
Effect of the Nature of the Electrolyte on the Intrinsic Viscosity and Huggins Coefficient of Homopolymers and Sample A50/M50

sample	electrolyte	$C_{electrolyte}$ (mol·L^{-1})	[η] (g·cm^{-3})	K_h
A100	LiCl	0.1	1520	0.32
		0.3	1060	0.35
		0.5	895	0.35
	CsCl	0.1	1515	0.36
		0.5	865	0.46
	$MgCl_2$	0.05	712	0.43
		0.1	606	0.45
		0.2	545	0.80
	$BaCl_2$	0.1	479	0.33
		0.2	439	0.50
M100	NaBr	0.1	997	0.77
		0.2	797	0.74
	NaI	0.1	778	0.64
		0.2	271	1.75
	NaSCN	0.1	521	1.37
		0.15	315	1.27
A50/M50	NaI	0.3	484	1.40
		0.4	713	0.76
		0.5	763	0.37
		0.8	846	0.48
		1.0	910	0.50

In the case of sample A50/M50, there is an increase in the hydrodynamic volume with salt concentration. The value of the CSC is shown to depend upon the nature of the electrolyte while the macromolecular coil expansion remains unaffected. The values of the Huggins coefficient for NaCl and NaI are quite comparable, suggesting that the solvent quality is the same (Θ solvent) once the intrinsic viscosity has reached its limiting value. Such a result is somewhat contradictory with that obtained for poly-MADQUAT and requires further experiments for a better understanding of this phenomenon.

III. Small-Angle Neutron Scattering. Semidilute solutions are characterized by a correlation length ξ that represents the average distance between interchain contact points or the blob size. When a contrast is established between the polymer and the solvent, the neutron scattering intensity $I(q)$ has an Ornstein–Zernicke form for $q\xi \ll 1$:[50]

$$I(q) \simeq 1/(1 + \xi^2 q^2) \qquad (2)$$

At larger q values, in the domain such as $q\xi \gg 1$, one probes the inside of the blobs, where the statistics depend on the chain conformation. Then, in this regime, one has for the scattering intensity[51]

$$I(q) = \text{constant}/q^n \qquad (3)$$

where n is a characteristic exponent of the chain conformation: $n = 2$ for Gaussian chains; $n = 5/3$ for three-dimensional excluded volume.

Figure 17 shows the log–log plots of the scattered intensity $I(q)$ versus q for both samples in NaI aqueous solutions. The curves are practically superimposed. The shape of the curves does not correspond to that of a homogeneous semidilute solution as described above. As a matter of fact, the expected Ornstein–Zernicke function should lead to a saturation of the signal in a log–log plot for $q\xi \ll 1$. In the present case, one observes a smooth shoulder for $q \simeq 4 \times 10^{-2}$ Å^{-1} and a sharp increase at $q < 3 \times 10^{-2}$ Å^{-1}. This anomalous increase of $I(q)$, which has already been observed in other cases but at lower q values,

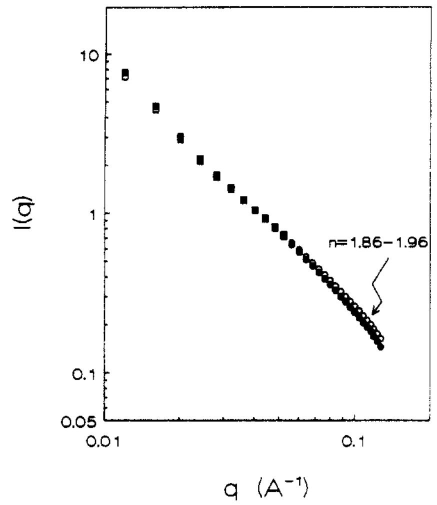

Figure 17. Scattered intensity versus q for sample A50/M50 in aqueous salt solution ($C \simeq 5 \times 10^{-2}$ g·cm^{-3}): (○,□) 0.6 M NaI; (●,■) 0.5 M NaI.

is not yet fully understood and has been attributed to the presence of heterogeneities (clusters) or to strong intermolecular interactions.[52] Note, however, that such an increase does not modify the results obtained at the larger q values ($q > 5 \times 10^{-2}$ Å^{-1}). A least-squares fit to the data (last 10 points of the curves of Figure 17) leads to values of $n = 1.86$ (for 0.6 M NaI) and $n = 1.96$ (for 0.5 M NaI), close to the characteristic value of a Gaussian coil ($n = 2$).

On the basis of a description of the system as a semidilute solution with additional large fluctuations on large length scales, one can try to estimate a correlation length. From the points corresponding approximately to the shoulder in the curves, one finds $\xi \simeq 30$ Å, a value which is in reasonable agreement with that found for a neutral polymer at a similar concentration.[53]

Further experiments are required to confirm these preliminary results.

Theoretical Background

While a large body of theoretical work has been developed on the structure of polyelectrolyte solutions, only few theories exist on polyampholytes.[22,54,55] Below, we recall briefly some theoretical predictions on the solution conformation of polyelectrolytes and more in detail the main conclusions of the recent model developed by Higgs and Joanny on polyampholytes.[22] These authors have predicted in terms of scaling laws the different regimes of behavior found for polyampholytes either neutral or with a net charge of one sign. Our experimental observations will be compared with these behavior predictions.

The hypotheses on which the models are based are the following: (i) weak coupling limit, i.e., $l_B/b \leq 0.3$ (where l_B is the Bjerrum length and b the length of a statistical unit); (ii) zero or low salt concentration, i.e., $\kappa^{-1} > l_B$ (κ^{-1} is the Debye–Hückel screening length).

I. Single Polyelectrolyte Chain in Dilute Solution.[56,57] The model of De Gennes et al.[57] predicts that in pure water a long chain of N monomers is formed of a succession of n small blobs of size

$$r \simeq b(b/l_B)^{1/3} \tag{4}$$

Within each blob, the chain is ideal: $r \simeq n^{1/2}b$. Strong Coulombic repulsive interactions exist between the blobs so that the overall conformation of the chain is extended with a size

$$R = b(l_B/b)^{1/3}N \tag{5}$$

Let us note that in the strong coupling limit ($l_B/b \simeq 1$) no precise predictions can be made. If the screening effects are neglected, it is expected that the chain is fully extended. However, the chain can be partly bent due to counterion condensation.

In the presence of salt and for distances smaller than κ^{-1}, the chain is stretched but it behaves globally as a neutral chain with short-range interactions between the monomers.[56]

$$R \simeq b^{3/5}(\kappa^{-1})^{2/5}N^{3/5} \tag{6}$$

II. Polyampholytes. The model[22] applies to a single chain having a fraction f of positively charged monomers and a fraction g of negatively charged monomers. The charged monomers are randomly distributed along the chain.

(a) Conformation of a Neutral Polyampholyte Chain ($f = g$). In Pure Water. We assume that there exists a collapsed state of the chain (by charge attractions) with a volume significantly smaller than the Gaussian chain volume ($N^{3/2}b^3$) but significantly larger than that of completely close-packed monomers (Nb^3). Thus, in this state, the macromolecule is at thermodynamic equilibrium and can easily change from one configuration to another. This collapsed state is stabilized by the third virial coefficient, which counteracts the electrostatic attractions.

If the polymer occupies a spherical region of radius R, the charge concentration in this region is $\simeq fN/R^3$. By analogy with the Debye–Hückel screening length κ^{-1}, one can define a screening length κ_p^{-1} due to the charge on the polymer given by

$$\kappa_p^{\,2} \simeq fNl_B/R^3 \tag{7}$$

As for polyelectrolytes, there exist different regimes depending on the dimensions of polymer chains. A long chain collapses into a globule consisting of close-packed blobs of size κ^{-1}. The blobs are either Gaussian or swollen depending on the second virial coefficient value. In a Θ solvent, the chain radius in the collapsed state is given by

$$R \simeq N^{1/3}b\left(\frac{b}{fl_B}\right)^{1/3} \tag{8}$$

In the case of finite concentration of chains, Higgs and Joanny predict a phase separation between a high-concentration phase of interpenetrating polymer chains and a dilute solution in which each chain is a collapsed globule.

In the Presence of Salt. The addition of salt tends to reswell the collapsed chain back to the dimensions of the uncharged chain. The electrostatic attractions are treated as a negative contribution to the excluded volume. There is therefore a Θ compensation point at the salt concentration at which the positive excluded volume interaction V balances the negative electrostatic contribution.

The effective excluded volume is given by

$$V^* = V - 4\pi l_B^{\,2}f^2/\kappa b^3 \tag{9}$$

At the Θ point ($V^* = 0$), the screening length is

$$\kappa = \kappa_\Theta = \left(\frac{l_B f}{b}\right)^2 \frac{1}{Vb} \tag{10}$$

This salt concentration marks the transition from collapsed to Gaussian or swollen chains.

(b) Conformation of a Nonneutral Polyampholyte Chain. The theory is restricted to the case $V = 0$ with $(f - g) \ll (f + g)$.

In Pure Water. The chain has the characteristics of both a polyelectrolyte (excess of charges: $f - g$) and of a neutral polyampholyte (neutral part: $2g \simeq f + g$). The overall conformation of the chain is determined by the respective values of the blob sizes relative to these two types. A critical net charge occurs at which the chain behaves like a classical polyelectrolyte in water:

$$(f - g) > (l_B/b)(f + g)^{3/2} \qquad (11)$$

In Salt Solution. The effective excluded volume is given by

$$V^* = \frac{\pi l_B^{\,2}(f + g)^2}{\kappa b^3} + \frac{4\pi l_B(f - g)^2}{\kappa^2 b^3} \qquad (12)$$

The polyelectrolyte term decreases like $1/\kappa^2$ while the polyampholyte term decreases like $1/\kappa$. For a large net charge, V^* becomes negative for $\kappa > \kappa_\Theta$, where

$$\kappa_\Theta = \frac{4(f - g)^2}{(f + g)^2}\frac{1}{l_B} \qquad (13)$$

The minimum of V^* occurs at $\kappa = 2\kappa_\Theta$. The chain becomes ideal as κ tends to infinity ($V^* \rightarrow 0$). Thus, the chain passes from linear to collapsed to ideal configurations with increasing salt concentration.

At a finite salt concentration, the polyampholyte effect dominates the polyelectrolyte effect at long distances if

$$(f - g)^2 < \frac{\kappa l_B}{4}(f + g)^2 \qquad (14)$$

Hence, the chain is expected to collapse at intermediate salt concentrations over a wider range of $(f - g)$.

For a small net charge, the polyampholyte term dominates and the chain behaves as in the case of a neutral polyampholyte.

Discussion

The homopolymers and copolymers of NaAMPS and MADQUAT investigated here have very high molecular weights (>10^7). In the following, we refer to the theoretical conclusions proposed for long chains (large N).

Homopolymers. PolyNaAMPS and poly-MADQUAT are pure polyelectrolytes and behave qualitatively, as predicted by the theory: the chains are stretched at very low ionic strength and contract progressively as the salt concentration is increased (eqs 5 and 6).

Neutral Polyampholyte (A50/M50). In the absence of salt, sample A50/M50 is totally insoluble in water. There is a phase separation between a polymer-rich phase and a dilute solution as predicted by Higgs and Joanny.[22] Addition of salt favors the solubilization of the chains. At the CSC, the sharp increase of the intrinsic viscosity marks the transition from a collapsed state to an ideal or swollen configuration (Θ transition). The plateau which is further observed corresponds to a regime of Gaussian or swollen conformation with excluded volume type interactions between monomers. The value of the exponent $n \simeq 2$ (from eq 3) found by SANS for this sample in the plateau region and the almost zero values of the second virial coefficients measured by light scattering[27,28] are in favor of a Gaussian configuration of the chain rather than a swollen state. At this stage, all the electrostatic interactions are screened by the small ions in solution.

Nonneutral Polyampholyte. In the case of polyampholytes with an excess of charges, the overall chain conformation is the result of the competition between polyelectrolyte and polyampholyte effects.

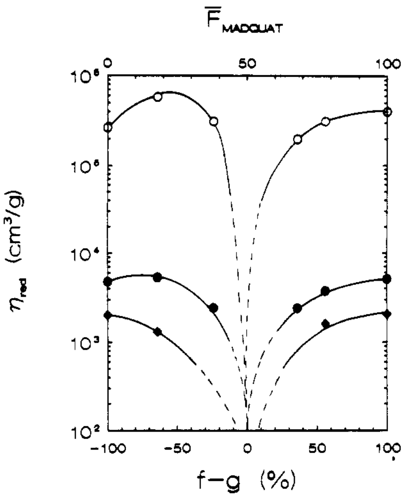

Figure 18. Reduced viscosity of aqueous (co)polymer solutions with the net charge at $T = 25$ °C. (○) H_2O ($C = 2.5 \times 10^{-4}$ g·cm^{-3}); (●) 0.02 M NaCl, (♦) 0.1 M NaCl ($C = 5 \times 10^{-4}$ g·cm^{-3}).

In pure water and for a large net charge (eq 11), the polyelectrolyte effect dominates and the chain has an extended configuration. The effective excluded volume goes through a minimum upon increasing salt (eq 12). Our experimental results corroborate this prediction. For an excess of charges $(f - g)$ from 20 to 60 a minimum in the optical transmission is observed at intermediate salt concentrations. This minimum can be associated with the formation of partial aggregation of chains resulting from the negative value of V^* at $\kappa > \kappa_\Theta$ (eq 13).

The theory also predicts that the polyampholyte effect dominates the polyelectrolyte effect at long distances, for a wide range of $(f - g)$ at a finite salt concentration (eq 14). This prediction was confirmed by McCormick et al.[19,20] on related polymers polymerized in aqueous solution. These authors found that the solution viscosity versus the net charge of the sample goes through a sharp minimum in pure water close to the neutral point; the minimum broadens in salt solution over a wider range of $(f - g)$. A minimum in viscosity was also observed by Alfrey et al.[58] and Katchalsky and Miller[8] on polyampholytes which were copolymers of a weak acidic monomer and a weak basic monomer. For our systems, the experiments could not be performed near the neutral point ($f - g = 0$) because of the insolubility of the samples in this domain. However, the results presented in Figure 18 are consistent with the theoretical predictions that are illustrated in a schematic manner by the dotted lines.

Limitations of the Comparison between Theory and Experiments. The general theories developed for polyelectrolytes or polyampholytes are usually valid under the following hypotheses: (i) the effect of the counterions on the conformation of the charged chains is neglected; (ii) the salt content is low ($\kappa l_B < 1$); (iii) the solutions are dilute.

Neglecting the effect of counter ions implies that the chains are weakly charged. This is obviously not the case for homopolymers of NaAMPS and MADQUAT, which contain only charged monomers. Part of the counterions are condensed, which affects the physical properties of the polyions. A more elaborate theory is needed to take these effects into account.[59]

One particularity of polyampholytes with respect to polyelectrolytes is that monomeric units of opposite sign tend to self-neutralize two by two.[27,28] Thus, a neutral

Table VI
Value of the Screening Length κ^{-1} at the CSC for Various Electrolytes for Sample A50/M50 ($C \simeq 10^{-2}$ g·cm^{-3}, T = 25 °C)[a]

electrolyte	CSC (mol·L^{-1})	κ^{-1} (Å)
NaCl	1.01	3.0
NaBr	0.58	4.0
NaI	0.36	5.1
$MgCl_2$	0.47	2.6
$BaCl_2$	0.38	2.8

[a] $\kappa^{-1} = 3.043 \times 10^{-10} I^{-1/2}$, with I the ionic strength ($I = {}^{1}/_{2}\sum_i z_i^{2} c_i$).

polyampholyte is free of inorganic counterions. For these samples, it seems reasonable to ignore the effect of counter ions.

The theories are only valid at low salt concentrations, which means that the Debye–Hückel screening length κ^{-1} is large with respect to the Bjerrum length ($l_B \simeq 7$ Å in water at 25 °C). The theory cannot be quantitatively accurate for the high salt concentrations needed to dissolve the highly charged polyampholytes. Table VI shows that the screening lengths κ^{-1} are indeed of the same order of magnitude as the radius of the ions (0.6–4 Å depending on the nature of the ion and whether it is crystalline[60] or hydrated[61]).

Concerning the range of polymer concentrations studied in the present work, the viscometric experiments were performed in the dilute regime, whereas the solubility data refer to the semidilute range.

Finally, the experimental data show that the chain behavior is very sensitive to the particular type of inorganic ions present. For instance, considerable differences are observed between the concentrations of NaCl, NaBr, or NaI required to dissolve the neutral polyampholyte (see Table II). This suggests that the ionic radius, the solvation of ions in water, and some specific ion–polymer interactions should be considered for a more complete theory. In spite of these reservations, the model of Higgs and Joanny[22] describes reasonably well the solution behavior of the polyampholytes investigated here.

Conclusion

Solubility and viscometry experiments were used to investigate the properties of polyampholytes in pure water and in salt solutions. Our results show that the solution behavior is essentially controlled by two parameters: the net electrical charge, fixed by the copolymer composition, and the ionic strength. Thus, a neutral polyampholyte is insoluble in pure water due to the chain collapse. It becomes soluble on addition of large amounts of salt with a more or less ideal configuration, because of a complete screening of the attractive interactions. Copolymers with a strong net charge behave more like polyelectrolytes. At intermediate copolymer compositions, the sample behavior depends on the duality between repulsive (polyelectrolyte effect) and attractive (polyampholyte effect) electrostatic interactions. Depending of the ionic strength, either one of these antagonist effects will dominate. For example, some nonneutral chains (the case for sample A60/M40) are in an extended polyelectrolyte configuration in pure water but collapse due to the polyampholyte effect at moderate salt concentrations. The results are found to be in good qualitative agreement with the recent theory of Higgs and Joanny on polyampholytes.[22]

The nature of the electrolyte was also shown to affect the solution properties. In particular, the larger the anion polarizability, the better the solubilization of the neutral polyampholyte. Divalent cations are more efficient than monovalent cations.

From the results, it can be inferred that the charge screening is of an atmosphere binding type rather than site binding. Finally, the viscometric behavior of samples in dilute solution suggests that the properties of highly charged polyampholytes essentially depend on the intramolecular ionic interactions.

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