Molecular Simulation

Monte Carlo Simulation of Polyampholyte Chains

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MONTE CARLO SIMULATION OF POLYAMPHOLYTE CHAINS

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Polyampholyte copolymers containing both positive and negative monomers regularly dispersed along the chain were studied. The Monte Carlo method was used to simulate chains with charged monomers interacting by screened Coulomb potential. The neutral polyampholyte chains collapse due to the attractive electrostatic interactions. The nonneutral chains are in extended conformations due to the repulsive polyelectrolyte effects that dominate the attractive polyampholyte interactions. The results are in good agreement with experiment.

KEY WORDS: Polyampholyte copolymers, Monte Carlo simulation, macromolecules, polyampholyte effect

I INTRODUCTION

Polyampholytes are macromolecules containing both positively and negatively charged monomers interdispersed along the same linear chain. They may be either electroneutral or present a net charge positive or negative. The behavior of this kind of charged polymer is still not well understood from a theoretical point of view [1, 2]. Although a wealth of experimental results on polyampholyte solutions exists in the literature [3, 4, 5] it is often impossible to obtain quantitative explanations of the results.

The conformation of a polyampholyte single chain in solution is a complex problem. A clear understanding of the single chain is necessary as a basis for polyampholyte solution theories at finite concentration. Few theoretical studies for polyampholyte solutions are available. Kholodenko [6] investigated a randomly charged chain in a Θ solvent and random distribution of charges. Edwards [7] has produced a scaling theory for the chain collapse without introducing the third virial coefficient. This coefficient turns out to be important for stabilizing the chain in its collapsed state, forbiding its close packing. Polyampholytes are interesting from a theoretical point of view as examples of chains that undergo a coil-globule transition [8], and due to its relation with several recent studies for the folding of proteins [9, 10]. In this paper, we use Monte Carlo method to generate macromolecules configurations in order to study the conformational properties of isolated polyampholyte macromolecules in a continuum 1:1 electrolyte solutions.

II THE MODEL

The model of polyampholyte is a pseudo $C_{300}(sp^3)$ chain with all the beads electrically charged. The beads of the polyion are connected by rigid bonds, 1, of unit length (0.154 nm) and the bond angle is the tetrahedral angle, 109,5°. All the distances will be expressed in reduced units, having as reference the carbon-carbon distance. The dihedral angles between the planes defined by three successive bonds are fixed at 30, 150 and 270° (the gauche and trans conformations), [11].

In this model, the interactions are the Coulombic screened like Debye-Hückel interactions between the beads. Each charged bead interacts with the other charged beads via a potential of mean force given by Debye-Hückel theory:

$$u(r_{ij}) = \frac{q_i q_j e^2}{4\Pi \varepsilon_0 \varepsilon_r r_{ij}} \exp(-\kappa r_{ij}) \tag{1}$$

where r_{ij} is the distance between beads i and j on the polyampholyte chain, q_i and q_j are the charges on beads i and j, respectively, e is the electronic charge, ε_0 the permittivity of vacuum, and ε_r the dielectric constant of the solvent. We take $\varepsilon_r = 78.5$ to represent water. The variable k in equation (1) is the inverse Debye-Hückel screening length:

$$\kappa^2 = \frac{e^2 N_A \Sigma_i q_i^2 C_i}{\varepsilon_r \varepsilon_0 k_B T} \tag{2}$$

where N_A is Avogadro's number, C_i is the concentration of species i in mol dm^{-3}, k_B is the Boltzmann constant, and the summation is over all ionic species in the
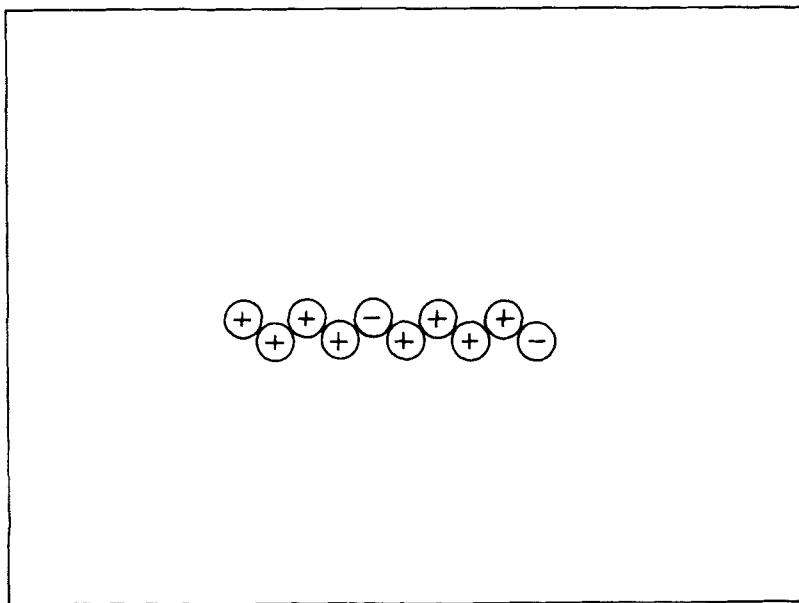

Figure 1 Regular arrangements of the charges for $q(-)/q(+) = 0.25$ and $N = 10$ beads.

added salt. Such a model for the polyion is essentially a model for repulsive (polyelectrolyte effect) and attractive (polyampholyte effect) intramolecular interactions. Every bead of the polyion can carry only one negative or one positive electrostatic charge depending on the ratio of negative and positive charges of the chain. The polyion charges are arranged in periodical sets of negative and positive beads. If $q(-)$ and $q(+)$ are the fraction of negative and positive charges, simulation for $q(-)/q(+) = 0.25$, for example, is made with macromolecules consisting of a repetition of a string of one negatively charged bead followed by four positive beads (see figure 1).

III METHOD

The Metropolis Monte Carlo method [2] was used to generate samples of 5,000 different chains for each experimental condition. Each macromolecule was generated directly beginning from one end and building the molecule using the Monte Carlo standard criterion in order to add each bead [2]. The conformations where some bead to bead distance appear to be less than 1 were rejected automatically (hard sphere short range potential). The chain obtained in such a manner is a correct canonical sample at the given temperature. For this reason no thermalization was needed such as in the slithering snake method [11]. This kind of polymer building was tested on previous data [11, 12] showing a perfect agreement with them. Of course the advantage of the method is an enormous gain of CPU time: for example, a 300 beads polyion is generated on a 100 MIPS Convex C220 computer in about $0.24\,s$ while the time will be $72\,s$ using the N^3 repetition method. The polyions Monte Carlo generated conformations were used to determine the end-to-end distance, R, given by:

$$R^2_{1,N} = (r_1 - r_N)^2 \tag{3}$$

where r_i is the distance between the first and the last bead of the chain. In the same way the radius of gyration, S, can be calculated by:

$$S^2 = \frac{1}{N} \sum_{i=1}^{N} (r_i - R_c)^2 \tag{4}$$

where $(r_i - R_c)$ is the distance between the center of mass of the molecule in its actual conformation and bead i.

The distribution functions for the end-to-end distance and for the radius of gyration are equal to the frequencies of R and S observed during the simulations.

The Monte Carlo simulations of the chains containing fractions $q(+)$ of positively charged monomers and fraction $q(-)$ of negatively charged monomers were performed at 300 K in 1:1 aqueous electrolyte solutions. The permittivity of the solutions was fixed at 78.5 and the salt concentration at 1.0, 0.1, 0.01 and 0.001 M. The ration $q(-)/q(+)$ varies from 0 to unity.

IV RESULTS AND DISCUSSION

Figures 2 and 3 present the dependence of the end-to-end distance and of the radius of gyration respectively with the ratio $q(-)/q(+)$. Figure 2 indicates that the
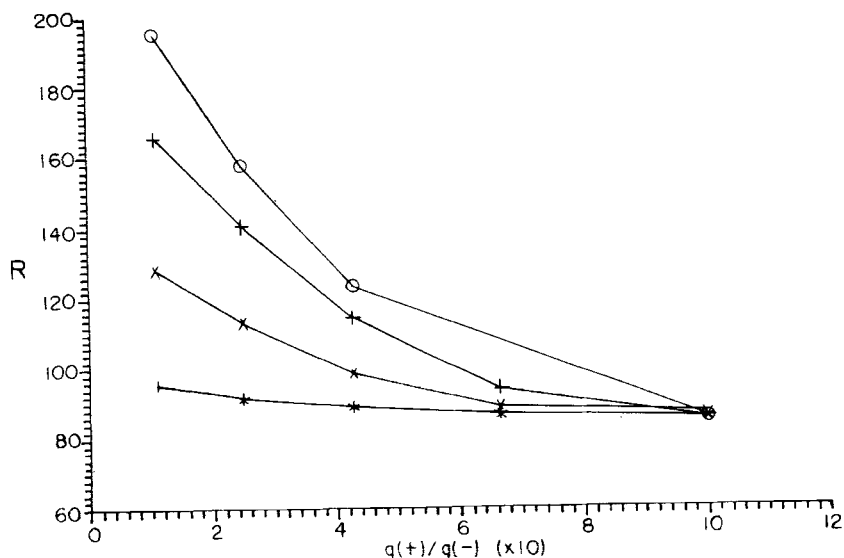
Figure 2 End-to-end distance (reduced units) versus the fraction $q(-)/q(+)$. (0) = 0.001 M, (+) = 0.01 M, (×) = 0.1 M, (*) = 1.0 M.

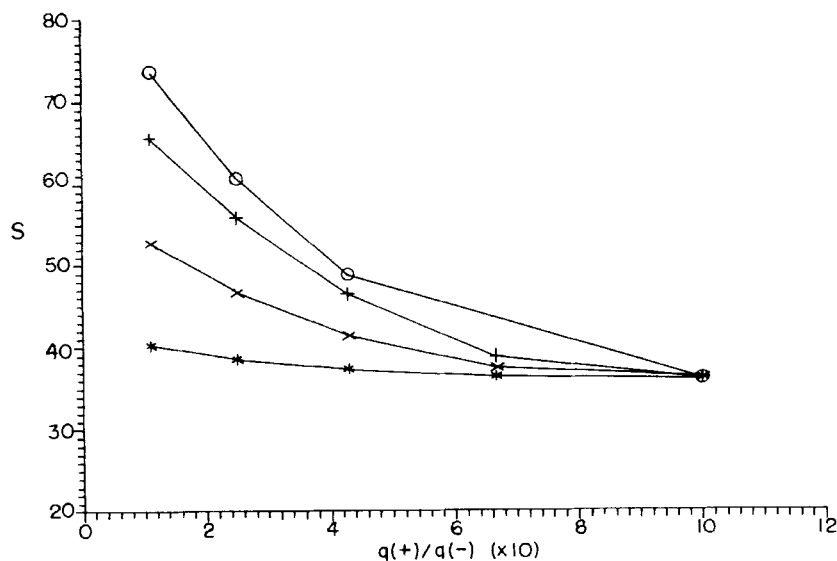**Figure 3** Radius of gyration (reduced units) versus the fraction $q(-)/q(+)$. (0) = 0.001 M, (+) = 0.01 M, (×) = 0.1 M, (*) = 1.0 M.
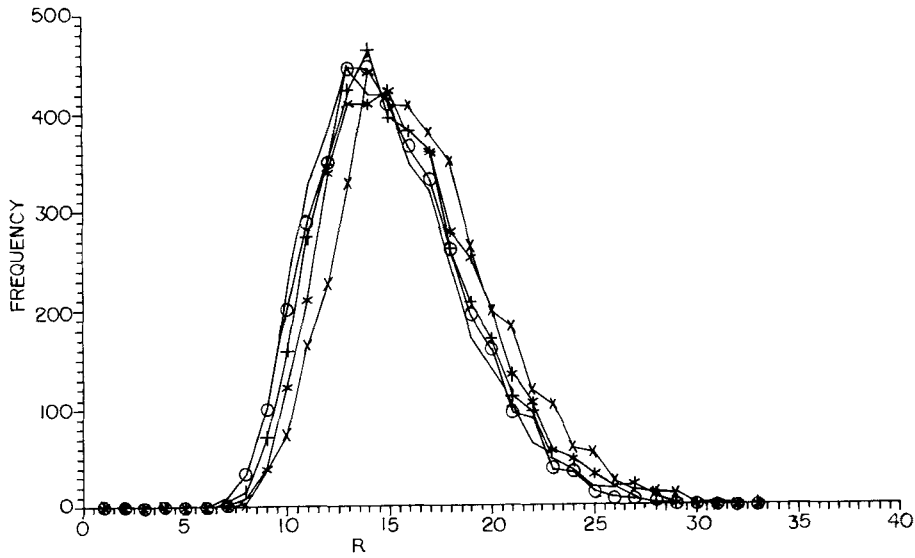
Figure 4 End-to-end distance distributions. Salt concentration is 1.0 M. $q(-)/q(+)$: (.) = 1.0, (0) = 0.67, (+) = 0.43, (*) = 0.11.
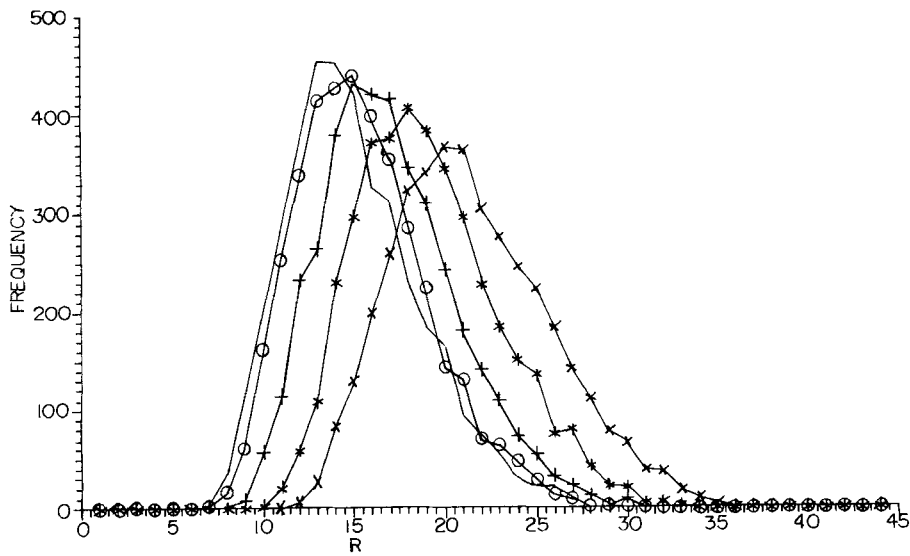
Figure 5 End-to-end distance distributions. Salt concentration is 0.1 M. $q(-)/q(+)$: (.) = 1.0, (0) = 0.67, (+) = 0.43, (*) = 0.11.

polyampholyte chain collapses into a globule as the $q(+)/q(-)$ approaches 1.0 (neutral chain), due to attractive electrostatic interactions.

The origin of this attraction is the screening effect that occurs in electrolyte solutions; according to recent theories [1], a positive or negative charge tends to be surrounded by an "atmosphere" of opposite sign charges. The neutral chains are in an collapsed conformation and present the same end-to-end distance value for all salt concentrations. The strong attraction between charges of opposite signs gives rise to frozen conformations in the collapsed state. The same comments can be made for the radius of gyration.

The results for the end-to-end distance distributions when the number of beads is 300 are shown in figs. 4 and 5 for $q(-)/q(+) = 0.11, 0.25, 0.43, 0.67$ and 1.0, for salt concentration equal to 1.0 and 0.1 M respectively. Figure 4 shows that the most probable end-to-end distance is nearly independent of $q(-)/q(+)$, indicating that the electrostatic interactions and the attractive forces (polyampholyte effect) are screened by the addition of salt. The addition of salt tends to reswell the collapsed state back to the most stable conformation of the uncharged macromolecule. In figure 5, a monotonic shift is observed for the most probable end-to-end distance when the $q(-)/q(+)$ is lowered from 1.0 (neutral chain) to 0.11 (nonneutral chain). The distributions become somewhat broader as $q(-)/q(+)$ is lowered, indicating that the chain adopt extended conformations due to the polyelectrolyte effect, i.e., repulsive interactions between the charged (same sign) beads.

The effects of added electrolytes on the end-to-end distance are shown in figure 6. Typical polyeletrolyte behavior (decrease in R with ionic strength) is observed for the macromolecules with $q(-)/q(+)$ in the range 0.11 to 0.43. Macromole-
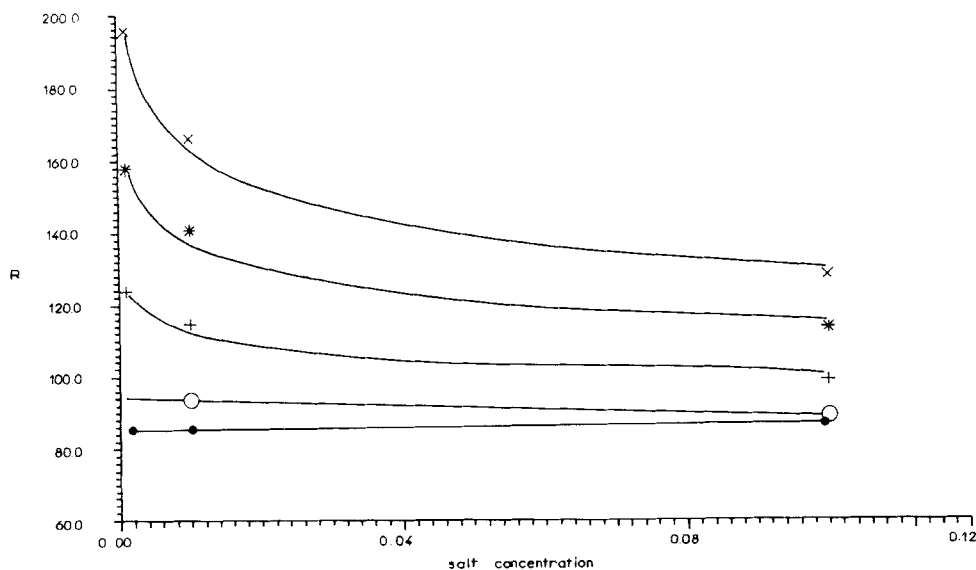

Figure 6   End-to-end (reduced units) versus salt concentration. $q(-)/q(+)$: (.) = 1.0, (0) = 0.67, (+) = 0.43, (*) = 0.25, (×) = 0.11.

cules with $q(-)/q(+) = 0.67$ and 1.0 display typical polyampholyte behavior. The value of R is quite independent from the ionic strength when $q(-)/q(+) = 0.67$, while, for $q(-)/q(+) = 1.0$, R increases with the ionic strength. Figure 6 can be compared with figures 3 and 4 of reference 3, where the authors plotted [η] versus [NaCl] for a series of copolymers of (2-acrylamido-2-methylpropil) dimethyl-ammonium cloride (AMPDAC) with 2-acrylamido-2-methylpropa-nesulfonate (NaAMPS). According to the authors, the viscosity decreases with ionic strength for the ADAS-0 and ADAS-10 homopolymer and 10 mol % AMP-DAC copolymer, respectively), the invariance of the viscosity for the copolymers ADAS-25 and ADAS-40, and the increasing viscosity for the copolymer ADAS-50 (50 mol % AMP-DAC). These behaviors are due to the shielding in the disruption of positive-negative charge attractions allowing coil expansion by enhanced solvation. In our model the charges are fixed on the beads and only intramolecular ionic interactions between the charged groups were taken into account: this model represent severe conditions for chain stiffness and for the charges distances from the backbone. Nevertheless a good qualitative agreement with the experimental results is found [4].

V CONCLUSIONS

Monte Carlo simulations were used to investigate the conformational properties of neutral and nonneutral polyampholyte macromolecules. Our results show that the macromolecules exist in collapsed conformations when the number of negatively charged monomers is equal to the number of the positively ones. The conformational properties of this chain is independent of the salt concentration in the range 0.001–1.0 M. Depending on the salt concentration, a competition between the extended conformation (polyelectrolyte effect) and the collapsed one (polyampholyte effect) is observed. Our results are in good qualitative agreement with the experimental results of McCormick and Johnson [4].

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