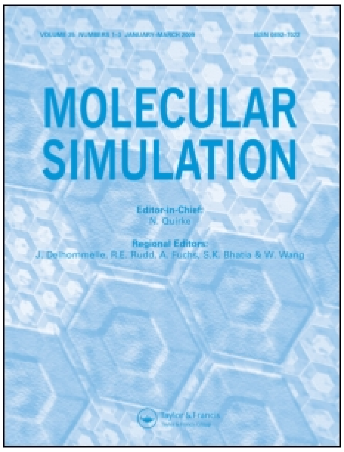

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Molecular dynamics simulations of polyampholyte solutions: osmotic coefficient

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Molecular dynamics simulations of polyampholyte solutions: osmotic coefficient

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Polyampholytes are charged polymers containing both positively and negatively charged monomers widely used in colloid stabilization, wetting, adhesion, lubrication, etc. Due to the randomly distributed positive and negative charges on polymer backbone, polyampholyte chains have both the contraction tendency by counter charges and the stretch tendency by similar charges, which causes difficulty to develop a reliable molecular thermodynamic model. In this work, osmotic coefficients of solutions containing neutral or non-neutral polyampholyte chains with different segment sizes and charged sequences were obtained by molecular dynamics (MD) simulation, in which the Langevin equation considering both the viscous force from solvent and the stochastic force from heat-bath is used. A molecular thermodynamic model based on chemical association theory was developed where the polyampholyte molecules are modeled as positively and negatively charged hard-sphere chains with a chain length l. Those chains and counter-ions are embedded in a continuum medium. The l-particle cavity correlation function for a polyion chain is linearly approximated by a product of nearest-neighbor two-particle cavity correlation functions, density dependence of which is analytically expressed as a function of a scaling parameter from the mean-spherical approximation (MSA). It is shown that the predicted osmotic coefficients by the model agree satisfactorily with those obtained from MD simulation for neutral polyampholytes.

Keywords: Polyampholyte; Molecular thermodynamic model; Molecular dynamics simulation; Langevin equation

1. Introduction

Polyampholytes are charged polymers containing both positively and negatively charged monomers. Many biopolymers such as proteins are polyampholytes. Also we have many synthetic neutral or non-neutral polyampholytes. In aqueous solution, they can exist in anionic, cationic or neutral state depending on the pH. They have a wide variety of applications in colloid stabilization, wetting, adhesion, lubrication, etc. Understanding their properties is essential to biological processes and industrial applications. In contrast to uncharged polymers and polyelectrolytes, due to the unique electrostatic interactions caused by all kinds of different distributions of anionic and cationic segments in polyion chains, polyampholytes remain one of the least understood systems in the field of complex fluids. There are increasing interests concerning polyampholytes. Developments including theory [1–7], simulation [8–15] and experiments [16] have been made during the past few years. Most of these deal with configuration properties of polyampholyte, while attention on thermodynamic properties is rare. Kalyuzhnyi and Cummings [17] applied polymer mean spherical approximation (PMSA) in the multidensity integral equation theory of Wertheim to study thermodynamic properties of polyelectrolytes and polyampholytes solutions, the osmotic coefficients of polyampholyte solutions can be predicted. However, no comparisons with simulation results have been made. In this work, we consider the polyampholytes as linear nonstructural polymers by neglecting their detail conformation. Osmotic coefficients of solutions containing neutral or non-neutral polyampholyte chains with different segment sizes and charged sequences were obtained by molecular dynamics (MD) simulation, in which the Langevin thermostat considering both the viscous force from solvent and the stochastic force from heat-bath is used. Similar to Jiang *et al.* [18,19] and Cai *et al.* [20] work for the development of the molecular thermodynamic model for polyelectrolyte solutions and

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Hu *et al.* [21] work for hard-sphere chain fluids, a molecular thermodynamic model for polyampholyte solutions based on chemical association theory [18,22] was developed. The predicted osmotic coefficients are agreed well with those results by MD or Monte Carlo simulations [23].

2. Molecular dynamics simulations

We adopt primitive model for polyampholyte solutions. For stabilizing the system, in MD method, we use the Langevin equation considering both the viscous force from solvent and the stochastic force from heat-bath as was brought forward by Grest and Kremer [24] and has been successfully used in polyelectrolytes simulation [25]. The equation of motion is

$$\ddot{r}_i = -\nabla U_i - \gamma \dot{r}_i + W_i(t) \tag{1}$$

where γ is a friction coefficient set equal to 1 in all simulations. $W_i(t)$ is a random force acting on particle i at time t which satisfies the equation

$$\langle W_i(t) W_i(t') \rangle = \delta_{ij}\delta(t-t')6k_{\mathrm{B}}T\gamma \tag{2}$$

U_i is the interaction energy of particle i with other particles

$$U_i = \sum\nolimits_{j\neq i} U_{ij} = \sum\nolimits_{j\neq i} U_{ij}^{e} + U_{ij}^{\mathrm{LJ}} + U_{ij}^{C} \tag{3}$$

where U_{ij}^{e} is the electrostatic interaction energy between particles i and j,

$$U_{ij}^{\mathrm{e}} = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\frac{z_i z_j}{r_{ij}} \tag{4}$$

In simulations, electrostatic energy is calculated using Ewald summation method [26,27]. The electrostatic properties such as virial, energy and forces can be decomposed into the real space contribution and the reciprocal space contribution. The half box length (L) is selected as cut-off distance in real space, and the value in error function is chosen to be $5/L$. The vector numbers are chosen automatically by the program so that the relative deviation of electrostatic energy is less than 0.01%. The virial of electrostatic contribution is set equal to the negative of electrostatic potential.

U_{ij}^{LJ} is the Lennard–Jones potential between particles i and j. We use a cut-off distance $r_{ij}^{\mathrm{c}} = 2^{1/6}\sigma_{ij}$ for excluded volume between all monomers.

$$U_{ij}^{\mathrm{LJ}} = \begin{cases} 4\varepsilon\left[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6} - (\sigma_{ij}/r_{ij}^{\mathrm{c}})^{12} + (\sigma_{ij}/r_{ij}^{\mathrm{c}})^{6}\right] & r_{ij} \le r_{ij}^{\mathrm{c}} \\ 0 & r_{ij} > r_{ij}^{\mathrm{c}} \end{cases} \tag{5}$$

where ε and σ are energy and size parameters, respectively. The connectivity of nearest neighbor monomers in a chain is maintained by a finite extension non-linear elastic (FENE) potential,

$$U_{ij}^{\mathrm{C}} = \begin{cases} -\frac{1}{2}kR_0^2\ln(1 - r_{ij}^2/R_0^2) & r_{ij} \le R_0 \\ 0 & r_{ij} > R_0 \end{cases} \tag{6}$$

where $k = 18\varepsilon/\sigma^2$ is the spring constant, and $R_0 = 2\sigma_{ij}$ is the maximum extension. At these conditions the total fluctuation of bond length is less than 5%.

The osmotic coefficients (Φ) can be obtained by the osmotic pressure (p) of the polyampholyte solutions which can be evaluated by the virial consisting of the above three contributions.

$$\Phi = \frac{p}{(\rho_c + \rho_m)k_{\mathrm{B}}T} \tag{7}$$

where ρ_c is the polyampholyte polyion density and ρ_m is the total counterion density in the solution.

We use the above MD method to obtain osmotic coefficient of polyampholyte solutions. The chain length of polyampholyte is set equal to 16. The chain numbers in the most simulations are 16. The reduced temperature is $k_{\mathrm{B}}T/\varepsilon = 1.2$. The reduced Bjerrum length l_{B} ($l_{\mathrm{B}} = e^2/4\pi\varepsilon_r\varepsilon_0 k_{\mathrm{B}}T\sigma$) is 0.833. It means that in the aqueous solution at the temperature 298.15 K the diameter of the charged particle is 0.86 nm. The time step is 0.015τ, $\tau = \sigma(m/\varepsilon)^{1/2}$. Most of simulations perform more than 800,000 time steps, among them the former 400,000 time steps are for equilibrium, and the latter for measurement of thermodynamic properties.

3. Molecular thermodynamic model

In solutions, the polyampholyte ion consists of at least two types of charged particles with different signs; besides, there are two types of counter ions. To develop a molecular thermodynamic model for polyampholyte solutions, similar to our previous work [18,19], we consider that the charged hard spheres are connected into a polyampholyte through chemical association as shown in figure 1. The reference system is composed of K species of charged hard spheres with number density $\rho_{i,0}$, hard-core diameter σ_i and charge z_ie, $i = 1,\ldots,K$, respectively. They are embedded in a continuum medium with a permittivity $\varepsilon_0\varepsilon_r$. The whole system is neutral

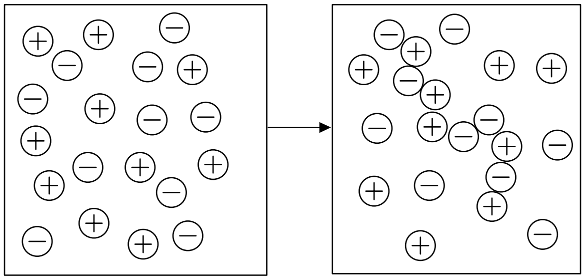

Figure 1. The formation of a polyampholyte molecule.

subject to

$$\sum_{i=1}^{K} \rho_{i,0} z_i = 0 \tag{8}$$

A polyion with a chain length l is constituted by l types of tangent-jointed charged hard spheres. The number density of polyions is ρ. Adopting the sticky hard sphere model, the Mayer function of tangent-jointed l segments can be expressed as:

$$f^{(l)}_{1,\ldots,l}(r_{12}, r_{23}, \ldots, r_{l-1,l}) = \begin{cases} -1 + \prod_{p=1}^{l-1} \sigma_{p,p+1} \delta(r_{p,p+1} - \sigma_{p,p+1})/(12\tau_{p,p+1}); & r_{p,p+1} \le \sigma_{p,p+1} \\ -1 + \exp\left[-\beta\varepsilon^{(l)}_{12,\ldots,l}(r_{12}, r_{23}, \ldots, r_{l-1,l})\right]; & r_{p,p+1} > \sigma_{p,p+1} \end{cases} \tag{9}$$

where $\tau_{p,\ p+1} = \exp(\beta\delta\varepsilon_{p,\ p+1}) - 1$ is an association parameter, $\delta\varepsilon_{p,\ p+1}$ is the association energy. The corresponding total correlation function is:

$$h^{(l)}_{1,\ldots,l}(r_{12}, r_{23}, \ldots, r_{l-1,l}) = -1 + \prod_{p=1}^{l-1} \sigma_{p,p+1} \times \delta(r_{p,p+1} - \sigma_{p,p+1})\lambda_{p,p+1}/12; \quad r_{p,p+1} \le \sigma_{p,p+1} \tag{10}$$

where $\lambda_{p,p+1}$ is a distribution parameter related to $\tau_{p,p+1}$. The association degree is defined by:

$$a = \frac{\rho^{(l)}}{\rho} = \frac{1}{\rho}\rho^{l} \int_{\sigma-}^{\sigma+} g^{(l)}_{12,\ldots,l}(r_{12}, r_{23}, \ldots, r_{l-1,l}) \mathrm{d}r_{12}\, \mathrm{d}r_{23} \cdots \mathrm{d}r_{l-1,l} \tag{11}$$

where $\rho^{(l)}$ is the number density of l-mer. The cavity correlation function of l-mer can then be derived as

$$y^{(l)}_{12,\ldots,l}(r_{12}, r_{23}, \ldots, r_{l-1,l}) = \prod_{p=1}^{l-1} \tau_{p,p+1}\lambda_{p,p+1} \tag{12}$$

According to statistical mechanics, we have

$$\frac{\delta(\beta A/V)}{\delta f^{(l)}_{12,\ldots,l}} = -\rho^{l} y^{(l)}_{12,\ldots,l}(r_{12}, r_{23}, \ldots, r_{l-1,l}) \tag{13}$$

Substituting equation (12) into equation (13) and integrating twice with respect to r and τ, we obtain

$$\frac{\beta[A(\alpha) - (\alpha = 0)]}{V} = -\rho\left[\alpha - \int_0^{\alpha} \alpha \,\mathrm{d}\ln y^{(l)}_{12,\ldots,l}(\sigma_{12}, \ldots, \sigma_{l-1,l})\right] \tag{14}$$

For simplicity, the l-particle cavity correlation function for a polyion chain is linearly approximated by a product of all nearest-neighbor two-particle cavity correlation functions $y^{(\mathrm{eff})}_{p,p+1}$,

$$y^{(l)}_{12,\ldots,l}(\sigma_{12}, \ldots, \sigma_{l-1,l}) = (1-\alpha)^{l} \prod_{p=1}^{l-1} y^{(\mathrm{eff})}_{p,p+1}(\sigma_{p,p+1}) \tag{15}$$

Substituting equation (15) into equation (14), differentiating βA with respect to V, and considering that the monomers are tangent jointed, when $\alpha = 1$, the osmotic pressure due to the formation of polyion chains can be obtained,

$$\beta\Delta p^{\mathrm{poly}} = \beta p(\alpha = 1) - \beta p(\alpha = 0) = -\rho\left[l - 1 + \sum_{p=1}^{l-1} \frac{\partial \ln y^{(\mathrm{eff})}_{p,p+1}(\sigma_{p,p+1})}{\partial \rho_0}\right] \tag{16}$$

where $\rho_0 = \sum_{i=1}^{K} \rho_{i,0}$ is the summation of number density of all particles. Correspondingly, Helmholtz function is

$$\frac{\beta\Delta A^{\mathrm{poly}}}{V} = \frac{\beta[A^{r}(\alpha = 1) - A^{r}(\alpha = 0)]}{V} = -\rho \sum_{p=1}^{l-1} \ln y^{(\mathrm{eff})}_{p,p+1}(\sigma_{p,p+1}) \tag{17}$$

The reference fluid is a solution of charged hard sphere mixture, its thermodynamic properties are adopted from MSA of Blum [28], which are expressed by the contributions of hard sphere mixture and electrostatic interactions, respectively. For the former, the Mansoori–Carnahan–Starling–Leland's equation of state is used,

$$\beta p(\mathrm{hs}) = \frac{\zeta_0}{\Delta} + \frac{18\pi\zeta_1\zeta_2 + \pi^2\zeta_2^3}{36\Delta^2} + \frac{\pi^2\zeta_2^3}{18\Delta^3} \tag{18}$$

$$\frac{\beta A^{r}(\mathrm{hs})}{V} = \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln\Delta + \frac{\pi\zeta_1\zeta_2}{2\Delta} + \frac{\pi\zeta_2^3}{6\zeta_3\Delta^2} \tag{19}$$

For the latter, the electrostatic contribution, it is expressed as [28]

$$\beta p^{\mathrm{EX}}(\mathrm{MSA}) = -\frac{\Gamma^3}{3\pi} - \frac{\alpha_0^2 P_K^2}{8\Delta^2} \tag{20}$$

$$\frac{\beta A^{\mathrm{EX}}(\mathrm{MSA})}{V} = -\frac{\alpha_0^2}{4\pi} \sum_{i=1}^{K} \frac{\rho_{i,0} z_i}{1 + \sigma_i\Gamma}\left(z_i\Gamma + \frac{\pi\sigma_i P_K}{2\Delta}\right) + \frac{\Gamma^3}{3\pi} \tag{21}$$

where

$$\zeta_k = \sum_{i=1}^{K} \rho_{i,0}\sigma_i^k; \quad \Delta = 1 - \pi\zeta_3/6; \quad \beta = 1/kT; \tag{22}$$

$$\alpha_0^2 = \beta e^2/\varepsilon_0\varepsilon_r$$

$$P_K = \frac{\sum_{i=1}^{K} \frac{\rho_{i,0}\sigma_i z_i}{1+\sigma_i\Gamma}}{\left(1 + \frac{\pi}{2\Delta}\sum_{i=1}^{K} \frac{\rho_{i,0}\sigma_i^3}{1+\sigma_i\Gamma}\right)} \tag{23}$$

Γ is a scaling parameter calculated by equation (23) combining with the following equation,

$$4\Gamma^2 = \alpha_0^2 \sum_{i=1}^{K} \frac{\rho_{i,0}}{(1+\sigma_i\Gamma)^2}\left(z_i - \frac{\pi\sigma_i^2 P_K}{2\Delta}\right)^2 \tag{24}$$

The nearest-neighbor two-particle cavity correlation function at tangent can be obtained from the radial distribution function and the direct correlation function of charged hard sphere mixtures under HNC approximation,

$$\ln y_{ij}^{(2)}(\sigma_{ij}) = \frac{1}{\Delta} + \frac{\alpha_0^2 z_i z_j}{4\pi\sigma_{ij}} + \frac{\pi\sigma_i\sigma_j\zeta_2}{4\sigma_{ij}\Delta^2} - \frac{a_i a_j \Gamma^2}{\pi\sigma_{ij}\alpha_0^2} - 1 \tag{25}$$

The above model is similar to that for polyelectrolyte solutions, the latter will be resumed when the polyions are constructed by charges with the same sign.

4. Results and discussions

Before discussing the osmotic properties of polyampholytes, we first study the polyampholytes without counterions or small ions which are interested by theorists owing to the simple model. Figure 2 is a comparison between the predicted results by theoretical model and that by MD simulation. The abscissa $\rho^* = \sum_{i=1}^{K}\rho_{i,0}\sigma_i^3$ is the reduced number density. The alternating and diblock copolymer polyampholyte composed of monovalent negative and positive ions with diameter σ. The temperature T^* is set equal to 1.8. The chain numbers in the simulations are 32. From the figure, we can see that the deviations of osmotic coefficients (or osmotic pressures) of polyampholyte solution between theoretical results and simulated results are small in middle-concentration and large in high concentration. It should be worth noting that there is a difference between MD simulation and molecular thermodynamic model, in MD simulations the particles are soft-spheres while in the theoretical model the particles are hard spheres, and it will bring about a few deviations for the osmotic coefficients.

However, real polyampholyte aqueous solution exist counterions which are dissociated from the backbone of polyampholyte chains. In the following, we present osmotic coefficients of neutral and non-neutral polyampholyte solutions all with counterions simulated by MD method and calculated by the molecular thermodynamic model.

4.1 Neutral polyampholyte solutions

Neutral polyampholytes carry the same numbers of positive and negative charges, the net charge is zero. Figure 3 shows the osmotic coefficients of two polyampholyte solutions, one is an alternative copolymer and another is a diblock copolymer composed of monovalent negative and positive ions with diameter σ. In figure 4, the polyampholyte chains are alternative copolymer while the diameters of negative and positive ions are different, they are 1.5σ and σ, respectively as well as the ions are bivalent. From the two figures, we can see that the predicted results by the molecular thermodynamic model agree with those by MD simulations. A higher deviation is observed in the intermediate densities for the higher valent ions as shown in figure 4, which may result from the MSA employed for the reference fluid. Literature studies [29] indicate that the MSA is quite accurate for systems with low coupling constant ($e^2 z_+ z_- / \varepsilon_0\varepsilon_r\sigma k_B T$) or

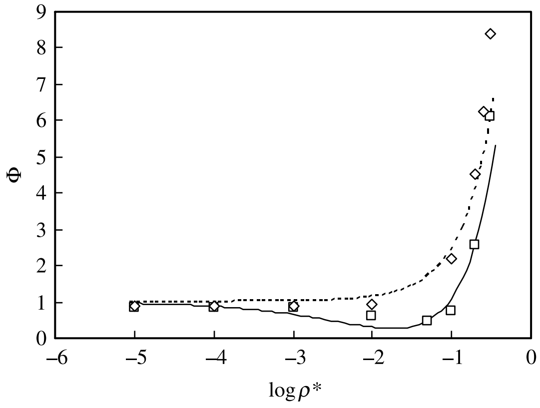

Figure 2. Osmotic coefficients of neutral polyampholyte solutions for alternating and diblock polyamplolytes composed of monovalent negative and positive ions with diameter σ, $T^* = 1.8$. Alternating polyampholyte: open diamonds (MD) and dashed line (theory). Diblock polyampholyte: open squares (MD) and solid line (theory).

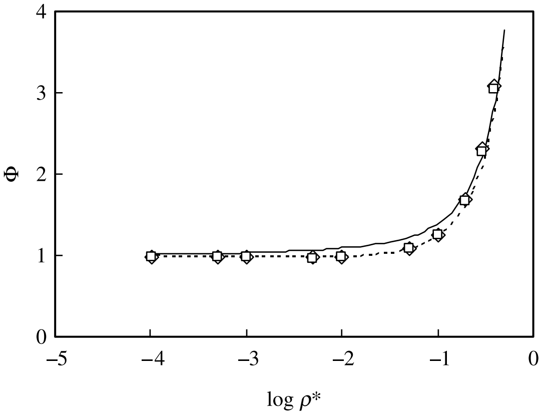

Figure 3. Osmotic coefficients of neutral polyampholyte solutions for alternating polyion and diblock polyion composed of monovalent negative and positive ions with diameter σ, $T^* = 1.2$. Alternating polyampholyte: open diamonds (MD) and solid line (theory). Diblock polyampholyte: open squares (MD) and dashed line (theory).

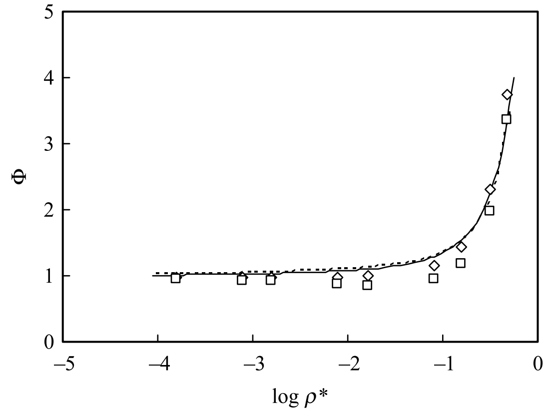

Figure 4. Osmotic coefficients of neutral alternating polyampholyte solutions at $T^* = 1.2$. Polyion composed of monovalent negative and positive ions with diameter 1.5σ and σ: open diamonds (MD) and solid line (theory); polyion composed of divalent negative and positive ions with diameter 1.5σ and σ: open squares (MD) and dashed line (theory).

higher densities, but deteriorates for systems with higher coupling constant (higher charge, lower temperature, or low dielectric constant) and lower densities.

For polyampholyte solutions, the configurations are affected by packing density. Figures 5 and 6 show the density dependence of the average square end-to-end distance and the asphericity ($\Delta = \sum_{i=1}^{3}(\lambda_i - \bar{\lambda})^2/6\bar{\lambda}^2$, where λ is the eigenvalue of the gyration tensor [30]), respectively. The results indicate that owing to the stronger electrostatic interaction in diblock polyampholyte chains, they occupy less volume and behave more spherical than that of alternative polyampholyte chains. As the number density increases, the screening of electrostatic effects enhances the more stretched chains. On the contrary, the density dependence for the alternative polyampholyte is not obvious, only when the density is high enough, the attraction effect is slightly enhanced.

4.2 Non-neutral polyampholytes

Now we study non-neutral diblock polyampholyte solutions; charges of the two blocks are different in sign and different in number. In figure 7, there are 10 negatively charged and six positively charged monovalent monomers, 12 negatively charged and four positively charged monovalent monomers and 14 negatively charged and two positively charged monovalent monomers, respectively, in the two blocks of the backbone. Diameters of all monomers and salt ions are σ. The reduced temperature is set equal to 1.2. From the figure, we can see that the predicted osmotic coefficients of all three different non-neutral polyampholyte solutions by the molecular thermodynamic model are the same. It is because the nearest-neighbor two-particle cavity correlation functions of $y_{++}(\sigma_{++})$ and $y_{--}(\sigma_{--})$ are not distinguished when the cations and anions in the chain are only different in their densities by MSA. The nearest-neighbor two-particle cavity correlation function in MSA is not concerned with the density of each species but with the total density of all species (see equation (25)), while the density of cations and anions in the chain are different in the non-neutral polyampholytes. In fact, the predicted osmotic coefficients

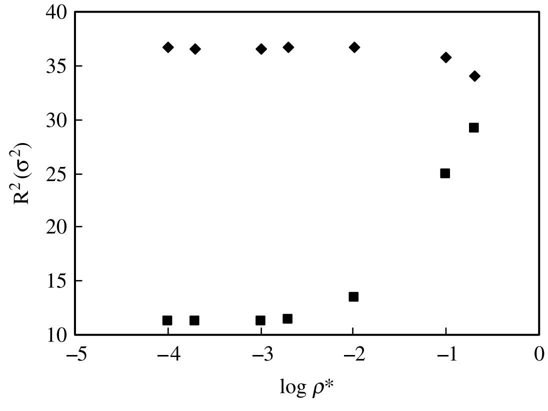

Figure 5. The Average square end-to-end distance of neutral polyampholytes. Squares: diblock polyampholyte; diamonds: alternating polyampholyte.

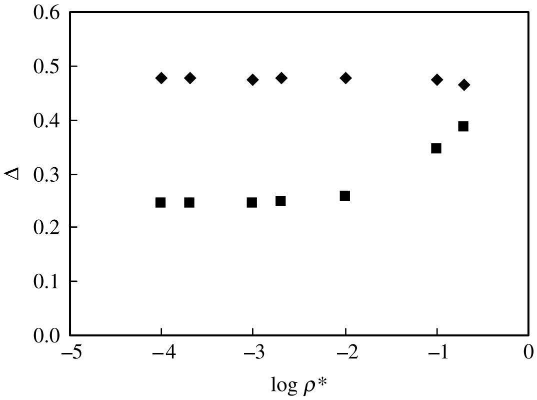

Figure 6. Asphericity of neutral polyampholytes. Squares: diblock polyampholyte; diamonds: alternating polyampholyte.

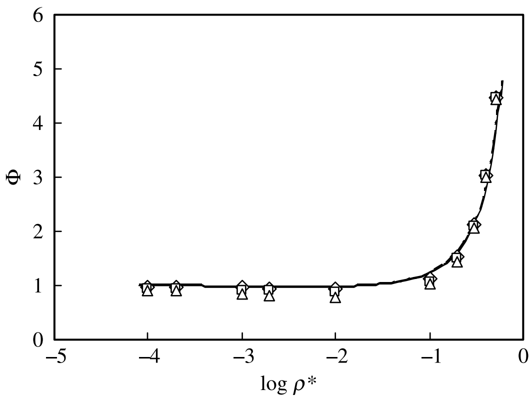

Figure 7. Osmotic coefficient of diblock polyampholyte solutions with polyion segment diameter 1σ and monovalent positive and negative counterions diameter 1σ at $T^* = 1.2$. Polyion with 10 monovalent negative and six monovalent positive ions: open diamonds (MD) and solid line (theory); polyion with 12 monovalent negative and four monovalent positive ions: open squares (MD) and dashed line (theory); Polyion with 14 monovalent negative and two monovalent positive ions: open triangles (MD) and dot dashed line (theory).

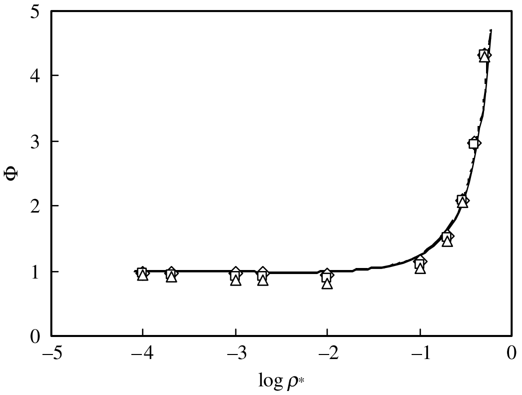

Figure 8. Osmotic coefficient of alternating polyampholyte solutions with polyion segment diameter 1σ and monovalent positive and negative counterions diameter 1σ at $T^* = 1.2$. Polyion with 10 monovalent negative and six monovalent positive ions: open diamonds (MD) and solid line (theory); polyion with 12 monovalent negative and four monovalent positive ions: open squares (MD) and dashed line (theory); polyion with 14 monovalent negative and two monovalent positive ions: open triangles (MD) and dot dashed line (theory).

agree well with the neutral diblock polymapholytes. For predicting the osmotic coefficients of the non-neutral polyampholytes the model should be improved in two aspects, the first is selecting better model of reference fluid than MSA, and the second is thinking over more correlations among the segments in the chain [20]. Figure 8 shows the osmotic coefficients of triblock polyampholyte solutions with polyion segment diameter 1σ and monovalent positive and negative counterions diameter 1σ at $T^* = 1.2$. Polyion is with two monovalent negative and 12 monovalent positive and two monovalent negative ions, polyion with four monovalent negative and eight monovalent positive and four monovalent negative ions, and polyion with six monovalent negative and four monovalent positive and six monovalent negative ions, respectively. The results of theory agree well with the neutral triblock polyampholyte.

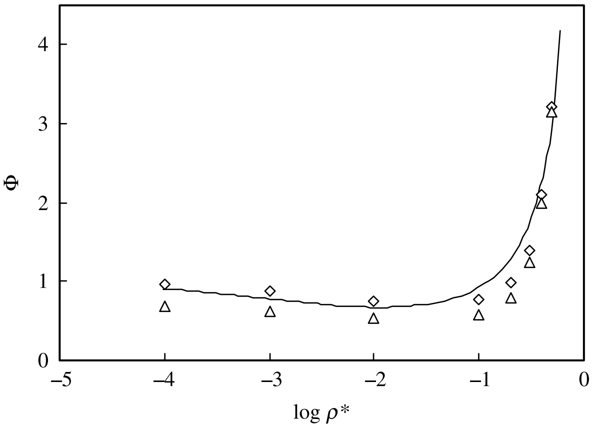

Figure 9. Osmotic coefficient of diblock polyampholyte solutions with polyion segment diameter 1σ and monovalent positive and negative counterions diameter 1σ at $T^* = 1.2$ and higher Bjerrum length ($l_B = 4.17$). Polyion with eight monovalent negative and eight monovalent positive ions: open diamonds (MD); polyion with 12 monovalent negative and four monovalent positive ions: open triangles (MD); solid line (theory).

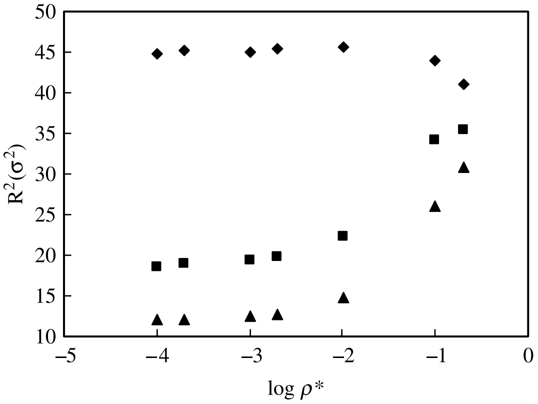

Figure 10. The Average square end-to-end distance of polyions for non-neutral diblock polyampholytes with different net charges. Diamonds: 12 net charges; squares: eight net charges; triangles: four net charges.

The systems mentioned above are weak coulomb coupling which are devoted to aqueous solutions. Figure 9 shows the osmotic coefficients of diblock at higher Bjerrum length ($l_B = 4.17$) which is corresponding to a strong coulomb coupling system. In the figure, the diblock of polyampholyte is eight negatively charged and eight positively charged monovalent monomers, 12 negatively charged and four positively charged monovalent monomers, respectively. Although the more deviations between Lennard–Jones potential and hard sphere potential at larger Bjerrum length with fixed temperature, the figure also show that the osmotic coefficients by theory agree well with the neutral polyampholytes.

Figures 10 and 11 show the density dependence of the average square end-to-end distance and the asphericity of polyions for non-neutral diblock polyampholytes with different net charges. Compared with figures 5 and 6 we can see that the more net charge, the behavior is closer to that of the alternating polyampholytes.

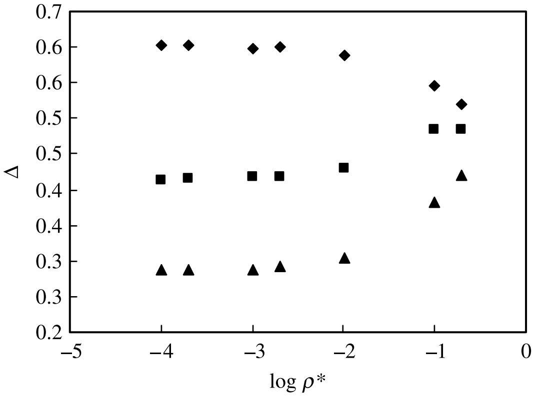

Figure 11. The asphericity of polyions for non-neutral diblock polyampholytes with different net charges. Diamonds: 12 net charges; squares: eight net charges; triangles: four net charges.

5. Conclusions

We have used MD method considering both the viscous force and the stochastic force to obtain the osmotic coefficients of polyampholyte solutions. We have also extended the chemical association theory of polyelectrolyte solutions to polyampholyte solutions to build a molecular thermodynamic model. Generally, the agreement between the predicted osmotic coefficients and the simulation results is satisfactory for neutral polyampholytes in weak or strong coulombic coupled systems indicating that the model developed in this work can be used for practical engineering purposes. However, in the case of higher valence of monomer ions and in the case of non-neutral polyampholytes, the density dependence by MD clearly shows a minimum. The model in this work does predict such a minimum, but only slightly that cannot be expressed obviously in the figures; the deviation is, therefore, a slightly higher. It is reasonable to suggest that maybe the deviation lies in the applicability of the MSA used in reference system, MSA is not completely suitable for ions with higher valence. However, other shortcomings in the model, for example, the correlations of none bond particles in the chain still need to be considered.

In order to further improve the prediction results of theoretical model for polyampholyte solutions, some factors should be considered. Firstly, according to the molecular thermodynamic model mentioned above, the thermodynamic properties of polyampholyte solution are only depended on the properties of the reference fluids, i.e. the thermodynamic and structural properties of charged hard sphere mixture. Especially, the cavity correlation functions of the reference fluid affects the behavior of the model seriously. However, the pair correlation functions from MSA is not accurate [29], using better pair correlation functions may improve the predicted results of theoretical model. Secondly, taking account the correlation between next-nearest-neighbor segments in polyion is an alternative approach [21]. Thirdly, the model does not deal with the screening of counterions and salt ions to polyions, which can be regarded as physical asscociation [20]. Considering screening may also improve accuracy of the molecular thermodynamic model.

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