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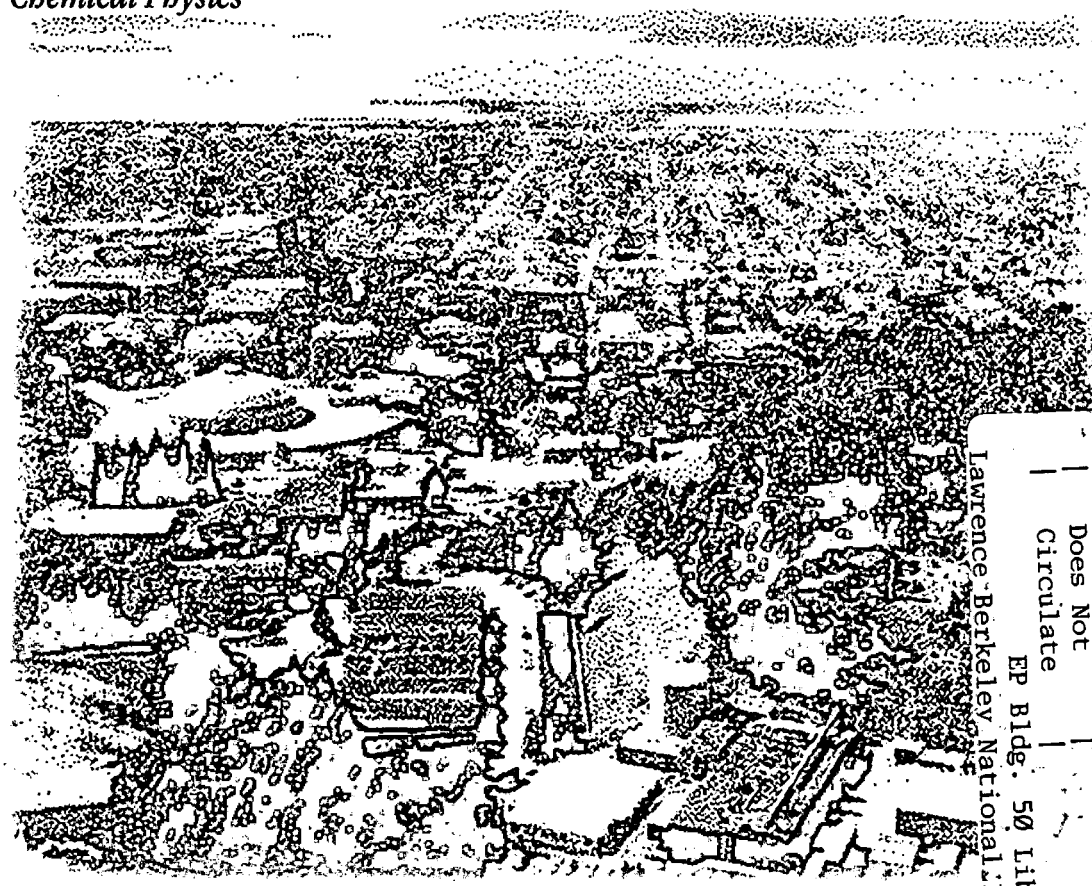

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A Molecular-Thermodynamic Model for Polyelectrolyte Solutions

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Polyelectrolyte solutions are modeled as freely tangent-jointed, charged hard-sphere chains and corresponding counterions in a continuous medium with permmitivity ε. By adopting the sticky-point model, the Helmholtz function for polyelectrolyte solutions is derived through the *r*-particle cavity-correlation function (CCF) for chains of sticky, charged hard spheres. The *r*-CCF is approximated by a product of effective nearest-neighbor two-particle CCFs; these are determined from the hypernetted-chain and mean-spherical closures (HNC/MSA) inside and outside the hard core, respectively, for the integral-equation theory for electrolytes. The colligative properties are given as explicit functions of a scaling parameter Γ that can be estimated by a simple iteration procedure. Osmotic pressures, osmotic coefficients and activity coefficients are calculated for model solutions with various chain lengths. They are in good agreement with molecular-simulation and experimental results.

1. Introduction

Natural and synthetic polyelectrolytes are distinguished by their high electostatic field and large molar mass of polyions [1-3]. It is widely recognized that the behavior of a

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polyelectrolyte in solution is very sensitive to the ionic environment. The electrostatic interactions often exert a dominant effect on a polyelectrolyte's thermodynamic properties.

Extensive efforts have been made to develop theories and models for these complex systems. Prevailing theories of polyelectrolyte solutions are mostly based on the cylindrical-cell model [4,5]; this model describes a polyelectrolyte solution as an ensemble of equal cylindrical cells with a uniformly charged rod-like polyion placed along the axis of each cell. Either the counterion-condensation formalism (CC), developed primarily by Manning [1,6,7], or the Poisson-Boltzmann approach (PB) [5,8] has been applied. However, Manning's oversimplified picture requires knowing *a priori* when the condensation occurs. Because Manning's results are independent of polyelectrolyte concentration, they are valid only at sufficiently low concentrations. PB theories provide a more detailed description of the small-ion distribution around the polyion. However, rod-like chains are not likely to reflect reality at experimentally interesting concentrations. The effect of chain connectivity on the small-ion distribution is also neglected. The error caused may be small only for highly charged polyelectrolytes in very dilute salt solutions [9]. Some revisions of PB have been made, e.g. the modified PB (MPB) by Outhwaite [10,11]. MPB theory embeds the classical Debye-Hückel mean electrostatic approach into the Bogoliubov-Born-Green-Kirkwood-Yvon integral equation; this procedure provides a mechanism to correct approximations in the PB theory. Alternatively, integral-equation theory, using the hypernetted chain (HNC) and the mean-spherical (MSA) closures inside and outside the hard core, respectively [12,13], and computer-simulation methods [14,15], have also been adopted. Because those more sophisticated methods neglect polyion-polyion interactions, they are rigorous only at infinite dilution.

Stretching of polyelectrolyte chains due to repulsion between backbone charges is not as intense as expected by most theories. The conformation of a polyion may not be strictly rod-like in many cases as discussed by Nagasawa et al [16]. Recently, using the MSA closure in the Wertheim-Ornstein-Zernike formalism, models have been developed by Kalyuzhnyi et al [17] and Blum et al [18] to study flexible linear polyelectrolytes.

However, no numerical results were given. In this work, we also adopt a flexible-chain model. Based on the sticky-point model of Cummings and Stell [19], the Helmholtz function for a polyelectrolyte solution is derived through the r-particle cavity-correlation function (CCF) for chains obtained from sticky charged hard spheres similar to those discussed by Zhou and Stell [20] and in our previous work [21]. The r-CCF is approximated by a product of effective nearest-neighbor two-particle CCFs. Blum's results [22-24] for electrolytes are used to determine those two-particle CCFs. Osmotic pressures, osmotic coefficients and activity coefficients are calculated and compared with simulation results.

2. Molecular-thermodynamic model

Polyelectrolyte solutions are modeled as freely tangent-jointed, charged hard-sphere chains with chain length r and corresponding counterions in a continuum whose permmitivity is ε, equal to that of the pure solvent. The monomer unit with size σ_m carries charge $Z_m e$. The corresponding number density is ρ_m. Charges of polyions are compensated by small ions (subscript k) whose charge and number density are Z_k and ρ_k, respectively. Electroneutrality requires that

$$\rho_m Z_m + \sum_k \rho_k Z_k = 0 \quad . \tag{1}$$

By adopting the sticky-point model of Cummings and Stell [19] for each nearest neighbor pair, the Mayer function for a group of r segments corresponding to a polyion can be expressed as

$$\begin{aligned} f_{12\cdots r}^{(r)} &= -1 + \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \left(\sigma_m \, \delta(r_{ij} - \sigma_m) \, \xi / 12 \right), & r_{ij} < \sigma_m \\ &= -1 + \exp\left(-\beta \, \varepsilon_{12\cdots r}^{(r)} \right), & r_{ij} > \sigma_m \end{aligned} \tag{2}$$

where ξ is a parameter measuring stickiness; $\varepsilon_{12\cdots r}^{(r)}$ is the attractive energy at distances beyond collision diameter σ_m. (In eq.(2), δ is a Kronecker delta.) The r-particle total correlation function $h_{12\cdots r}^{(r)}$ is related to the r-particle radial distribution function $g_{12\cdots r}^{(r)}$

through $h^{(r)}_{12\cdots r} = g^{(r)}_{12\cdots r} - 1$:

$$h^{(r)}_{12\cdots r} = -1 + \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \left(\sigma_m\, \delta(r_{ij} - \sigma_m)\, \lambda / 12\right), \qquad r_{ij} < \sigma_m \tag{3}$$

where λ is a distribution parameter related to sticky parameter ξ.

The degree of association α for the monomers is defined by

$$\alpha = r\rho_r / \rho_m = r(\rho_m)^{r-1} \int_{\sigma^-}^{\sigma^+} g^{(r)}_{12\cdots r}(r_{12}, r_{23}, \ldots r_{r-1,r})\, \mathrm{d}r_{12}\, \mathrm{d}r_{23} \ldots \mathrm{d}r_{r-1,r} / r! \tag{4}$$

where ρ_r is the density of chains.

To obtain the Helmholtz density A/V, we use its functional derivative with respect to the Mayer function for an r-particle group which is related to the r-particle CCF by

$$\frac{\partial(\beta A / V)}{\partial f^{(r)}_{12\cdots r}} = -\rho_m^r y^{(r)}_{12\cdots r}(r_{12}, r_{23}, \ldots, r_{r-1,r}) / r! \tag{5}$$

Integrating this equation yields [20,21]

$$\begin{aligned} \frac{\beta[A(\alpha) - A(\alpha = 0)]}{N_0} &= -c_1 \int y^{(r)}_{12\cdots r}(r_{12}, r_{23}, \ldots, r_{r-1,r})\, \mathrm{d}[\alpha / y^{(r)}_{12\cdots r}(r_{12}, r_{23}, \ldots, r_{r-1,r})] \\ &= -c_1 \left[\alpha - \int \alpha\, \mathrm{d}\ln y^{(r)}_{12\cdots r}(r_{12}, r_{23}, \ldots, r_{r-1,r})\right] \end{aligned} \tag{6}$$

$$c_1 = \frac{\rho_m}{r\zeta_0} \tag{7}$$

where N_0 and ζ_0 are the total number and total-number density of monomers prior to association including counterions. As usual, $\beta = 1/kT$.

The key to obtaining the Helmholtz function is provided by information on the r-particle CCF for an r-mer chain. In principle, the r-particle CCF could be determined by the inter-segment potential function (or the Mayer function) by integral-equation theory. However, at present this is not possible for polymers. Following our previous work [21], we propose to calculate the r-particle CCF as the product of two contributions: a chemical contribution $(1-\alpha)^r$ dependent on the degree of association, and a physical contribution expressed by the product of nearest-neighbor effective two-particle CCFs y^{ref}_{ij} $(j = i+1)$:

$$y_{12\cdots r}^{(r)}(r_{12}, r_{23}, \ldots r_{r-1,r}) = (1-\alpha)^r \prod_{\substack{i=1 \\ j=i+1}}^{r-1} y_{ij}^{\mathrm{ref}}(r_{ij}) \tag{8}$$

where superscript "ref" refers to the reference system without association. Using this approximation, we obtain the Helmholtz function,

$$\frac{\beta[A(\alpha) - A(\alpha=0)]}{N_0} = c_1[\alpha(r-1) + r\ln(1-\alpha)] \quad . \tag{9}$$

However, this equation is of no use when $\alpha = 1$. Therefore we propose an alternate procedure: we first calculate osmotic pressure Π and then obtain Helmholtz function A by integration.

$$\Pi = (\zeta_0)^2 \left(\frac{\partial(A/N_0)}{\partial(\zeta_0)} \right)_T \quad . \tag{10}$$

Considering that association takes place at tangent position, $r_{ij} = \sigma_m$, we have

$$\frac{\beta[\Pi(\alpha) - \Pi(\alpha=0)]}{\zeta_0} = -\alpha c_1 \left[r - 1 + \sum_{\substack{i=1 \\ j=i+1}}^{r-1} \frac{\partial \ln y_{ij}^{\mathrm{ref}}(\sigma_m)}{\partial \ln \zeta_0} \right] \tag{11}$$

where c_1 is defined by eq.(7). When $\alpha = 1$, the osmotic pressure is then expressed as

$$\beta\Pi = \beta\Pi(\alpha=0) - c_1\zeta_0 \left(r - 1 + \sum_{\substack{i=1 \\ j=i+1}}^{r-1} \frac{\partial \ln y_{ij}^{\mathrm{ref}}(\sigma_m)}{\partial \ln \zeta_0} \right) \quad . \tag{12}$$

Substitution of eq.(12) into eq.(10), followed by integration, yields the residual Helmholtz function A^r (relative to ideal gas at same temperature and density):

$$\frac{\beta A^r}{N} = c_2 \frac{\beta A^r(\alpha=0)}{N_0} - c_1 c_2 \sum_{\substack{i=1 \\ j=i+1}}^{r-1} \ln y_{ij}^{\mathrm{ref}}(\sigma_m) + [c_2 - 1 - c_1 c_2 (r-1)] \ln \zeta \tag{13}$$

$$c_2 = \frac{\zeta_0}{\zeta} \tag{14}$$

where N and ζ are the total number and the total-number density of polyions and counterions. Osmotic coefficient ϕ and activity coefficient γ can be expressed by

$$\phi = c_2 \left\{ \phi(\alpha = 0) - c_1 \left(r - 1 + \sum_{\substack{i=1 \\ j=i+1}}^{r-1} \frac{\partial \ln y_{ij}^{\mathrm{ref}}(\sigma_m)}{\partial \ln \zeta_0} \right) \right\} \tag{15}$$

and

$$\ln \gamma = \frac{\beta A^r}{N} + \frac{\beta \Pi}{\zeta} - 1 \tag{16}$$

3. The effective nearest-neighbor cavity correlation function

To obtain thermodynamic properties for polyelectrolyte solutions from eqs. (12), (15) and (16), we need the cavity correlation function and its derivative with respect to number density of the reference system, i.e, the charged hard-sphere mixture without association including counterions. For that system, the distribution functions can be calculated from Blum's MSA theory[22-24].

The direct correlation function at σ_{ij} for ions *i* and *j* is expressed by

$$c_{ij}(\sigma_{ij}^{+}) = -\frac{\alpha_0^2 Z_i Z_j}{4\pi\sigma_{ij}} \tag{17}$$

where $\sigma_{ij} = \sigma_i + \sigma_j$; α_0^2 is the Bjerrum length defined by

$$\alpha_0^2 = \frac{\beta e^2}{\varepsilon} \tag{18}$$

The pair correlation function at σ_{ij} is expressed by

$$g_{ij}(\sigma_{ij}^{+}) = \frac{1}{\nabla} + \frac{\pi\sigma_i\sigma_j\zeta_2}{4\nabla^2\sigma_{ij}} - \frac{D_n a_i a_j}{4\pi\sigma_{ij}} \tag{19}$$

$$\zeta_2 = \sum_l \rho_l \sigma_l^2 \tag{20}$$

where *l* counts all the monomers prior to association including counterions. Both D_n and a_i depend only on scaling parameter Γ (refer to eqs.(B-45,56,59) in ref.[24]). They are estimated by the following iterative procedure [23,24]:

$$4\Gamma^2 = \alpha_0^2 \sum_l \rho_l \left(\frac{1}{1+\Gamma\sigma_l} \right)^2 \left(z_l - \frac{\pi P_n \sigma_l^2}{2\nabla} \right)^2 \tag{21}$$

$$\nabla = 1 - \pi\zeta_3 / 6 \tag{22}$$

$$\zeta_3 = \sum_l \rho_l \sigma_l^3 \tag{23}$$

$$P_n = \frac{\sum_l \frac{\rho_l \sigma_l z_l}{1+\Gamma\sigma_l}}{1+\frac{\pi}{2\nabla}\sum_l \frac{\rho_l \sigma_l^3}{1+\Gamma\sigma_l}} \tag{24}$$

Because P_n is small, it can be omitted in eq.(21) without significant error. Eq.(21) is then rewritten,

$$4\Gamma^2 = \alpha_0^2 \sum_l \frac{\rho_l z_l^2}{(1+\Gamma\sigma_l)^2} \tag{25}$$

Compared with eq.(22), eq.(25) is much more convenient to yield Γ.

We adopt the hypernetted-chain closure (HNC) inside the core,

$$y_{ij}(r) = \exp[h_{ij}(r) - c_{ij}(r)] \tag{26}$$

Because of continuity, the effective nearest-neighbor cavity correlation function at tangent $y_{ij}^{\mathrm{ref}}(\sigma_m)$, as well as the corresponding derivative with respect to density, can be obtained from eqs.(17) and (19):

$$\begin{aligned}\frac{\partial \ln y_{ij}^{\mathrm{ref}}(\sigma_m)}{\partial \ln \zeta_0} &= \frac{\zeta_3}{\nabla^2} + \frac{\pi\sigma_m^2\zeta_2(2\zeta_3+\nabla)}{4\sigma_m\nabla^3} \\ &\quad - \frac{\zeta_0}{4\pi\sigma_m}\left(a_i a_j \frac{\partial D_n}{\partial \zeta_0} + D_n a_i \frac{\partial a_j}{\partial \zeta_0} + D_n a_j \frac{\partial a_i}{\partial \zeta_0}\right)\end{aligned} \tag{27}$$

$$\frac{\partial D_n}{\partial \zeta_0} = \frac{D_n}{\zeta_0} - 2\sum_l \frac{\rho_l \sigma_l z_l^2}{(1+\Gamma\sigma_l)^3} \cdot \frac{\partial \Gamma}{\partial \zeta_0} \tag{28}$$

$$\frac{\partial a_i}{\partial \zeta_0} = -\frac{\alpha_0^2 z_i (1+2\Gamma\sigma_i)}{2\Gamma^2(1+\Gamma\sigma_i)^2} \cdot \frac{\partial \Gamma}{\partial \zeta_0} \tag{29}$$

$$\frac{\partial \Gamma}{\partial \zeta_0} = \frac{1}{\zeta_0} \frac{\alpha_0^2 \sum_l \frac{\rho_l z_l^2}{(1+\Gamma\sigma_l)^2}}{8\Gamma + 2\alpha_0^2 \sum_l \frac{\rho_l \sigma_l z_l^2}{(1+\Gamma\sigma_l)^3}} \tag{30}$$

Pertinent thermodynamic properties can therefore be explicitly expressed as functions of scaling parameter Γ.

4. Results and discussion

We calculated the osmotic pressures, osmotic coefficients and activity coefficients for several polyelectrolyte solutions. Monomer unit size and charge are: $\sigma_m = 0.857\text{nm}$ and $Z_m = -1$. Charges of polyions are compensated by those of counterions with size $\sigma_c = 0.857\text{nm}$ and charge $Z_c = +1$. At present we consider only salt-free systems; number densities of monomer units and counterions are therefore the same: $\rho_m = \rho_c$. Stevens and Kremer [25] have published corresponding molecular-dynamics (MD) simulation results for such flexible linear polyelectrolyte solutions. Instead of a hard-sphere potential, in their work, the excluded volume was included via a Lennard-Jones potential. Nevertheless, our predictions coincide well with simulation results. This favorable comparison implies that the electrostatic potential plays a dominant role in polyelectrolyte systems.

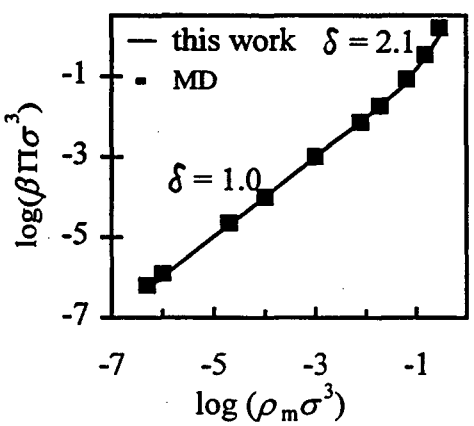

Fig.1. Density dependence of the osmotic pressure with $r = 16$.

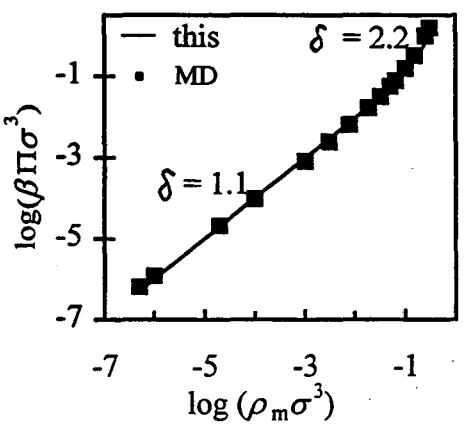

Fig.2. Density dependence of the osmotic pressure with $r = 32$.

In Fig.1, the osmotic pressure is plotted as a function of monomer density with chain length $r = 16$. Comparison with simulation results is also shown. Calculated results agree almost perfectly with simulations. Two scaling regimes are found where $\beta\Pi \sim \rho_m{}^{\delta}$. At lower density, δ=1.0, close to δ=9/8 experimentally found by Wang and Bloomfield [26] and predicted by Odijk's scaling theory [27]. At higher density, above a crossover value $\rho_m\sigma^3 = 0.08$, δ=2.1, close to δ=9/4 as experimentally observed [26]. The scaling

behavior in the higher density regime is also close to that of semidilute solutions of neutral polymers, implying that counterion condensation takes place at higher density. Because the charges of the polyion are screened, the polyions are nearly neutral polymers.

Our model is also valid at very low concentration, lower than the minimum concentration required for accurate experimental measurement. The low-density limit for Π is $\beta\Pi = \rho_m(1+1/r)$, as obtained by Stevens and Kremer [25].

For chain length r = 32, similar behavior is shown in Fig.2 but with δ=1.1 at low density and δ=2.2 at high density. The scaling relation for r = 64 is shown in Fig.3 where δ=1.0 at low and δ=2.2 at high density. All scaling parameters reported here agree well with those predicted from simulation studies and with experimental data. Agreement between calculated osmotic pressures and simulation results is again near perfect. Moreover, osmotic pressures depend only weakly on chain length. Crossover densities between two regimes also depend weakly on chain length. Our results indicate that polyions may adopt a stretched, rodlike chain conformation at low concentrations and an expanded, random chain conformation at high concentration; in the latter case, counterions condensation may occur.

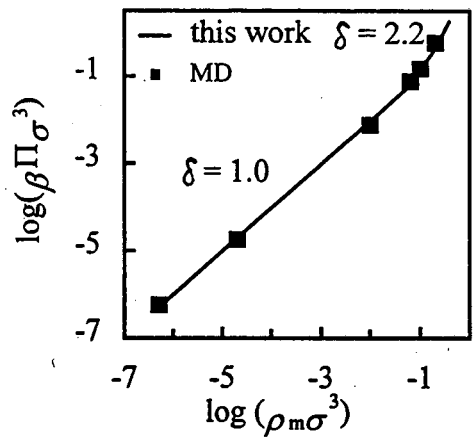

Fig.3. Density dependence of the osmotic pressure with r = 64.

Fig.4 and Fig.5 show osmotic coefficients and activity coefficients for chain length r=32. For the former, there is a little discrepancy between our results and those of Stevens and Kremer [25] in the low-density limit. The discrepancy may be due to statistical errors in MD simulations. No data are available for comparison of our activity coefficients. Our results show that the chain length has almost no effect on activity coefficients or osmotic pressures.

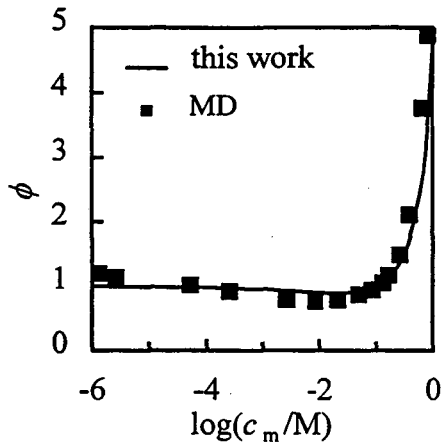

Fig.4. Concentration dependence of the osmotic coefficient with $r = 32$.

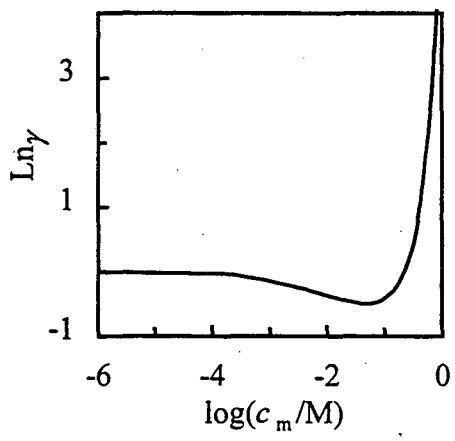

Fig.5. Concentration dependence of the activity coefficient with $r = 32$.

The results obtained here suggest that our model can predict thermodynamic properties for polyelectrolyte solutions. It can serve as a basis for the development of more realistic models; particular attention must be given to the effects of counterion size, charge and Bjerrum length. Studies toward that end are in progress.

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