

Influence of Aggregation and Dialysis on Conductivity of Salt-Free Polyelectrolyte Solution in the Dilute/Semidilute Region

King-Fu Lin,* Szu-Nang Yang, Hon-Long Cheng, and Yu-Hui Cheng

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

Received November 18, 1998; Revised Manuscript Received May 4, 1999

ABSTRACT: The conductivity of sodium poly(styrenesulfonate) solution was found to increase during dialysis against water as indicated by the in-situ conductivity measurements at a concentration of $c = 0.1$ g/L, which is in the dilute/semidilute region. To interpret this unexpected phenomenon, the domains of polyion chains and their aggregates are assumed to have a uniformly charged density. Although the aggregation resulted from the higher attractive forces rather than the repulsion between the polyion chains, their size was determined by the counterbalance of ionic osmotic forces due to the fact that the interior of aggregated domains has more counterions than the exterior. When the polyelectrolyte solution was dialyzed against water, extra osmotic forces acted on the solution due to Donnan's effects. On the basis of the mean field theory and above arguments, the increase of conductivity during dialysis was interpreted in terms of the aggregation of polyions in the aqueous solution.

Introduction

The aggregation of polyelectrolyte chains in the aqueous solutions has raised great research interest over the past two decades. In the presence of a high concentration of low molecular weight salt that screens off charges from polyelectrolytes, the polyions may be homogeneously dispersed. Odijk¹ has pointed out that the theoretical predication on the solution behavior of polyelectrolytes with added salt was straightforward, whereas no satisfactory theory in the absence of salt was available. The polyelectrolyte solutions with no or low added salt have been often regarded as a heterogeneous solution in which the polyions formed a multichain cluster (or domain).^{2–11} For example, Ise et al.² observed a single broad peak in the small-angle X-ray scattering of polyelectrolyte dilute solution and suggested the presence of quasi-lattice-like ordering domains. In the dynamic light scattering of polyelectrolyte solutions with no or low added salt, a double-exponential correlation function interpreted as consisting of fast and slow modes was frequently reported.^{4–11} The fast mode was interpreted as a coupled diffusion of polyions and counterions. The slow mode was interpreted as the diffusion of multichain domains and regarded as evidence of the existence of polyions' aggregation.¹⁰ It was also demonstrated that the slow mode appeared along with a slight increase of apparent equivalent conductivity of poly(L-lysine-HBr) when the external NaBr salt concentration is decreased below a certain critical value.¹²

The conformation of polyelectrolyte chains in the aqueous solution is not yet clear. Theoretical efforts on interpretation of polyion expansion focused on two models, i.e., the chain model and spherical model.^{13,14} The first chain model was made by Kuhn et al.¹⁵ in 1948. They assumed that in dilute solutions the counterions escape from the polyion domain so that they do not influence the mutual repulsion of the fixed charges carried by polyions. This simplified chain model leads to a rod limit of polyions in the extremely dilute solution. The model has been shown to be oversimplified because

a significant fraction of counterions remained in the polyion domain.¹⁴ Odijk et al.^{1,16} had modified the chain model by describing the expansion of polyelectrolytes according to the wormlike chain model,¹⁷ counterion condensation theory,¹⁸ electrostatic persistence length,¹⁹ and polymer scaling law.²⁰ However, the model could only apply to the semidilute region of polyelectrolyte solution with added salt. On the other hand, the spherical model was first proposed by Hermans and Overbeek,²¹ who assumed that the polyelectrolyte chains formed as a sphere with a uniformly charged density in aqueous solution with added salt. The expansion coefficient of polyelectrolyte chains was calculated accordingly by using the Poisson–Boltzmann equation under high salt concentration. Flory^{22,23} also treated the swelling of polyion in the presence of salt as a uniformly charged sphere. He proposed a Donnan assumption that the major driving forces of the swelling process was the osmotic forces, which are mainly due to an excess of mobile ions in the interior of the polyion domain and partly (but negligibly) due to the mixing of solvent and polymer segments. However, the spherical model is unrealistic since the polyion chains become increasingly asymmetric as they expand. Nevertheless, in the absence of salt, due to the heterogeneous nature of polyelectrolyte solution, no existing theory so far is satisfactory to interpret its solution properties.

Conductometry is an important tool to investigate the solution properties of polyelectrolytes. In this study, when the sodium poly(styrenesulfonate) (NaPSS) aqueous solution at a concentration of 0.1 g/L was dialyzed against water, the conductivity was found to increase with time. The increase of conductivity during dialysis of polyelectrolyte solution was never reported in the literature before. So, the experiment was repeated several times and came out with a consistent result. To interpret this phenomenon, we have assumed that the polyions may aggregate and form a uniformly charged domain. Thus, on the basis of the mean field theory, the increase of conductivity during dialysis was interpreted satisfactorily.

Experimental Section

Sodium poly(styrenesulfonate) purchased from Aldrich has a number-average molecular weight of 226 000 and a M_w/M_n ratio of 2.57, measured by gel permeation chromatography (Testhigh Series III RI detector with $H_2O/CH_3OH/NaNO_3/NaH_2PO_4$ buffer solution as a mobile phase). The calibration curve was obtained from the monodispersed poly(ethylene oxide) standard sample. The purification of NaPSS followed the procedure provided by ref 11 with some modifications.

In general, 1 g of NaPSS was dissolved in 0.2 M HCl (250 cm^3). The solution was then dialyzed in a Spectra/Pro regenerated cellulose membrane tube (molecular weight cutoff at 3500) against water (ultrapure, 18.3 M Ω), which was purified by the Barnstead Easypure RF system. The dialysis tube was cleaned by heating in a detergent solution, followed by extensive rinsing with ultrapure water. The solution was dialyzed until the conductivity of the repeatedly refreshed water surrounding the dialysis tube closed to 1 $\mu S/cm$. Then it was converted to the NaPSS solution by potentiometric titration with 0.1 M NaOH and dialyzed again to remove the excess NaOH. The solution was then freeze-dried to a solid product, which retained up to 10 wt % H_2O as measured by thermogravimetric analyzer (Du Pont model 9900-954 TGA).

To prepare the 0.1 g/L NaPSS aqueous solution samples for the in-situ conductivity measurements during dialysis, the freeze-dried NaPSS sample with corrected weight (subtracting the water content) was dissolved in the ultrapure water. For comparison, a 0.1 g/L unpurified NaPSS aqueous solution was also prepared. Two batches for dialysis of unpurified and purified NaPSS individually were prepared as follows: 100 mL of NaPSS solution was loaded into a cleaned dialysis tube, which was then immersed in a beaker containing 1.5 L of ultrapure water. During the dialysis, the beakers were thermostated at 30 $^{\circ}C$ with a deviation of 0.01 $^{\circ}C$. One of the beakers with purified NaPSS sample was performed conductivity measurement under a nitrogen atmosphere by using a conductivity cell, with platinized electrodes and a cell constant of 3.64 cm^{-1} , immersed inside the dialysis tube. The other beaker with unpurified sample was performed conductivity measurement in open air. The signal was recorded on a Radiometer Copenhagen CDC-230 conductivity meter, and the data were automatically stored by the personal computer during dialysis.

The purified NaPSS was also used to measure the conductivity at various concentrations. A concentration of 0.8 g/L, the highest concentration in this study, was prepared first. The other concentrations were prepared by the successive dilution with ultrapure water. The concentrations of NaPSS after prepared were rechecked by the spectrophotometric method at a wavelength of 261.5 nm.¹¹ The conductivity measurements were conducted in a beaker thermostated at 30 $^{\circ}C$ with a deviation of 0.01 $^{\circ}C$.

Results

Figure 1 shows the specific conductivity of 0.1 g/L unpurified NaPSS solution as a function of the dialysis time. In the beginning, the conductivity decreased from 33 to 29 $\mu S/cm$ rapidly and then turned to increase. After 50 h, the increasing rate was higher, and the conductivity versus time follows the S-pattern until 275 h and then stayed at 38.1 $\mu S/cm$. The increase ratio by dialysis from the lowest to highest conductivity was 31.4%. Because the increased conductivity by dialysis was an unexpected result, the experiment was repeated several times, and the results were quite consistent. To ensure that the increase of conductivity was not caused by the condensing CO_2 and impurities, the next experiment was conducted in a nitrogen atmosphere with the purified NaPSS.

Figure 2 shows the specific conductivity of 0.1 g/L purified NaPSS solution versus the dialysis time. In the

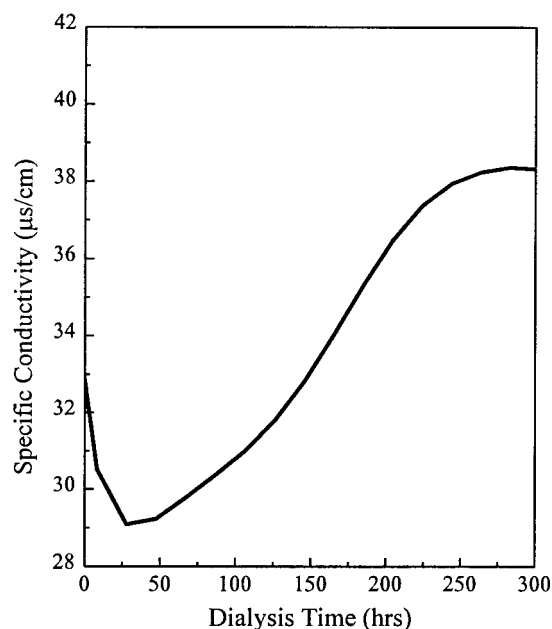


Figure 1. Specific conductivity of 0.1 g/L unpurified NaPSS aqueous solution as a function of the dialysis time at 30 $^{\circ}C$.

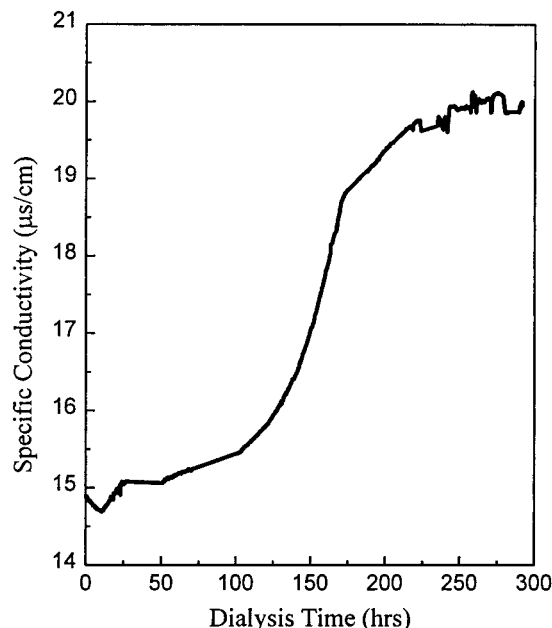


Figure 2. Specific conductivity of 0.1 g/L purified NaPSS aqueous solution as a function of the dialysis time at 30 $^{\circ}C$.

initial stage, the conductivity was decreased slightly from 14.9 to 14.7 $\mu S/cm$ but picked up to 15.1 $\mu S/cm$ before 25 h. In comparison with the unpurified one, the purification process has decreased the conductivity from 33 $\mu S/cm$ ($\Lambda = 68 S cm^2/monomol$) to 14.9 $\mu S/cm$ (30.7 $S cm^2/monomol$), which was considered to be due to the removal of low molecular weight species of NaPSS and impurities. Moreover, the initial decrease of conductivity for purified NaPSS resulted from the diffusion of water into the solution across the dialysis tube, because the purified NaPSS had the molecular weight too high to diffuse out in a short time. After dialysis for 25 h, the conductivity was increased from 15.1 to about 20 $\mu S/cm$. Similar to the unpurified NaPSS, the increase of conductivity followed an S-pattern, and the total processing time to reach the maximum conductivity was 275 h. The increase ratio of specific conductivity by

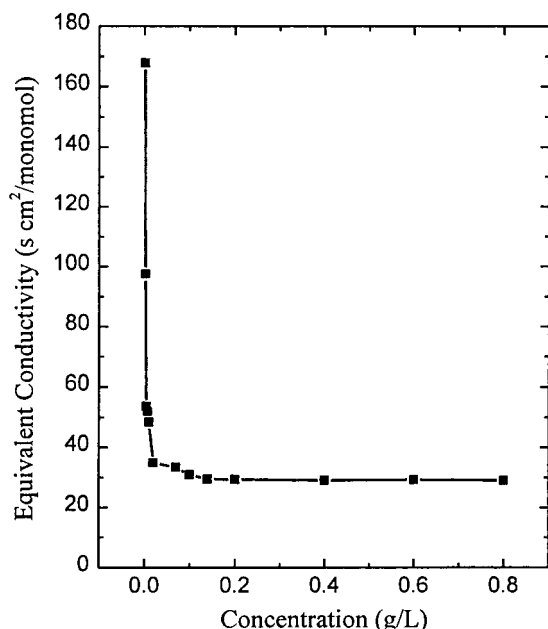


Figure 3. Equivalent conductivity of purified NaPSS aqueous solution as a function of concentration at 30 °C.

dialysis is 36%, which was apparently caused by the osmotic pressure induced by dialysis.

Figure 3 shows the equivalent conductivity of purified NaPSS as a function of concentration at 30 °C. It may be divided into three regions. At $c > 0.14$ g/L, the equivalent conductivity barely changed. In the region 0.14 g/L $> c > 0.02$ g/L, the equivalent conductivity increased with decreasing concentration at a slope of ~ -45.7 (S cm²/monomol) (L/g). At $c < 0.02$ g/L, the equivalent conductivity was abruptly increased at a slope of ~ -6990 (S cm²/monomol) (L/g).

Discussion

According to de Gennes et al.,²⁴ the onset of concentration, c_G^* , that the fully stretched chain cannot orient freely any more, may be defined by

$$c_G^* \cong \frac{M}{N_A l^3} \quad (1)$$

where M is molecular weight of the polyelectrolyte, N_A is the Avogadro number, and l is the contour length of polyions. For NaPSS, l (Å) may be estimated by the following equation¹⁸

$$l \cong \frac{2.46M}{M_m} \quad (2)$$

where M and M_m are molecular weights of the polyelectrolyte and of the monomer unit, respectively. From eqs 1 and 2, c_G^* of NaPSS in our system was estimated as 0.019 g/L. On the other hand, Odijk¹ has defined a dilute/semidilute region in $c^* > c > c_G^*$, where c^* may be estimated by the following equation

$$c^* \cong \frac{M_m}{16\pi N_A Q b l} \quad (3)$$

where $Q = e^2/\epsilon RT$ is the Bjerrum length (e is the electronic charge and ϵ is the dielectric constant of water) and b is the charge spacing of the polyion chain.

For water at 30 °C, Q is 7.02 Å ($\epsilon = 78.5$). For NaPSS with a degree of sulfonation $\alpha = 1$, b is 2.46 Å. Thus, from eq 3, we obtain $c^* = 0.147$ g/L. By referring to Figure 3, the equivalent conductivity of the NaPSS solution was increased with decreasing concentration abruptly for $c < c_G^*$, the regime of which the polyions have negligible interaction with each other.¹ For $c^* > c > c_G^*$ where the polyions remain rigid and interact strongly, the equivalent conductivity was decreased with the concentration at a moderate slope. For $c > c^*$, the equivalent conductivity was almost constant. Accordingly, the concentration of 0.1 g/L at which the dialysis was conducted in this study is in the dilute/semidilute region.

Uniformly Charged Domains. To interpret the conductivity data, it is convenient for us to describe the swelling polyions and their aggregates as a uniformly charged domain and an undrained particle. Some of the dissociated counterions were trapped inside the domains and screened by the polyions. It is rationale to assume that those counterions bound inside the domains have no contribution to the conductivity. Only those outside the domains have a chance to move out and contribute to the conductance.

In coagulation, the free energy of mixing between polyions and water, ΔG_m , is larger than zero. To simplify the case, the effect of counterions on ΔG_m was not included first. Owing to the Donnan-type equilibrium, ΔG_m will be counterbalanced by the free energy difference, ΔG_i , due to the difference in counterion concentration in and out the aggregated domains. That is, $\Delta G_m + \Delta G_i = 0$. Therefore,

$$\left(\frac{\partial \Delta G_m}{\partial n_1} \right)_{n_2, T, P} + \left(\frac{\partial \Delta G_i}{\partial n_1} \right)_{n_2, T, P} = 0 \quad (4)$$

or

$$(\Delta \mu_1)_m = (\mu_1^{\text{out}})_i - (\mu_1^{\text{in}})_i \quad (5)$$

where $(\Delta \mu_1)_m$ is the chemical potential of water due to the mixing and $(\mu_1^{\text{out}})_i - (\mu_1^{\text{in}})_i$ is the chemical potential difference of water resulting from the difference in counterion concentration in and out the aggregated domains. The free energy change of mixing between polyions and water in local-scale coagulation may be expressed by $\Delta G_m = \Delta H_m - T\Delta S_m$, with

$$\Delta S_m = -R \left(n_1 \ln \phi_1 + \frac{n_2}{m} \ln \phi_2 \right) \quad (6)$$

and

$$\Delta H_m = RT\chi_1 n_1 \phi_2 \quad (7)$$

where n_1 and n_2 are the number of moles of water and polyions in the solution, ϕ_1 and ϕ_2 are the volume fractions of the water and polyions, m is the averaged number of polyions in an aggregated domain, and χ_1 is the interaction parameter expressed as

$$\chi_1 = \frac{z\Delta\omega_{12}V_1}{RTV_s} \quad (8)$$

where z is the number of contacts per water molecule, V_1 and V_s are the molar volumes of water and segments of polyions, and $\Delta\omega_{12}$ is the change in energy of

formation of the unlike contact pair expressed as

$$\Delta\omega_{12} = \omega_{12} - \frac{1}{2}(\omega_{11} + \omega_{22}) \quad (9)$$

where ω_{12} , ω_{11} , and ω_{22} are the energy of bond formation for those respective pair contacts. Because the solution forms aggregated domains, the interaction energy ω_{22} between polymer segments must be substantially high. Some researchers have suggested that the hydrophobic backbone of polyelectrolytes might be responsible for the aggregation.^{25–28} However, it has been questioned that, in the case of strongly charged polyelectrolytes, the effect of the poor solvation of a chain backbone should be fully overcompensated by the strong solvation of numerous charged groups along the chain.²⁹ A “pure electrostatic interaction” mechanism of domain formation was also suggested as often indicated that the intermediary of oppositely charged counterions is responsible for the attractive interaction between polyions in aggregated domains.^{2,5,6,9} We believed that both mechanisms contribute to ω_{22} so that it may be divided into two components, $\omega_{22,\text{Wan der Waal}}$ and $\omega_{22,\text{electrostatic}}$. Thus, the chemical potential of water due to mixing of polyions and water in small-scale coagulations can be derived as follows,

$$(\Delta\mu_1)_m = \frac{\partial\Delta G_m}{\partial n_1} = RT \left[\left(\chi_1 - \frac{1}{2} \right) \phi_2^2 - \frac{V_1}{mxV_s} \phi_2 \right] \quad (10)$$

and

$$\chi_1 > \frac{1}{2} + \frac{V_1}{mxV_s\phi_2} \quad (11)$$

where x is the number of segments in a polymer chain.

On the other hand, to estimate the $(\mu_1^{\text{out}})_i - (\mu_1^{\text{in}})_i$, the following conditions may be assumed: (1) the molar volume of the water is equal to that of the counterions (Na^+), and (2) the osmotic coefficient, ζ , may be expressed by³⁰

$$\zeta = (2\xi)^{-1}, \quad \xi = Q/b = e^2/\epsilon kTb > 1 \quad (12)$$

and

$$\zeta = 1 - \frac{\xi}{2}, \quad \xi < 1 \quad (13)$$

where ξ is the charge density parameter and Q is the Bjerrum length. If f is the ratio of counterions that diffused out of the aggregated domains compared to the total dissociated counterions, then

$$(\mu_1^{\text{out}})_i - (\mu_1^{\text{in}})_i \cong RT\zeta(\phi_c^{\text{in}} - \phi_c^{\text{out}}) \quad (14)$$

where ϕ_c^{in} is the volume fraction of counterions inside the domains, expressed as

$$\begin{aligned} \phi_c^{\text{in}} &= \frac{mx\alpha(1-f)}{(n_1m/n_2) + (mxV_1/V_s) + mx\alpha(1-f)} \\ &\cong \frac{n_2x\alpha(1-f)}{n_1} \end{aligned} \quad (15)$$

if $n_1 \gg n_2xV_1/V_s$ and ϕ_c^{out} is the volume fraction of

counterions outside the domains, expressed as

$$\phi_c^{\text{out}} \cong \frac{n_2x\alpha f}{n_1} \quad (16)$$

where α is the degree of sulfonation in NaPSS. By inserting eqs 10, 14, 15, and 16 into eq 5, f may be expressed as

$$f = \frac{1}{2} - \frac{1}{2\alpha\zeta} \left[\left(\chi_1 - \frac{1}{2} \right) \phi_2 - \frac{V_1}{mxV_s} \right] \quad (17)$$

Thus, less than half of the dissociated counterions diffused out of the polyion-aggregated domains. A very recent paper by Schmitz³¹ has also predicted that the counterion concentration within a cluster is greater than the external concentration according to the juxtaposition of potential fields for multibody interaction systems. From eq 17, f is increased with the osmotic coefficient ζ and the degree of sulfonation α . Manning³⁰ pointed out that ζ is the fraction of counterions that is free and does not interact with the polyion including the Debye–Huckel interactions. According to his ref 31, $\zeta = 0.175$ ($\xi = 2.85$) may be obtained for the salt-free NaPSS ($\alpha \sim 1$) aqueous solution at 30 °C. Besides, f decreased with increasing χ_1 (or ω_{22}), ϕ_2 , m , and x .

The equivalent conductivity of polyelectrolyte solution, Λ ($\text{S cm}^2/\text{monomol}$), may be expressed as

$$\lambda \cong \mathcal{J}(fu_0 + u_{\text{aggregate}}) \quad (18)$$

where \mathcal{J} is a faraday of electricity, u_0 is the mobility of counterions which is the same as in solutions of simple electrolytes, and $u_{\text{aggregate}}$ is the average mobility of segments in polyion aggregates. If the coagulated domains of polyions were treated as a spherical particle carrying $q = mx\alpha f e$ negative charges and only electrophoretic mobility was considered here, $u_{\text{aggregate}}$ may be derived by balancing the electric force (qE) with the viscous force ($6\pi\eta Rv$):³²

$$qE = 300(6\pi\eta Rv) \quad (19)$$

$$u_{\text{aggregate}} = \frac{v}{mx e E} = \frac{1}{mx e} \frac{q}{1800\pi\eta R} = \frac{\alpha f}{1800\pi\eta R} \quad (20)$$

where η is the viscosity of water and R is the radius of domains. Equation 20 has many different forms depending on drainage of the particle³³ and the thickness of electrical double layers in the particle surface.³² Since we have assumed that the particles are an undrained sphere and $\kappa R \ll 1$ (κ is the reciprocal Debye screening length) can be applied to the salt-free polyelectrolyte solution (low electric charge density in solution) in the dilute/sedilute region, eq 20 may be applied to our system. Thus, by inserting eqs 17 and 20 into eq 18, Λ may be expressed by

$$\begin{aligned} \Lambda &= \mathcal{J} \left(u_0 + \frac{\alpha}{1800\pi\eta R} \right) \\ &= \left(\mathcal{J} u_0 + \frac{\mathcal{J}\alpha}{1800\pi\eta R} \right) \left\{ \frac{1}{2} - \frac{1}{2\alpha\zeta} \left[\left(\chi_1 - \frac{1}{2} \right) \phi_2 - \frac{V_1}{mxV_s} \right] \right\} \end{aligned} \quad (21)$$

Equation 21 indicates that the equivalent conductivity is decreased with the concentration and molecular weight of polyelectrolytes, the trend of which is consis-

tent with the experimental data reported by Wandrey³⁴ for the NaPSS aqueous solution in the dilute/semidilute region. By referring to Figure 3, the slope that the equivalent conductivity decreased with concentration may be expressed by

$$\text{slope} = -\frac{1}{2\rho\alpha\zeta}\left(\chi_1 - \frac{1}{2}\right)\left(u_0 + \frac{\alpha}{1800\pi\eta R}\right) = -45.7 \text{ (S cm}^2\text{/monomol) (L/g)} \quad (22)$$

where ρ is the mass density of NaPSS. The equivalent conductivity of sodium ion at 30 °C is 55.6 (S cm²/mol).³⁵ If $\rho \sim 1$ (the mass density of NaPSS, g/cm³) and $\alpha \sim 1$ are assumed, we obtained $f \sim 0.435$, $u_{\text{aggregation}} \sim 0.117u_0$, and $\chi_1 \sim 227$ by inserting $\phi = 0.0001$ and $\Lambda = 30.7$ (S cm²/monomol) into eqs 21 and 22. Apparently, $\omega_{22,\text{electrostatic}}$ should be responsible for the high value of χ_1 . $\omega_{22,\text{Wan der Waal}}$ contributed little to χ_1 . The early work on the phase separation of polyelectrolyte solutions by Michaeli et al.³⁶ also suggested that the electrical interactions only may suffice to bring about phase separation. On the other hand, eq 21 also suggests that the equivalent conductivity be decreased with the domain size and the number of polyions in an aggregated domain.

The foregoing derivation has eliminated the effects of counterions on ΔG_m , although their contributions to ΔG_m may be included in the high value of χ_1 . To consider the dissociated counterions as the third component that is assumed to be well dispersed in the aqueous solution, eq 10 may be modified as

$$\frac{\partial \Delta G_m}{\partial n_1} = KT \left[\ln \phi_1 + \left(1 - \frac{V_1}{mxV_s}\right) \phi_2 + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \frac{\chi_{23}\phi_2\phi_3 V_1}{xV_s} \right] \quad (23)$$

where χ_{ij} is pair interaction parameters corresponding to χ_1 in eq 8. Thus,

$$f \cong \frac{1}{2} - \frac{1}{2\zeta} \left[\frac{\ln \phi_1}{\phi_3} + \left(1 - \frac{V_1}{mxV_s}\right) \frac{\phi_2}{\phi_3} + (\chi_{12}\phi_2 + \chi_{13}\phi_3) \frac{\phi_2 + \phi_3}{\phi_3} - \frac{\chi_{23}\phi_2 V_1}{xV_s} \right] \quad (24)$$

As a result, the conductivity may be modified as

$$\Lambda = \left(u_0 + \frac{\alpha}{1800\pi\eta R} \right) \left\{ \frac{1}{2} - \frac{1}{2\zeta} \left[\frac{\ln \phi_1}{\phi_3} + \left(1 - \frac{V_1}{mxV_s}\right) \frac{\phi_2}{\phi_3} + (\chi_{12}\phi_2 + \chi_{13}\phi_3) \frac{\phi_2 + \phi_3}{\phi_3} - \frac{\chi_{23}\phi_2 V_1}{xV_s} \right] \right\} \quad (25)$$

The trends that f and Λ decreased with m but increased with α and ζ are similar to those indicated by eqs 17 and 21. Besides, f is also less than one-half.

Effect of Dialysis on Conductivity and Aggregation. When the polyelectrolyte solution is dialyzed against water, a chemical potential difference of water, $(\mu_1^w)_d - (\mu_1^s)_d$, across the membrane will be produced, resulting from the difference of number of polyion domains and concentration of unbound counterions between solution and water side of the membrane. Since the molecular weight of polyions was much higher than the cutoff molecular weight, few polyions with their

counterions diffused across the membrane to the water side. Thus, we assumed that their concentration in the water side can be neglected so that $(\mu_1^w)_d = \mu_1^0$. However, water can diffuse across the membrane to dilute the solution. As a result, n_1' , the moles of water molecules in the solution after dialysis, will be larger than n_1 and ϕ_2' (the volume fraction of polyions after dialysis) will be slightly less than ϕ_2 . Thus, $(\mu_1^w)_d - (\mu_1^s)_d$ may be expressed by

$$(\mu_1^w)_d - (\mu_1^s)_d = \mu_1^0 - (\mu_1^s)_d = -(\Delta\mu_1^s)_d = RT \left(\frac{n_2}{m'n_1'} + \frac{n_2\alpha\zeta f}{n_1'} \right) \quad (26)$$

Therefore, the osmotic pressure π_1 that applied to the solution will be

$$\pi_1 = -(\Delta\mu_1^s)_d / V_1 \quad (27)$$

Since the total pressure on the solution has been increased by an osmotic pressure, the chemical potential of water in the system will be changed to

$$\left(\frac{\partial \Delta G_m}{\partial n_1'} \right)_{n_2, P+\pi_1} + \left(\frac{\partial \Delta G_i}{\partial n_1'} \right)_{n_2, P+\pi_1} = \int_P^{P+\pi_1} V_1 dP = V_1 \pi_1 \quad (28)$$

i.e.,

$$(\Delta\mu_1^s)_m + (\mu_1^{\text{in}})_i - (\mu_1^{\text{out}})_i + (\Delta\mu_1^s)_d = 0 \quad (29)$$

By inserting eqs 14, 15, 16, 23, and 26 into eq 29, we obtain

$$\left[\ln \phi_1' + \left(1 - \frac{V_1}{m'xV_s}\right) \phi_2' + (\chi_{12}\phi_2' + \chi_{13}\phi_3') \times (\phi_2' + \phi_3') - \frac{\chi_{23}\phi_2'\phi_3' V_1}{xV_s} \right] = \frac{n_2\alpha\zeta(1-2f')}{n_1'} + \left(\frac{n_2}{m'n_1'} + \frac{n_2\alpha\zeta f'}{n_1'} \right) \quad (30)$$

By rearrangement of eq 30, f' may be expressed as

$$f' \cong 1 - \frac{1}{\zeta} \left[\frac{\ln \phi_1'}{\phi_3'} + \left(1 - \frac{2V_1}{m'xV_s}\right) \frac{\phi_2'}{\phi_3'} + (\chi_{12}\phi_2' + \chi_{13}\phi_3') \frac{\phi_2' + \phi_3'}{\phi_3'} - \frac{\chi_{23}\phi_2' V_1}{xV_s} \right] \quad (31)$$

Since $2V_1/m'xV_s \ll 1$, $f' \sim 2f$ may be obtained from eqs 31 and 24 assuming that only small amount of water diffuses into the dialysis tube. Thus, the conductivity Λ' of solution at equilibrium may be represented by

$$\Lambda' \cong \left(u_0 + \frac{\alpha}{1800\pi\eta R} \right) \left\{ 1 - \frac{1}{\zeta} \left[\frac{\ln \phi_1'}{\phi_3'} + \left(1 - \frac{2V_1}{m'xV_s}\right) \frac{\phi_2'}{\phi_3'} + (\chi_{12}\phi_2' + \chi_{13}\phi_3') \frac{\phi_2' + \phi_3'}{\phi_3'} - \frac{\chi_{23}\phi_2' V_1}{xV_s} \right] \right\} \quad (32)$$

which is also approximately twice the value of Λ in eq 25. The foregoing prediction on the increase of conductivity by dialysis is larger than the experimental observation shown in Figure 2. This discrepancy might

be caused by three factors: (i) the friction force (or pressure drop) inside the membrane of dialysis tube reduces the osmotic pressure that directly applies on the solution; (ii) diffusion of NaPSS across the dialysis tube to water side gradually in a long period of dialysis (275 h), which not only decreases the concentration of NaPSS in the solution but also decreases the osmotic pressure; and (iii) decrease of NaPSS concentration by diffusion of water across the dialysis tube to the solution.

Concluding Remarks

Uniformly charged aggregation model of polyions is a crude model, because it neglects many important factors affecting the coagulation such as volume shrinkage of polyelectrolyte solution during mixing and drainage of domains. However, it has successfully interpreted the unsolved conductivity problems of salt-free polyelectrolytes in the dilute/semidilute region, such as the increase of equivalent conductivity by decreasing the concentration and molecular weight. It also clarifies the dispute about the nature of attractive interactions between the polymer segments in aggregates. In addition, it provides another interpretation for the long-disputed coagulation phenomenon of polyions observed by dynamic light scattering. Above all, it interprets the observed unexpected phenomenon that the conductivity of salt-free polyelectrolyte solution is increased by dialysis in the dilute/semidilute region.

Acknowledgment. The authors acknowledge the financial support of the National Science Council in Taiwan, Republic of China, through Grant NSC 87-2216-E-002-001.

References and Notes

- (1) Odijk, T. *Macromolecules* **1979**, *12*, 688.
- (2) Ise, N. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 323. Matsuoka, H.; Ise, N.; Okubo, T.; Kunugi, S.; Tomiyama, H.; Yoshikawa, Y. *J. Chem. Phys.* **1985**, *83*, 378. Sogami I.; Ise, N. *J. Chem. Phys.* **1984**, *81*, 6320.
- (3) Lin, S. C.; Lee, W. I.; Schurr, J. M. *Biopolymers* **1978**, *17*, 1041.
- (4) Schmitz, K. S.; Lu, M.; Gauntt, J. *J. Chem. Phys.* **1983**, *78*, 5059.
- (5) Drifford, M.; Dalbiez, J. P. *Biopolymers* **1985**, *24*, 1501.
- (6) Schmitz, K. S.; Ramsay, D. J. *J. Colloid Interface Sci.* **1985**, *105*, 389.
- (7) Sedlak, M.; Konak, C.; Stepanek, P.; Jakes, J. *Polymer* **1987**, *28*, 873.
- (8) Forster, S.; Schmidt, M.; Antonietti, M. *Polymer* **1990**, *31*, 781.
- (9) Sedlak, M.; Amis, E. J. *J. Chem. Phys.* **1992**, *96*, 817.
- (10) Walkenhorst, R.; Dorfmueller, Th.; Eimer, E. *Ber. Bunsenges. Phys. Chem.* **1995**, *99*, 1137.
- (11) Tanahatue, J. J.; Kuil, M. E. *J. Phys. Chem. B* **1997**, *101*, 9233.
- (12) Shibata, J.; Schurr, J. M. *Biopolymers* **1979**, *18*, 1831.
- (13) Hodgson, D. F.; Amis, E. J. In *Polyelectrolytes Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993; Chapter 3.
- (14) Morawetz, H. *Macromolecules in Solution*, 2nd ed.; Wiley-Interscience: New York, 1974; Chapter 7.
- (15) Kuhn, W.; Kunzle, O.; Katchalsky, A. *Helv. Chim. Acta* **1948**, *31*, 1994. Katchalsky, A.; Kunzle, O.; Kuhn, W. *J. Polym. Sci.* **1950**, *5*, 283.
- (16) Odijk, J.; Houwaart, A. C. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 627.
- (17) Kratky, O.; Porod, G. *Recl. Trav. Chim.* **1949**, *68*, 1106.
- (18) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
- (19) Odijk, J. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 477. Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
- (20) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, 1979.
- (21) Hermans, J. J.; Overbeek, J. T. G. *Recl. Trav. Chim.* **1948**, *67*, 761.
- (22) Flory, P. J. *J. Chem. Phys.* **1953**, *21*, 162.
- (23) Flory, P. J.; Osterheld, J. E. *J. Phys. Chem.* **1954**, *58*, 653.
- (24) De Gennes, P. G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Paris)* **1976**, *37*, 1461.
- (25) Borue, V. Y.; Erukhimovich, I. Y. *Macromolecules* **1988**, *21*, 3240.
- (26) Joanny, J. F.; Leibler, L. *J. Phys. (Paris)* **1990**, *51*, 545.
- (27) Khokhlov, A. R.; Nyrkova, I. A. *Macromolecules* **1992**, *25*, 1493.
- (28) Moussaid, A.; Schosseler, F.; Munch, J. P.; Candau, S. J. *J. Phys. (Paris)* **1993**, *25*, 573.
- (29) Sedlak, M. *J. Chem. Phys.* **1994**, *101*, 10140. Ermi, B. D.; Amis, E. J. *Macromolecules* **1996**, *29*, 2701.
- (30) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
- (31) Schmitz, K. S. *Langmuir* **1997**, *13*, 5849.
- (32) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*, 2nd ed.; Marcel Dekker: New York, 1986; Chapter 13.
- (33) Leeuwen, H. P. V.; Cleven, R. F. M. J.; Valenta, P. *Pure Appl. Chem.* **1991**, *3*, 1251.
- (34) Wandrey, C. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 869.
- (35) Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford University Press: Oxford, 1994; Chapter 24.
- (36) Michaeli, I.; Overbeek, J. T. G.; Voorn, M. J. *J. Polym. Sci.* **1957**, *23*, 443.

MA9817976