Macromolecules **2003,** *36,* 9128−9134

Ion Migration through a Polymer Solution: Microviscosity

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Received June 6, 2003; Revised Manuscript Received October 2, 2003

ABSTRACT: The ion migration in polymer solutions of different molecular weights is investigated by conductometry for various inorganic salts. The electric conductivity κ declines with increasing the number concentration of polymer c_p at a given salt concentration c_s. All reduced conductivities for salts of the same valency type collapse into a single curve for a given polymer molecular weight and can be well represented by the simple exponential $\kappa = \kappa_0(c_s)\exp(-[\kappa]c_p)$. Here κ_0 is the conductivity of the salt solution in the absence of polymers, and $[\kappa]$ can be regarded as an intrinsic attenuation factor. Our result indicates that the reduction of the ion mobility is mainly attributed to hydrodynamic interactions between the probe ion and polymer segments, and the specific ion effect plays a minor role. The intrinsic attenuation factor is found to be independent of the salt concentration but to vary with polymer molecular weight M_w, $[\kappa] \propto M_w$. This consequence reveals that the ion interacts with all segments of a polymer as it migrates through the coil or the network, and hence the conductivity reduction depends mainly on the polymer weight concentration.

I. Introduction

The transport of an individual particle, such as protein and colloid, in polymer solutions is of fundamental interest and also relevant to many technological applications. For example, capillary electrophoresis involves the migration of a charged object through a semidilute polymer solution.[1] Other examples include separation and chromatography. In these processes one of the most important properties is the translational mobility of the particle through a microscopically inhomogeneous medium under the externally applied field.

One of the old methods for determining the viscosity of a polymer solution, particularly cross-linking macromolecules such as slime,[2] is the falling ball viscometer. It comprises the migration of a heavy particle through the microscopically inhomogeneous solution due to gravitational forces. In those applications, there are two length scales: the particle size R and the characteristic length corresponding to the inhomogeneity of the solution ξ. If the former is large compared to the latter, then the particle feels a homogeneous medium during motion. As a consequence, the Stokes−Einstein relation, which links the diffusivity of the particle to the bulk viscosity of its surroundings, is generally valid.[3,4] However, when R becomes comparable to or smaller than ξ, the particle is able to experience the inhomgeneous microstructure. In other words, the particle may sense the solvent viscosity and the polymer resistances intermittently during its motion in polymer solutions. Under this condition, the bulk viscosity (friction) in the Stokes−Einstein relation must be replaced by the effective viscosity (microviscosity), which is generally smaller than the macroscopic viscosity in aqueous solutions.

About two decades ago, de Gennes[5] and Langevin and Rondelez[6] proposed that when the particle size is smaller than the correlation length ξ, which represents the average mesh size of the fluctuating polymer network, the particles move easily and they feel essentially the solvent viscosity. In a good solvent, the correlation length ξ describes the average distance between entanglement points[5] and is a decreasing function of the polymer concentration c, $\xi/R_g \simeq (c/c^*)^{-3/4}$ in the semidilute regime. Here R_g denotes the radius of gyration of the polymer chain with molecular weight M_w and $c^* \sim M_w/(4\pi/3)R_g^3$ is the overlap concentration. Recently, Tong et al.[7] performed sedimentation measurements of small colloidal particles with a radius $R \approx 4$ nm through a nonadsorbing polymer solution by ultracentrifugation. The interaction between particles was negligible because of sufficiently dilute colloidal suspensions. For semidilute solutions, i.e., above overlap concentration c^*, their experiments reveal that the particle feels the single-chain viscosity rather than the solvent viscosity as $R \lesssim \xi$. On the other hand, when $R \gg \xi$, the particle experiences the macroscopic viscosity of the polymer solution. In the literature the measured viscosity η is often fitted by a stretched exponential function

$$\frac{\eta}{\eta_0} = \exp[(\gamma c)^{\upsilon}] \tag{1}$$

where η_0 is the solvent viscosity and the exponent υ is usually in the range $0.5 \le \upsilon \le 1$.[7,8] Since the viscosity is inversely proportional to the sedimentation coefficient (the settling velocity per unit field), one anticipates that the mobility of the particle in the polymer solution also follows the stretched exponential behavior.

For charged particles in neutral flexible polymer solutions, the mobility can be determined by applying an external, electric field. Radko and Chrambach[9,10] have studied electrophoretic migration of charged particles through solutions of entangled polymers. The measured mobility of the particle μ can be well described by the stretched exponential function

$$\frac{\mu}{\mu_0} = \exp(-\alpha c^{\upsilon}) \tag{2}$$

where μ_0 is the particle electrophoretic mobility in the absence of the polymer. Both the prefactor α and the

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10.1021/ma034769i CCC: $25.00

scaling exponent υ were found to vary with the particle radius and the polymer molecular weight. The passage of rigid, spherical proteins in the range of $R = 2-5$ nm through poly(ethylene glycol) in the molecular weight range of $(0.6-8) \times 10^6$ gives that $\alpha \propto R$ and $\upsilon \simeq 3/4$. According to the literature for PEO properties,[11] the radius of gyration can be estimated as $R_g \approx 24-204$ nm. For the polymer concentrations investigated, the average mesh size is larger than the particle size, i.e., $R < \xi$.[9] On the other hand, the electrophoresis of carboxylated polystyrene latex spheres of $R = 55$, 140, and 215 nm radius in solutions of linear polyacrylamide of $(0.4-1) \times 10^6$ molecular weight, in the concentration range $c = 0.1-1$ wt %, yields that $\upsilon \simeq 1$ and α declines with increasing the particle size. The radius of gyration for polyacrylamide of $M_w = 10^6$ is $R_g = 44$ nm. Since the mesh size is $\xi \approx 9-22$ nm, this case corresponds to $R > \xi$.[10]

The aforementioned studies indicate that the mobility of the probe particle μ in polymer solutions depends significantly on its size. The interplay between the probe size R and the mesh size ξ further complicates the retardation effect in the probe mobility. For example, a mnemonic image frequently implied in theoretical models is a fish moving through a fishnet. To minimize the geometric hindrance due to the polymer network, we investigate the asymptotic condition that the probe size is small compared to the mesh size, i.e., $R \ll \xi$. This limiting case can be satisfied by considering the migration of ions through a polymer solution under an externally applied electric field. When the ion concentrations are dilute enough, the ion−ion interactions can be ignored, and the reduction of the electric conductivity corresponds to the retardation of the ion mobilities. Under such a circumstance, the probe particles, i.e., small ions, encounter an inhomogeneous microenvironment during their motion. The resistances are attributed to the solvent viscosity and the interactions between ions and polymer segments. The latter may be of hydrodynamic or chemical nature.

In this paper, we investigate the obstruction effect of water-soluble polymers on the inorganic ion migration in aqueous solutions by electric conductometry. The effects of polymer concentrations (from dilute to semidilute regime), polymer molecular weight (10^3-10^5), ion species (valency 1−3), and salt concentrations (1−10 mM) are studied. The validity of the stretched exponential expression for the electric conductivity is examined and explained. Moreover, the relevance between our results and microviscosity and the validity of the Stokes−Einstein relation are also discussed.

II. Experimental Section

Materials. Seven different molecular weights of linear poly(ethylene glycol) (PEG) were used. Normal molecular weights of 1000 and 2000 g/mol were purchased from Riedel-deHaen and 3000, 6000, 10 000, 20 000, and 35 000 g/mol from Fluka. Two different molecular weights of poly(vinyl alcohol) (PVA), $M_w = 3.1 \times 10^4$ and 1.3×10^5, were bought from Fluka. Two different molecular weights of poly(vinylpyrrolidone) (PVP), $M_w = 10^4$ and 3.6×10^5, were purchased from Sigma. The inorganic salts used include KCl, KI, Na_2SO_4, $MgSO_4{\cdot}7H_2O$, and $CuSO_4$ (Merck, 99%); K_2SO_4 and $LaCl_3$ (Riedel-deHaen, 99%); $CaSO_4$ (Wako, Japan, 99%); $CaCl_2$ (Shimakyu's, Japan, 99%); and $MgCl_2$ (Sigma, 99%). All salts were of analytical grade. All substances were used without further purification.

All salt solutions were prepared quantitatively and equilibrated at least 7 h at room temperature. The water used in the preparation of the solutions was obtained first from distillation, which was then fed into the reverse osmosis system. After suitable amount of polymer was added, all solutions were stirred magnetically for about an hour before measurement.

Conductivity and Viscosity Measurements. A conductivity meter (MPC227) and an InLab 730 electrode, both from Mettler-Toledo (Switzerland), were used to obtain the electric conductivity of polymer solutions. The temperature was control at 25 ± 0.2 °C using a FIRSTEK B-402L circulating water bath. A Brookfield DV III cone and plate viscometer was used for all the bulk viscosity measurements. The cone spindle (CP-40) angle is 0.8°, and it offers viscosity determinations ranging from 0.1 to 3070 cP. The sample volume was 0.5 mL. All measurements were conducted at 25 °C.

III. Results and Discussion

The electrophoretic migration of the probe particle through the microscopically inhomogeneous medium, i.e., polymer solutions, has been investigated. We consider the limiting case that the characteristic size of the polymer solution, the radius of gyration or the mesh size, is large compared to the size of the probe particle. By measuring the electric conductivity, we are able to obtain the variation of the mobility of the ion probe with neutral polymer concentrations for various inorganic salts and polymer molecular weights.

In dilute electrolyte solutions the electric current is simply the sum of the current carried by individual ions if the ion−ion interaction is ignored. It is known as Kohlrausch's law of independent migration of ions.[12] As a result, based on the additivity of all conductivity contributions $\kappa_\pm$, the electric conductivity of an electrolyte solution κ is given by

$$\kappa = \Sigma_\pm \kappa_i = \Sigma_\pm z_i e \mu_i c_i \tag{3}$$

where z_i (valency) is the number of fundamental charges carried by species i and c_i the number concentration associated with species i. The fundamental charge is $e = 1.6 \times 10^{-19}$ C. The electrical mobility μ_i is defined as the velocity attained by the ion under unit electric potential gradient. We have performed conductivity experiments for various kinds of inorganic salts (z_+:z_- electrolyte), such as KCl (1:1), $CaCl_2$ (2:1), Na_2SO_4 (1:2), $LaCl_3$ (3:1), and $MgSO_4$ (2:2). Figure 1 demonstrates the conductivity curves, which depict the variation of the conductivity with the polymer number concentration c_p (mM) for a given salt concentration. We observe that the electric conductivity declines as the concentration of PEG with $M_w = 2 \times 10^4$ is increased for the salt concentration, $c_s = 10$ mM. On the basis of the limiting mobilities at 25 °C,[12] i.e., at infinite dilution in aqueous solutions, one is able to estimate the electric conductivity in the absence of polymers according to eq 3. Our experimental results agree reasonably well with the theoretical calculations. Note that the total ion concentration of $LaCl_3$ is the highest and that of KCl is the lowest.

Empirical observations indicate that the product of the limiting conductivity and the solvent viscosity (η) is very approximately constant for the same ions in different solvents. This is known as Walden's rule[12] and can be expressed as

$$\frac{\mu_i}{|z_i|e} = \frac{1}{f_i} \propto \frac{1}{\eta} \tag{4}$$

where the friction coefficient (resistivity) f_i is the force required to drag the particle through the liquid at unit

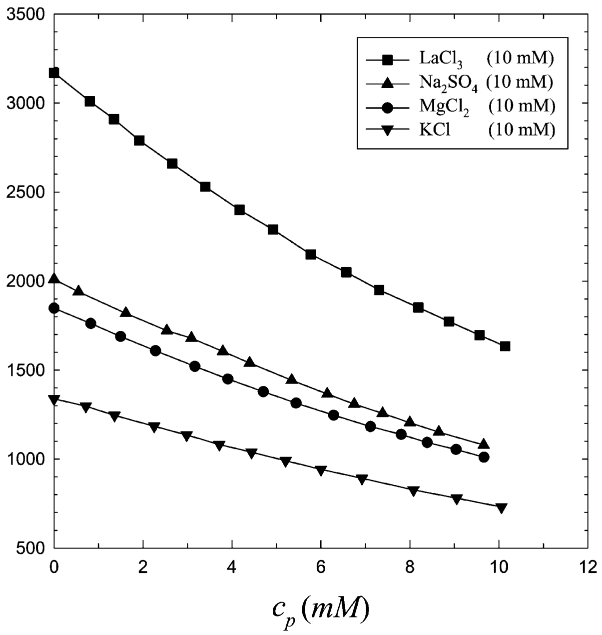

Figure 1. Variation of the electric conductivity with the polymer number concentration for inorganic salts $LaCl_3$, Na_2SO_4, $MgCl_2$, and KCl at concentration 10 mM. The molecular weight of PEG is 2 × 10^4.

speed. Equation 4 can be rationalized in terms of the well-known Stokes' law, which states that the friction on a rigid sphere of radius R in creeping flow is $f = 6\pi\eta R$. The mobility calculated based on the crystallographic radius of a small ion (such as Na^+) is often greater than the experimental result. An effective radius of hydrated ion is then invoked to explain this discrepancy.[12] This approach is called the solvent-berg model. Note that the conditions for the validity of Stokes' law are not fulfilled for small ions. Another widely accepted theory, called the dielectric friction model, considers the dielectric response of the polar solvent to the ion motion. The continuum theory incorporating the relaxation of the polarized fluid in the vicinity of the moving ion predicts the total friction factor is proportional to the solvent viscosity.[13] Therefore, eq 4 provides a useful picture for explaining the decrement of conductivity due to polymer addition. Equations 3 and 4 indicate that the retardation of ion migration is attributed to the increase in the fluid resistance, i.e., the effective viscosity η due to polymers.

It is well-known that addition of water-soluble polymers leads to an increase of the bulk viscosity of the solution. It is caused by solvent immobilization, like suspended hard spheres, in dilute solutions and by polymer entanglements in concentrated solutions. In general, the variation of the bulk viscosity with the polymer concentration can be approximated by the stretched exponential expression, as depicted in eq 1. For PEG with molecular weight 2 × 10^4, we obtain $\gamma = 37.5$ mL/g and $\upsilon = 0.621$, as shown in Figure 2. Addition of enough amount of salt, such as $c_s = 0.9$ M KCl or 0.45 M K_2SO_4, may substantially reduce the bulk viscosity because the solution has been shifted from good solvent regime toward Θ solvent. It is similar to the salting-out effect. Under such a condition, the bulk viscosity can still be fitted by eq 1 with $\gamma = 28.3$ mL/g and $\upsilon = 0.669$. Nevertheless, Figure 2 clearly shows that the solution viscosity at $c_p \approx 10$ mM ($c = 20$ g/mL) is increased at least by about 20 times that of water. In

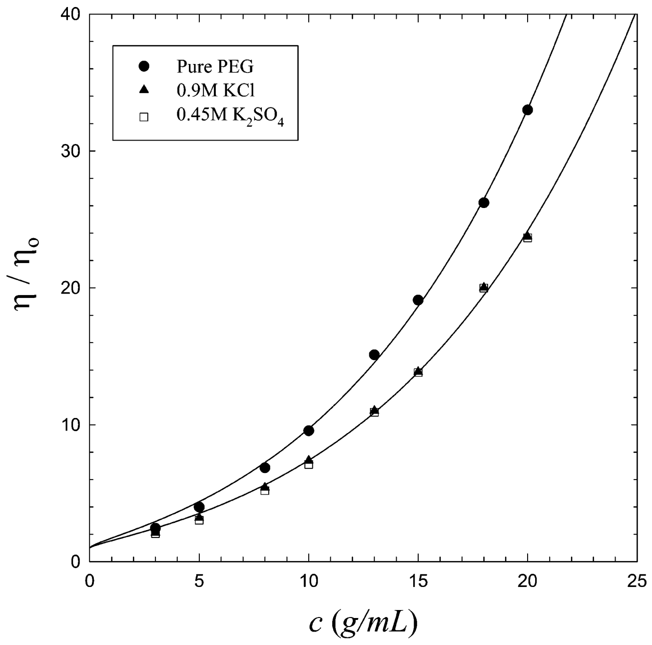

Figure 2. Plot of the bulk viscosity against the polymer concentration with or without salt addition. The molecular weight of PEG is 2 × 10^4. The salt concentration is 0.45 M for K_2SO_4 and 0.9 M for KCl. The solid lines represent the fitting result of eq 1 with two parameters γ and ν.

other words, if eq 4 is applicable for polymer solutions, one would obtain very significant conductivity reduction, and the conductivity ratio is $\kappa/\kappa_0 < 0.05$. Here κ_0 denotes the conductivity in the absence of polymer. However, this inference does not agree with the experimental results depicted in Figure 1. In fact, the electric conductivity reduction is less than 50% at $c_p \approx 10$ mM.

Equation 4 indicates that the mobility is inversely proportional to the viscosity. A reasonable explanation for the failure of eq 4 is that the bulk viscosity is unable to represent the effective viscosity felt by the ions during their migration. In fact, for dilute gels, the bulk viscosity is actually infinite, but the ion diffusivity is altered only slightly.[18] According to the conductivity experiments, the ion feels mainly the solvent viscosity, which is enhanced due to the presence of the polymer. In other words, the ion migration is primarily resisted by the hydrodynamic interactions between the ion and the polymer segments. Therefore, it is the microscopic (local) viscosity that is relevant rather than the macroscopic (bulk) viscosity. The typical example for the important role played by microviscosity is the self-diffusion of the probe particle in the concentrated polymer solution. The probe includes colloidal particle,[14,15] polymer,[16] molecule,[3,17] and small ions.[18] Note that the diffusion coefficient can be related to the friction coefficient and therefore the mobility by the Nernst–Einstein equation

$$D_i = \frac{k_B T}{f_i} = \frac{\mu_i}{|z_i|e} k_B T \tag{5}$$

where k_B is the Boltzmann constant and T the absolute temperature. Substituting the Stokes' law eq 4 into eq 5 for the friction coefficient, one has the Stokes–Einstein equation. It is found that the diffusivity is significantly underestimated if one adopts the bulk viscosity of the polymer solution in the Stokes–Einstein equation. This is because the probe sees a local environment of a sea of solvent molecules with polymer molecules serving to obstruct the motion of this particle furthermore. Consequently, the microviscosity η can be determined through the measurement of the diffusivity D, $\eta = \eta_0(D_0/D)$. Here D_0 is the diffusivity in the absence of polymers. Previous studies showed that the diffusivity retardation of macromolecular probe due to the presence of polymers can also be described by the stretched exponential, $D/D_0 = \exp(-\alpha c^{\upsilon})$.

On the basis of eq 4 and the concept of microviscosity, one would anticipate that the relation between electric mobility and microviscosity is given by

$$\frac{\mu_i}{\mu_{i,0}} = \frac{\eta_0}{\eta} \tag{6}$$

where $\mu_{i,0}$ is the electric mobility of species i in the absence of polymers. According to eqs 3 and 6, one can arrive at the conclusion that the electric conductivity reduction is inversely proportional to the effective viscosity (or the friction coefficient) increment

$$\frac{\kappa}{\kappa_0} = \frac{\eta_0}{\eta} \tag{7}$$

Note that eq 7 is valid if the hydrodynamic resistance plays the major role in conductivity reduction. Furthermore, eq 7 implies that the same amount of polymer addition provides the same microenvironment and thereby leads to the same microviscosity for the probe particle, which satisfies the conditions $R \ll R_g$ and $R \ll \xi$. As a consequence, we expect that the normalized conductivity curve κ/κ_0 associated with various inorganic salts, e.g., as illustrated in Figure 1, should collapse into a single curve for a polymer of the same molecular weight. Figure 3a shows that salts of various valency types, including 1:1, 1:2, 2:1, and 3:1, give quite similar conductivity curves for PEG of $M_w = 2 \times 10^4$. However, one obtains different conductivity curves if the molecular weights of polymers are different. As illustrated in Figure 3a, the conductivity reduction is less significant at $M_w = 6 \times 10^3$. For the valence type 2:2, we also find that a single conductivity curve can represent well the data for different inorganic salts ($MgSO_4$, $CaSO_4$, and $CuSO_4$), as shown in Figure 3b. Nevertheless, the conductivity reduction of the valency type 2:2 is more substantial than that of 1:z with $z = 1-3$. We speculate that the difference is caused by the electrostatic interactions between ions and polymer segments such as ion–dipole interaction. In fact, a careful examination of Figure 3a reveals the differences of the conductivity curves between KCl and $LaCl_3$. The latter shows a relatively large conductivity reduction.

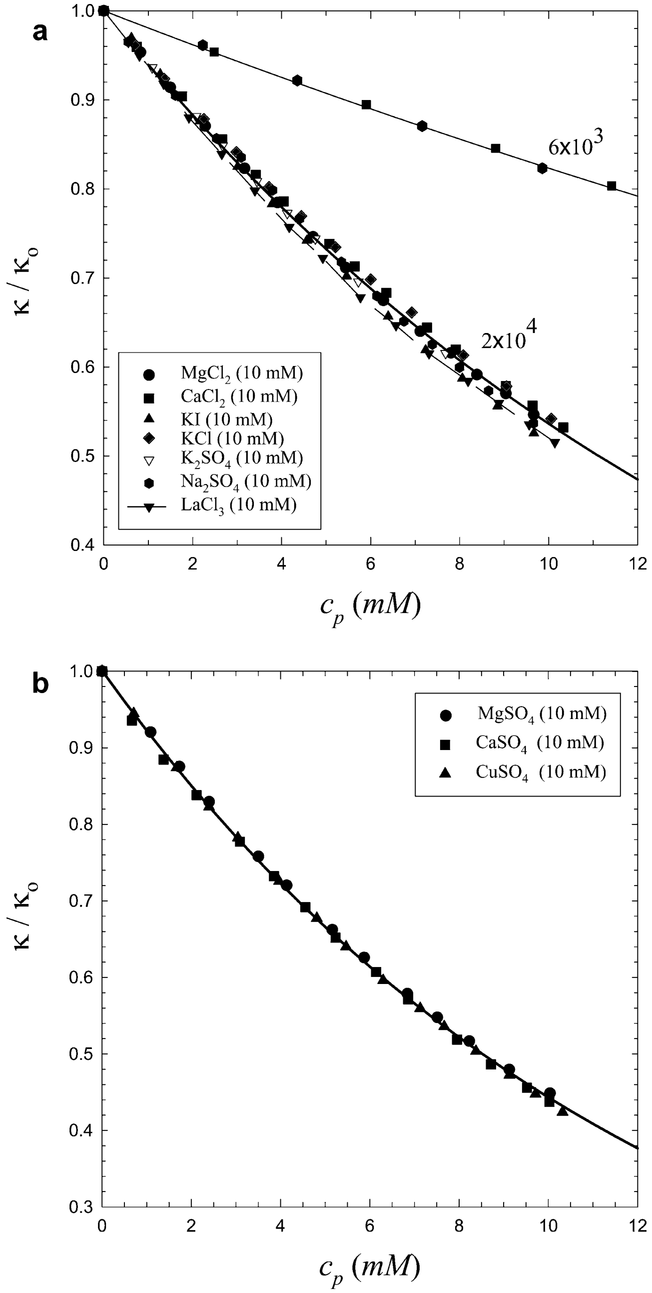

Figure 3. Variation of the reduced conductivity with the polymer number concentration. (a) The inorganic salt includes KCl, KI, Na_2SO_4, K_2SO_4, $MgCl_2$, $CaCl_2$, and $LaCl_3$ for PEG of molecular weight 6×10^3 and 2×10^4 at salt concentration 10 mM. (b) The inorganic salt is of valency type 2:2 and consists of $MgSO_4$, $CaSO_4$, and $CuSO_4$ at 10 mM for PEG of molecular weight 2×10^4.

In the current study, the polymer concentration is increased from dilute to semidilute regimes. For example, the overlap concentrations are $c^* \sim 3.2$ wt % (1.6 mM) for $M_w = 2 \times 10^4$ and $c^* \sim 7.8$ wt % (3.9 mM) for $M_w = 6 \times 10^3$. The radius of gyration is estimated from $R_g^2 = 4.08 \times 10^{-18} M_w^{1.16}$ (cm^2).[19] In dilute polymer solutions, the ion feels the solvent viscosity and the polymer resistance intermittently. The probability of encountering the coil is proportional to the polymer number concentration. This situation is somewhat similar to sedimentation of a small heavy particle through a dilute suspension of neutrally buoyant spheres.[20] The decrement of mobility can be estimated from hydrodynamic interactions between the heavy particle of radius a and the suspended sphere of radius b

$$\mu = \mu_0\left[\mathbf{I} - \frac{15}{4}\frac{ab^3}{r^4}\hat{\mathbf{r}}\hat{\mathbf{r}} + O\left(\frac{a}{r}\right)^7\right] \tag{8}$$

where $\mathbf{I}$ is the identity tensor and $\hat{\mathbf{r}}$ is the unit vector along the spheres' line of centers. Note that for bead–spring polymer models, such as in the Kirkwood–Riseman theory,[21] the hydrodynamic interactions between two beads are described by the Oseen (point force)[22] or Rotne–Prager tensors. Hence, those calculations have involved complicated, long-range $O(r^{-1})$

interactions. However, it was shown that the long-range r^{-1} hydrodynamic interactions between diffusing particles cancel on average in the absence of direct forces between the diffusing particles.[23] As a result, the leading term arises from wakes generated by the moving ions being reflected off of the polymers and returning to the ions, which gives the $O(r^{-4})$ approximate solution in eq 8 obtained by Mazur and van Saarloos[22,24] for free suspended hard spheres. If the polymer were highly charged, so that the small ions and polymer did interact strongly, then one would have to consider the effects of the r^{-1} hydrodynamic interactions.[25] Since the disturbance to the velocity field of the heavy sphere, due to the presence of a single neutrally buoyant particle, decays like r^{-4}, it is possible to obtain the hydrodynamic resistance by volume integral over pairs of particles in dilute suspensions. Therefore, the mobility reduction is given by[20]

$$\mu = \mu_0[1 - (k_{\mathrm{m}}v)c_{\mathrm{p}}] + O(c_{\mathrm{p}}^{\,2}) \tag{9}$$

where c_{p} denotes the number density of suspended particles and v is the volume of the suspended particle. The mean mobility coefficient k_{m} depends on the size ratio $\lambda = b/a$.[20] When $\lambda \lesssim 4$, the background spheres behaves as an effective fluid with Einstein viscosity correction, $k_{\mathrm{m}} = {}^5\!/_2$. On the other hand, $k_{\mathrm{m}} = 2\lambda$ for $\lambda \gg 1$ because of contributions from near-contact portions of the trajectories. In our case, however, the ion can penetrate into the polymer coil, which consists of a lot of correlated beads in terms of the bead–spring model. Moreover, ion migration involves significant thermal motion (similar to Brownian diffusion), and thereby the probe ion may run into most of the segments of a polymer coil. As a result, the polymer coil cannot be simply regarded as a hard sphere with radius R_{g}. Nevertheless, eq 9 provides a physical picture of mobility retardation and also indicates that the effective volume of the coil plays an important role.

If we regard the polymer as N effective beads with radius about b, then the mobility retardation is essentially $k_{\mathrm{m}}v \sim Nb^3$, which is proportional to the polymer molecular weight. In accordance with eqs 3 and 9, one can deduce the conductivity curve of the dilute polymer solution

$$\kappa = \kappa_0(1 - [\kappa]c_{\mathrm{p}}) + O(c_{\mathrm{p}}^{\,2}) \tag{10}$$

where $[\kappa]$ can be considered as the intrinsic attenuation factor and corresponds to a characteristic volume associated with the polymer coil for hydrodynamic friction acting on the ion probe. Figure 4 demonstrates that the reduced conductivity κ/κ_0 is linear with respect to the polymer number concentration c_{p} in the dilute regime, i.e., $c_{\mathrm{p}} \lesssim c_{\mathrm{p}}^*$. Moreover, the intrinsic attenuation factor rises with increasing the molecular weight. The values of $[\kappa]$ are about 0.03, 0.06, and 0.11 mM^{-1} for $M_{\mathrm{w}} = 10^4$, 2×10^4, and 3.5×10^4, respectively. This result reveals the scaling law $[\kappa] \propto M_{\mathrm{w}}$. As the polymer concentration is increased further, Figure 3a,b shows an evident deviation from the linear dependence for $c_{\mathrm{p}} > c_{\mathrm{p}}^*$. In other words, the hydrodynamic interactions between polymer coils become considerable in the semidilute regime. However, it is difficult to obtain corrections in eq 10 directly due to higher-order terms.

A decade ago, Phillies[4,26,27] had presented a hydrodynamic scaling model for probe diffusion in semidilute polymer solutions. On the basis of the self-similarity assumption, a stretched exponential expression is derived. Following the same scenario, we are able to extend the expression for conductivity reduction in the dilute limit, eq 10, to the semidilute regime. The self-similarity hypothesis asserts that the retardation of the probe by the polymer matrix is proportional to their friction coefficient.[4] In terms of conductivity (or mobility), one has

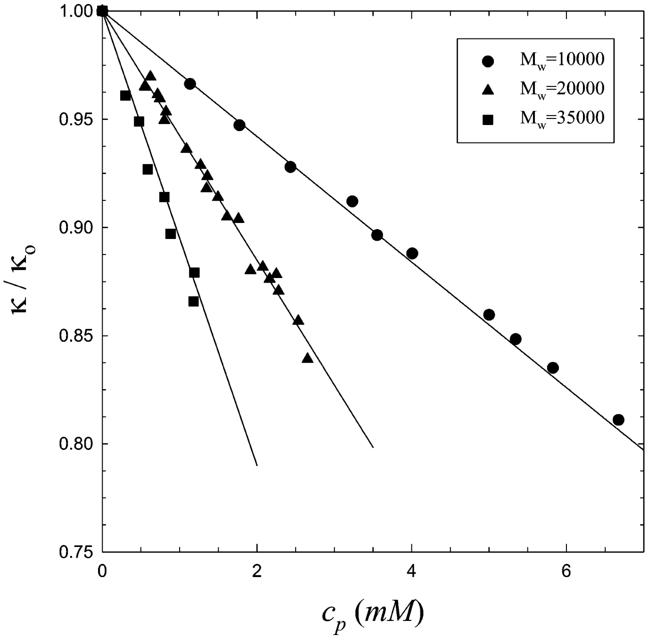

Figure 4. Plot of the reduced conductivity κ/κ_0 against the polymer concentration c_{p} in the dilute regime $c_{\mathrm{p}} \lesssim c_{\mathrm{p}}^*$. The molecular weight of PEG includes 10^4, 2×10^4, and 3.5×10^4.

$$\frac{\mathrm{d}\kappa}{\mathrm{d}c_{\mathrm{p}}} = -[\kappa]\kappa \tag{11}$$

where c_{p} is the number concentration of polymers. When $c_{\mathrm{p}} \ll c_{\mathrm{p}}^*$, one can approximate $\kappa \approx \kappa_0$ and eq 10 is recovered. Integration of eq 11 can be carried out to yield

$$\frac{\kappa}{\kappa_0} = \exp(-\int_0^{Z_{c_{\mathrm{p}}}}[\kappa]\,\mathrm{d}c_{\mathrm{p}}) \tag{12}$$

Since $[\kappa]$ varies solely with the molecular weight and is independent of c_{p}, one obtains a simple exponential

$$\frac{\kappa}{\kappa_0} = \exp(-[\kappa]c_{\mathrm{p}}) \tag{13}$$

Equation 13 can be examined by our experimental results. By plotting $-\ln(\kappa/\kappa_0)$ against c_{p}, one should obtain a straight line passing through the origin with a slope $[\kappa]$ if eq 13 is applicable. Figure 5 illustrates the variation of the reduced conductivity curve, $-\ln(\kappa/\kappa_0)$, with the polymer concentration c_{p} (mM) for PEG in the range of $M_{\mathrm{w}} = 10^3$–3.5×10^4. The salt concentration is $c_{\mathrm{s}} = 10$ mM for $CaCl_2$ in Figure 5a and Na_2SO_4 in Figure 5b. The data can be well represented by straight lines for various molecular weights. This consequence confirms the validity of eq 13, which depicts that the mobility retardation in polymer solutions follows simple exponential decay with respect to the polymer concentration. The slope $[\kappa]$ rises with increasing M_{w}. We collect the values of intrinsic attenuation factor $[\kappa]$

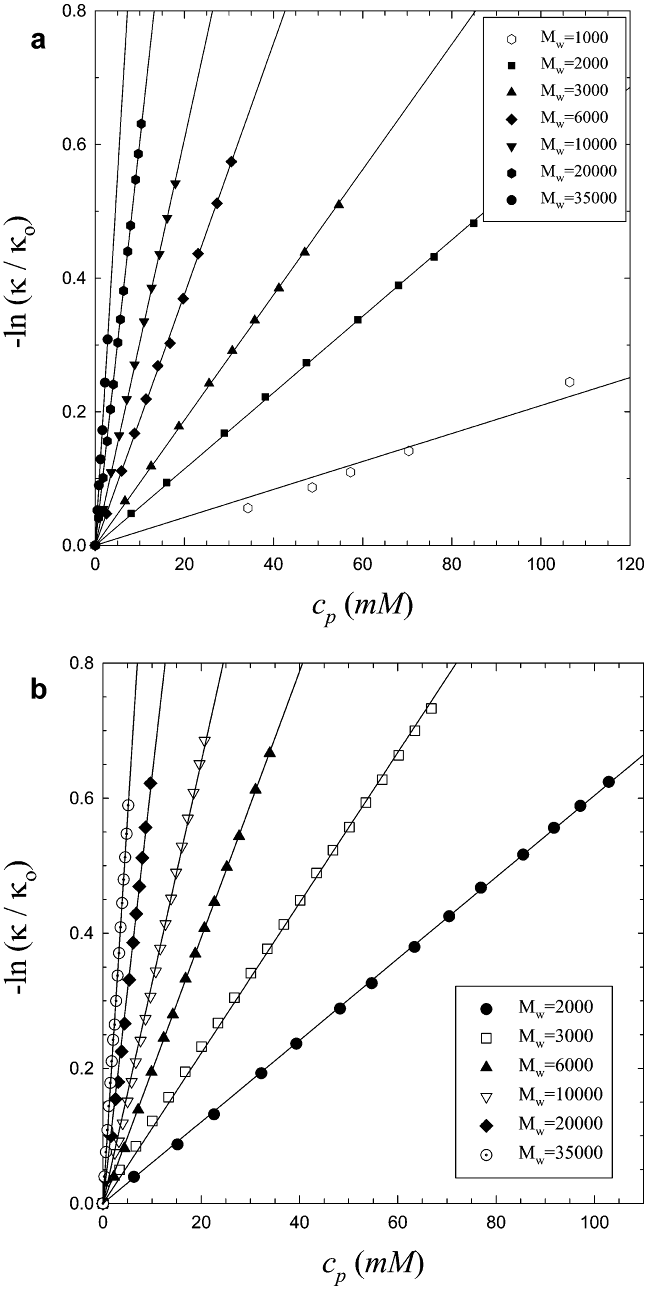

Figure 5. Plot of the reduced conductivity $\ln(\kappa/\kappa_0)$ against the polymer number concentration c_p for PEG with molecular weight in the range $10^3-3.5 \times 10^4$. (a) $CaCl_2$ at 10 mM; (b) Na_2SO_4 at 10 mM. The slope of the straight line denotes the intrinsic attenuation factor.

associated with different molecular weights and plot ln[κ] against ln M_w. If [κ] is scaled as $M_w{}^x$, a straight line results, and the slope corresponds to the exponent x. Figure 6 confirms the scaling law $[\kappa] \propto M_w$ for $CaCl_2$ and Na_2SO_4 in PEG solutions. That is, $x = 1$. Moreover, we find that this scaling law is also valid in water-soluble polymers PVA (poly(vinyl alcohol)) and PVP (poly(vinylpyrrolidone)), as demonstrated in the inset of Figure 6. In semidilute solutions, polymer coils overlap significantly and form fluctuating network due to entanglement. The probe ion migrates through a sea of polymer segments and cannot distinguish which polymer this particular segment belongs to. Consequently, we expect that the hydrodynamic resistances increase linearly with the segment concentration. However, since the mean distances between polymer segments decrease as well, the hydrodynamic interactions between segments become substantial and lead to the hydrodynamic screening effect. The interplay of resistance and screening yields a simple exponential decay of mobility. Note that in the absence of hydrodynamic screening, the mobility would eventually become zero, as indicated in eq 9.

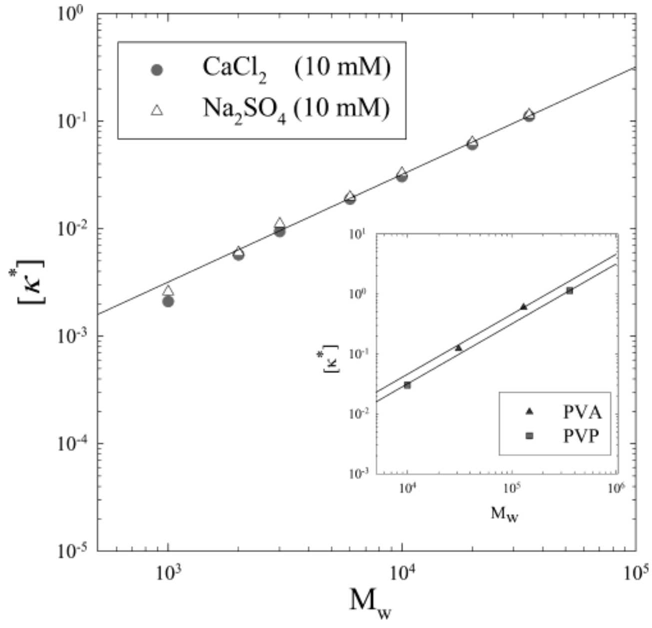

Figure 6. Variation of the intrinsic attenuation factor [κ] with the polymer molecular weight of PEG for Na_2SO_4 and $CaCl_2$. The slope of the straight line is one. The inset is meant for the polymers PVA (poly(vinyl alcohol)) and PVP (poly(vinylpyrrolidone)).

For inorganic ion migration in polymer solutions, we have obtained the result, eq 13. The intrinsic attenuation factor is linearly dependent on the molecular weight. In terms of polymer weight concentration c, eq 13 can be rewritten as

$$\kappa = \kappa_0(c_s)\exp(-\alpha c) \qquad (14)$$

where $\alpha = [\kappa]/M_w$. The constant α is therefore independent of M_w but may vary with the valency type due to ion−dipole interaction. Nevertheless, its value is in the range $\alpha \simeq 2.9-3.3$ mL/g for 1:z and $\alpha \simeq 4.1$ for 2:2. Figure 7 illustrates that the conductivities of $CaCl_2$ solutions with the same polymer weight concentration c fall in the same line for $M_w = 3 \times 10^3$, 10^4, and 3.5×10^4. This consequence indicates that the conductivity reduction and the mobility retardation are mainly caused by the hydrodynamic resistance associated with polymer segments of a polymer for a given valency type. The velocity disturbance induced by ion migration is then screened by hydrodynamic interactions between polymer segments.

The heuristic derivation of eqs 13 and 14 points out that the nature of self-similarity may be inherent in the hydrodynamic resistance and screening associated with segments in the polymer network. This statement is manifested through the M_w dependence of [κ] and c_p. To further verify this conclusion, we anticipate that [κ] should be independent of the concentration of probe ions. For dilute electrolyte solutions, the ion−ion interaction can be negligible. As a result, the conductivity should grow linearly with the salt concentration for a given polymer concentration. The slope of the straight

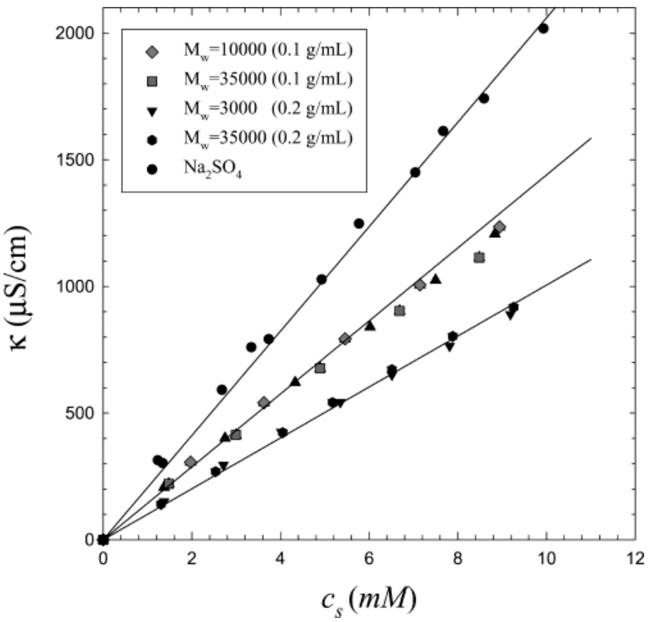

Figure 7. Variation of the electric conductivity with the salt concentration of $CaCl_2$ for different weight concentrations (0.1 and 0.2 g/mL). The molecular weight of PEG includes $M_w = 3 \times 10^3$, 10^4, and 3.5×10^4.

line is proportional to the ion mobility and hence decreases with increasing the polymer concentration. Therefore, the ratio of the slopes for two polymer concentrations should be $\exp(-\alpha\Delta c)$ according to eq 15. Here Δc is the concentration difference. Figure 7 confirms this conjecture. The slope ratio of $c = 0.1$ g/mL to $c = 0$ is approximately equal to that of $c = 0.2$ g/mL to $c = 0.1$ g/mL, i.e., $\exp(-\alpha\Delta c) \simeq 0.7$. The α value extracted from the two straight lines in Figure 7 is approximately $\alpha \approx 3.58$, which agrees reasonably well with those obtained from Figure 5. This consequence validates eq 15 by the fact that the dependence of the conductivity on the electrolyte concentration is through κ_0, and the exponential term is only related to the polymer weight concentration.

We have investigated the retardation of small ion mobility (diffusivity) due to the presence of water-soluble polymers by electric conductometry. It has to be explained by microviscosity instead of bulk viscosity in the Stokes−Einstein relation. The mobility reduction is mainly attributed to the hydrodynamic resistances associated with all segments of a polymer. For inorganic salts, the reduced conductivity (mobility) κ/κ_0 can be well described by a simple exponential, which is derived on the basis of the self-similarity assumption. Nonetheless, our preliminary result for the migration of ionic surfactants through polymer solutions reveals that the stretched exponential has to be invoked to depict the conductivity reduction. Thus, the surfactant−polymer interaction may involve significant nonhydrodynamic characteristics as well and is currently under investigation.

Acknowledgment. H.-K.T. thanks the National Council of Science of Taiwan for financial support under Grant NSC 91-2214-E-008-002.

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MA034769I