Studies of Transport Phenomena and Electrostatic Interactions in Polyacrylate Gels

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Received: March 5, 1999; In Final Form: May 17, 1999

The transport of uncharged electroactive probes, 1,1′-ferrocenedimethanol and 4-hydroxy-TEMPO, and electroactive cations, Tl^+, was studied in polyacrylate hydrogels using steady-state voltammetry at platinum and mercury film microelectrodes. It was found that, for concentrations of polymer less than 1.5%, the diffusion coefficient of uncharged probes does not differ significantly from that observed in aqueous solutions without a polymeric network. For the probe cation, strong electrostatic interactions were observed between Tl^+ and anionic polymeric networks; those interactions resulted in a significant decrease in the diffusivity of Tl^+ cations. Experimental data for Tl^+ transport in sodium polyacrylate gels were compared with predictions of Manning's theory for polyelectrolyte solutions. Electrostatic interactions between Tl^+ and anionic polyacrylate three-dimensional gel network were found stronger than those predicted for solutions of an equivalent polyelectrolyte. Electrostatic effects for gels were found even stronger when Tl^+ cations served as counterions in thallium polyacrylate gels; the transport of Tl^+ counterion was more suppressed in those gels than for a Tl^+ probe in sodium polyacrylate, especially for small values of charge separation distance in polymeric units. The mobility of a counterion forming a gel, Na^+, was also studied using conductance measurements, and appropriate expressions for conductivity as a function of poly(acrylic acid) neutralization degree were developed based on Manning's line charge model. Experimental conductivity data for Na^+ agreed with predictions of the model.

Introduction

Polymeric gels are three-dimensional networks of connected polymeric segments swollen by a solvent. Since in some cases a gel can contain up to 99% solvent, this is a rather unusual way in which large amounts of liquid can be maintained "solid". Therefore, gels possess many advantages characteristic of both the liquid and solid state of matter. Physical properties and applications of polymeric gels have been reviewed by several authors.[1−5] The potential usefulness of polymeric gels for drug delivery systems,[6,7] selective sorbents,[8,9] and such electrochemical devices as batteries and sensors[10−16] is well recognized and seems to be very promising, thus justifying more detailed studies of their properties.

The knowledge of diffusion coefficients of ions and molecules as a fundamental measure of molecular mobility in gels and electrostatic interactions in polyionic gels is of great importance in such applications as gel electrolytes for batteries, gel-based sensors, gels in separation techniques and polymeric gels as "solid-state" storage for liquids, and their controlled release. The values of diffusion coefficients of ions and molecules may also be used to probe the structure of a variety of gel networks, to mimic transport across natural and synthetic membranes, and to model flow through porous media.

Transport properties of probe molecules in gels have been studied using such techniques as light scattering spectroscopy,[17−19] pulsed-field-gradient spin−echo NMR spectroscopy[20−22] and radioactive tracer methods.[23,24] However, these techniques require relatively high concentration of diffusing species and the latter two are limited to NMR or radioactive probes. The application of electroanalytical techniques for transport studies in gels would permit a decrease in the concentration of monitoring probes and would extend the list of ions and molecules that can be investigated. The instrumentation is inexpensive and the method is very fast.

Recently steady-state voltammetry at microelectrodes has been employed for diffusion measurements in polyelectrolyte solutions[25−32] and colloidal systems.[33,34] The usefulness of the voltammetry with microelectrodes in the characterization of polymeric gels based on room-temperature ionic liquids has been shown by Carlin and co-workers,[13] voltammetric studies with interdigitated electrodes in polymeric gels have been presented by Tatistcheff et al.,[35] scanning electrochemical microscopy was used to study diffusivity and concentration of electroactive species in polyacrylamide gel films by Pyo and Bard,[36] and Collinson and co-workers applied voltammetry with micro- and regular size electrodes to characterize silica gels with encapsulated redox probes.[37,38]

The aim of this work is to study transport of ions and molecules in polyacrylate gels. Poly(acrylic acid), PAA, forms gel networks as a result of neutralization with a strong base, for example, NaOH. Using an appropriate proportion of a strong base and PAA solutions one can obtain a polyacrylate gel characterized by an unique charge separation distance and, consequently, a unique and well-defined charge density of the polymer structure. Those two parameters control electrostatic properties of the gel. Therefore, polyacrylate gels can be treated as model systems and can be used to mimic properties of a wide range of polyionic gels characterized by various charge densities.

Since polyacrylate is an anionic polymer, very strong attractive electrostatic interactions are expected between polymeric networks and any cations present in a solution or a gel.

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Therefore, two effects are of interest in these studies: first, the effect of the very viscous gel structure on transport of ions and molecules and, second, the effect of electrostatic interactions between polyacrylate networks and counterions (or any probe ions of the opposite charge) on transport of those ions in gels. The influence of electrostatic interactions on transport properties in polyacrylate gels is compared with theoretical predictions for polyelectrolyte solutions proposed by Manning.[39,40] Additionally, a new general model for calculations of conductivity in polyionic gels is developed based on Manning's theory. The main experimental approach is steady-state voltammetry with microelectrodes supported by conductance measurements.

Experimental Section

Chemicals. Poly(acrylic acid) (PAA, average MW 4×10^6), acrylic acid (AA), sodium hydroxide, and lithium perchlorate were purchased from Aldrich. Thallium hydroxide (10%, aqueous solution) and thallium nitrate were purchased from Alfa. 1,1′-ferrocenedimethanol (Fc(CH$_2$OH)$_2$) and 4-hydroxy-2,2,6,6-tetramethyl-1-pipperidinyloxy (4-hydroxy-TEMPO, an uncharged radical) were purchased from Fluka and Sigma, respectively. All chemicals were used as received. Ultrapure water (Milli-Q, Millipore Corporation) of a conductivity of about 0.056 mS/cm was used in all experiments.

Gel Preparation. Polyacrylate gels were prepared by neutralization of 0.5, 1.0 or 1.5% aqueous solutions of poly(acrylic acid), PAA, with the appropriate amount of either 10% NaOH[35] or 10% TlOH solution. Electroactive probes, 1,1′-ferrocene-dimethanol (2 mM), 4-hydroxy-TEMPO (2 mM) and TlNO$_3$ (2 mM), and supporting electrolyte, LiClO$_4$ (100 mM), were added to PAA solution prior to neutralization.

Conductance Measurements. The conductance of sodium polyacrylate solutions and gels was measured using a conductance meter, YSI Model 35, with a YSI 3417 conductivity cell. The cell constant was determined using conductivity standard solutions purchased from Fisher; its value was (1.005 ± 0.034) /cm.

Voltammetry. Electrochemical measurements were performed using an EG&G PARC Model 283A potentiostat, controlled via software by a PC computer. All experiments were carried out in a three electrode system. A platinum wire and a silver/silver chloride reference electrode were used as counter and reference electrodes, respectively. Working microelectrodes were 5, 10, and 25 μm radii platinum disk electrodes (Project Ltd., Warsaw, Poland) and a mercury film (silver-amalgam-based) microelectrode. The latter electrode was prepared by deposition of a mercury layer at the surface of a silver amalgam microdisk (12.5 μm in radius); preparation of this electrode is described in detail.[41] The size of the Hg microelectrode was determined from the steady-state current for reduction of Tl$^+$ cation of known concentration (2 or 12.9 mM) in 0.1 M LiClO$_4$ aqueous solution. The platinum microelectrodes were initially polished with aluminum oxide on a wet pad. The surfaces of all microelectrodes were inspected optically with a Nikon, Model Epiphot 200, inverted microscope for reflected light. If necessary, solutions were deoxygenated and blanketed with argon.

Results and Discussion

Conductivity of Polyacrylate Gels. Physical properties of polyacrylate gels, including transport properties, depend on the charge density of the polyanion which, in turn, depends on the neutralization degree parameter α, which is the ratio of the number of ionized carboxylate groups to the total number of monomers (AA). In other words, the mobility of ions in these
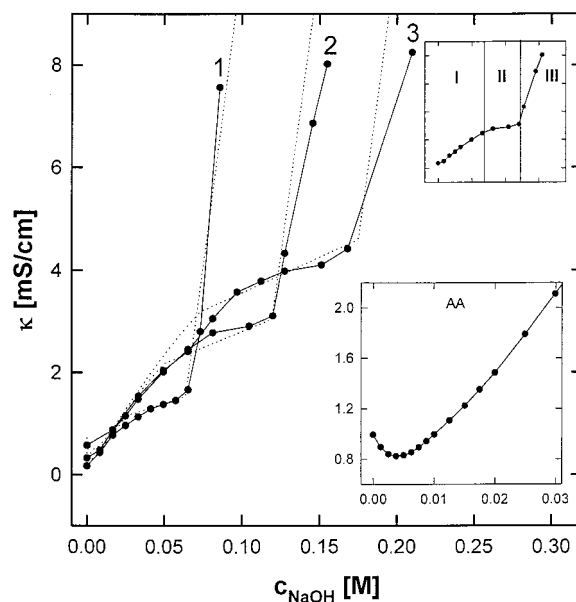

Figure 1. Experimental (solid lines and filled circles) and theoretical (dotted lines) conductometric titration curves for various PAA concentrations: (1) 0.5, (2) 1.0, and (3) 1.5%. The upper inset shows schematically three characteristic parts of titration curve of polyacid with strong base (see text for details). The lower inset presents typical conductometric titration curve for molecular acid—aqueous solution of acrylic acid—of concentration equivalent to concentration of monomers in 1% PAA solution.

systems is a function of the amount of added strong base. Such dependence can be studied conductometrically. Figure 1 presents conductometric curves obtained from titration of various concentrations of PAA solution with NaOH. It can be seen that all titration curves qualitatively exhibit similar shapes; they consist of three characteristic regions marked as I, II, and III (see the upper inset in Figure 1). For relatively small concentration of NaOH ($\alpha \ll 1$), the conductivity of the system increases because of ionization of the polymeric chain and the presence of Na$^+$ ions. In this stage of titration, the number of ionized groups of the polyacrylate chains is relatively small. Thus, the intensity of an electrostatic field generated by these chains is low and it does not significantly influence mobilities of counterions. With an increasing degree of neutralization ($\alpha < 1$), titration curves become flatter because of the significant decrease in mobility of a fraction of the counterions which condense onto the polyion. In this region the electrostatic interactions between oppositely charged species are strongest and the structure of the gel is highly ordered. This part of the curves ends at the stage of full neutralization ($\alpha = 1$). After this point, the excess of strong base causes a significant increase in conductivity of the system and results in the damage of the gel structure due to the excess of very mobile hydroxide ions. The formation of the polyacrylate gel is accompanied by strongly limited fluidity of the system, significant increase of its macroscopic viscosity, and a change in the color, from slightly milky for the PAA solution to transparent for the gel. Although we did not monitor quantitatively changes of viscosity of the system during gel formation, those listed macroscopically observed symptoms have been used for discovering when the gel is formed. For 1% PAA at 25 °C the formation of the gel was observed after addition of very low concentration of NaOH, approximately 8.5 mM.

Basically, the formation of the polyacrylate gels and the changes in their conductivity during conductometric titration are due to the acid—base reaction. However, this process differs
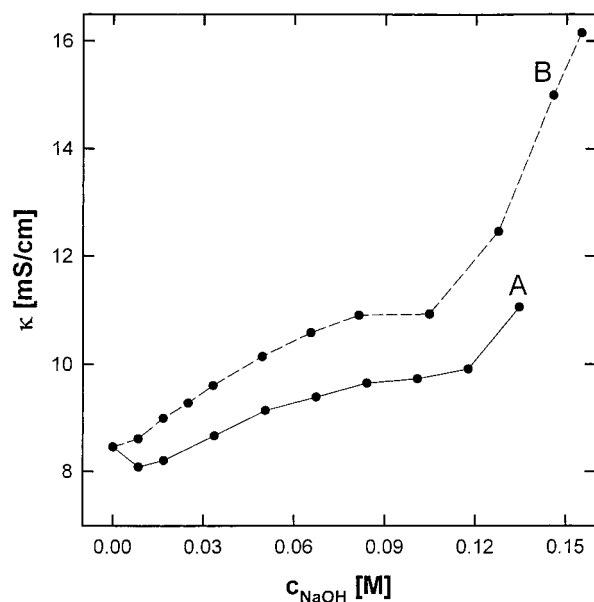
Figure 2. Experimental (A, solid lines and filled circles) conductometric titration curve for 1% aqueous solution of PAA with 0.1M LiClO$_4$. The broken line (B) shows the conductometric titration curve obtained by adding the value of conductivity of 0.1 M LiClO$_4$ in 1% aqueous solution of PAA to conductivities of salt-free 1% PAA titrated by NaOH (curve 2 in Figure 1).

significantly from the titration of a weak acid with a strong base. To show the totally different behavior of ions in gels and solutions, one can compare the titration curves described above with that for acrylic acid shown in the lower inset in Figure 1. The latter is a "V-shaped" titration curve typical for simple acids.

The characteristic shape of titration curves for PAA remains the same after addition of a large amount of neutral electrolyte, 0.1 M LiClO$_4$, to the polyacid solution. This is illustrated in Figure 2. In this figure the solid line refers to measurements in 1% PAA containing 0.1 M LiClO$_4$. It can be seen that for small concentrations of NaOH a local minimum is formed. This local decrease in conductivity is probably caused by the replacement of H$^+$ ions from dissociation of PAA, by less mobile Na$^+$ ions. Interestingly, such a minimum does not appear for the salt-free PAA (or it appears for significantly smaller concentrations of added base). In Figure 2 the broken line represents the conductometric curve obtained by adding the conductivity of LiClO$_4$ in 1% aqueous solution of PAA to the conductivities of the salt-free polyacrylate gels (curve 2 in Figure 1). The difference suggests that some fraction of lithium ions participates in electrostatic interactions with charged carboxylic groups. It should be mentioned here that the addition of a neutral electrolyte, such as LiClO$_4$, inhibits strongly the formation of the gel; the polyacrylate network becomes more liquid.

Theoretical Description. The conductivity of a given ionic system is a function of mobilities of ions in this system

$$\kappa = F^2 \sum_i z_i^2 c_i u_i \qquad (1)$$

where the summation covers all ionic species, z_i, c_i, and u_i are charge, local concentration, and mobility of ith ionic species, respectively, and F is the Faraday constant.

The mobility is related to the diffusion coefficient by the following expression

$$u_i = \frac{D_i}{RT} \qquad (2)$$

where D_i is diffusion coefficient of the ith species, and R and T have their usual meanings. This relation is valid for very low ionic strengths.

From eqs 1 and 2 one can obtain

$$\kappa = \frac{F^2}{RT} \sum_i z_i^2 c_i D_i \qquad (3)$$

This expression can be applied to the calculation of conductivities of polyacrylate gels; however, appropriate expressions for the diffusion coefficients of ions in such systems must be found.

Assuming that polyacrylate gels can be treated in an identical way as polyelectrolyte solutions, the appropriate expressions for ion diffusivities can be adopted, after some minor modifications, from Manning's line charge model for monovalent ions.[39,40] According to this model, the behavior of ions is determined by the value of parameter ξ, related to the charge density of the linear polyion, and given by

$$\xi = F^2/(4\pi\epsilon\,\epsilon_0\,N_A RTb) \qquad (4)$$

where ϵ is the relative permittivity of the solvent, ϵ_0 is the permittivity of vacuum, N_A is the Avogadro constant, and b is the length of the polyion per ionized group (the charge separation distance).

For $\xi < 1$, condensation does not occur and all ions are subject to electrostatic interactions according to the Debye–Hückel approximated model. For $\xi > 1$, a fraction of counterions is condensed onto the polyion chain. Thus, the ξ parameter and the amount of added salt determine mobility of ions in such systems.

In our case, the amount of added strong base determines the b-value and, thus, the value of the parameter ξ. Since

$$\alpha = \frac{N}{N_{tot}} = \frac{c_{H^+} + c_b}{N_{tot}\,c_{PAA}^0} \qquad (5)$$

$$b = \frac{L}{N} = \frac{L}{N_{tot}\alpha}, \quad \text{thus} \quad \xi = \frac{F^2\,N_{tot}}{4\pi\epsilon\epsilon_0\,N_A RTL}\alpha = \xi_0\alpha \quad (6)$$

where N, N_{tot}, L, c^0_{PAA}, c_b, and c_{H^+}, are the number of ionized groups in the polymeric chain, the total number of monomers in the polymeric chain (approximately 55 507), the length of the polymer, initial concentration of PAA, actual concentration of added base, and actual concentration of H$^+$ ions from the dissociation of PAA or partially neutralized PAA, respectively.

Therefore, the mobility of ions (i.e., counterions–Na$^+$, H$^+$, and Li$^+$, if present, and coions–ClO$_4^-$, if present, and OH$^-$, if excess NaOH) in the polyacrylate gel is a function of the concentrations of added strong base and neutral electrolyte. Because of the enormous sizes of polyions compared to other ions, their diffusion coefficient is assumed to be negligible small. It means that they are treated as immovable macromolecules.

As mentioned above, conductometric titration curves of PAA solutions and gels consist of three characteristic regions which are (i) $\alpha < 1$ and $\xi < 1$ (no condensation) (ii) $\alpha \leq 1$ and $\xi > 1$ (condensation of counterions), and (iii) $\alpha = 1$, $\xi = \xi_0$, and $\xi_0 > 1$ (condensation of counterions, excess strong base).

Appropriate expressions for ions concentrations, ions diffusion coefficients, and conductivity of the system can be written for all three regions. Those expressions along with their derivations are presented in the Appendix.

Calculated conductometric titration curves are presented in Figure 1 (dotted lines). According to our calculations, the slight

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increase in conductivity in region II is a result of the mobility of condensed counterions along the polyion chain. In this part of the conductometric titration curves, the conductivity due to mobility of this type of ions is the most significant fraction of the overall conductivity. The observed increase in the conductivity of the system may also partially originate from the finite conductance of the polymeric chains. We have assumed the diffusivity of polyions is very small; however, they have the enormous charge. These two factors compensate each other, and the result may be observed as an increase in the total conductivity.[42] We have found that the best fits of theoretical to experimental data are obtained for k (see eqs 26 and 37 in the Appendix) equal to 0.2, 0.25, and 0.28 for 0.5, 1.0, and 1.5% PAA solutions, respectively. It can also be seen that the largest discrepancy between predicted and measured values of conductivity, particularly for the third region of the titration curves, is observed for the highest concentrations of PAA and for the highest concentrations of NaOH. This is probably due to the decrease in diffusivities of ions caused by the increase in local viscosity which was not taken into account in the model.

Since the model developed for conductivity of polyacrylate gels is based on the electrostatic characteristic of the gel (eqs 4 and 6), it can be applied to predict conductivity of any polyionic system of a given charge density.

Voltammetry in Polyacrylate Gels. In our studies, diffusion coefficients of electroactive probes D are determined from the diffusion-limited steady-state current I_{ss} at disk microelectrodes[43]

$$I_{ss} = 4nFDc^b r_e \qquad (7)$$

where c^b is the bulk concentration of electroactive species, r_e is the radius of the microelectrode, n is the number of electrons transferred, and F is the Faraday constant. Since the steady-state current at microelectrodes is directly proportional to the flux of electroactive species, the voltammetric signal is very sensitive to changes in the value of the diffusion coefficient.

Uncharged Electroactive Probes, 1,1′-Ferrocenedimethanol and 4-Hydroxy-TEMPO. Voltammograms for the oxidation of 1,1′-ferrocenedimethanol in polyacrylate gels were very well defined and reproducible, with a coefficient of variation (calculated for 5 voltammograms) of less than 2%. Typical steady-state cyclic voltammograms obtained in 1% polyacrylate gel containing 0.1 M LiClO₄ at various Pt microdisks are presented in Figure 3. Steady-state voltammograms for oxidation of 4-hydroxy-TEMPO were of the same quality with coefficient of variation (calculated for 3 voltammograms) of less than 2%. The height of the oxidation waves of both probes in aqueous solutions with excess supporting electrolyte at Pt microelectrodes is controlled by diffusional mass transport.[26] It means that electrode processes of considered probes are not coupled to any chemical reactions. We examined the nature of the oxidation waves of 2 mM 1,1′-ferrocenedimethanol in 1% polyacrylate gel neutralized with 89.1 mM NaOH (with 0.1 M LiClO₄). For a process controlled by diffusion, the steady-state current I_{ss} should be proportional to the microelectrode radius r_e, see eq 7. The ratio I_{ss}/r_e for a given concentration of the substrate and in the same solution should be constant, independent of microelectrode radius. We compared wave heights for three sizes of Pt microdisks in 1% polyacrylate gel with 0.1 M LiClO₄. The ratio I_{ss}/r_e was 0.474, 0.480, and 0.485 nA/μm for microdisks of radius of 5, 10, and 25 μm, respectively. This indicates that the current of the oxidation of 1,1′-ferrocenedimethanol probe in polyacrylate gels is diffusion controlled under the applied experimental conditions. A similar dependence was obtained for 4-hydroxy-TEMPO.
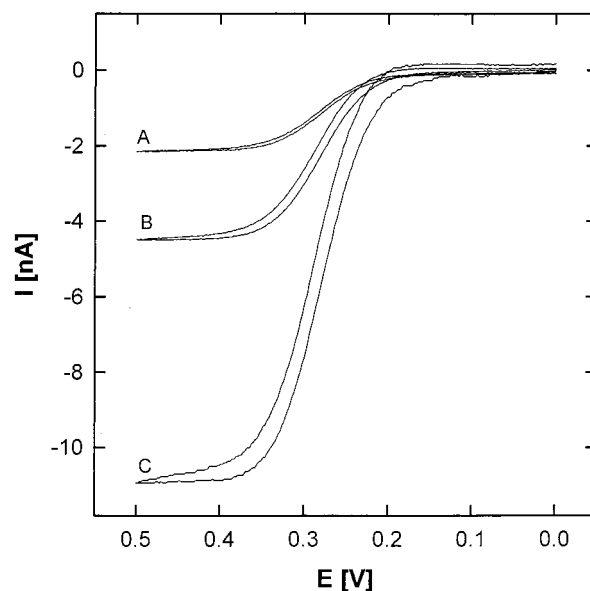

Figure 3. Cyclic voltammograms of 1,1′-ferrocenedimethanol (2 mM) obtained in 1% polyacrylate gel containing excess supporting electrolyte (0.1 M LiClO₄) for various radii of Pt microdisks: (A) 5, (B) 10, and (C) 25 μm. Reference electrode: Ag/AgCl. Scan rates: (A, B) 10 and (C) 4 mV/s. $T = 22$ °C.

We have also monitored the chronoamperometric current for the oxidation of 2 mM 1,1′-ferrocenedimethanol in 1% polyacrylate gel neutralized with 89.1 mM NaOH (with 0.1 M LiClO₄). During long-time chronoamperometric experiments (up to 100 s) we have observed no changes in the steady-state current. This indicates a semiinfinite diffusion field in the system and indirectly suggests that the structure of polyacrylate gels consists of channels that form a continuous network.

We determined diffusion coefficient values for both uncharged electroactive probes, 1,1′-ferrocenedimethanol and 4-hydroxy-TEMPO, in polyacrylate gels without and with added LiClO₄, and compared them with those from aqueous solutions. Since polyacrylate gels are electrolytes of relatively high conductivity and both electroactive probes are uncharged, the magnitude of the steady-state current is not influenced by migration and is controlled solely by diffusion even without excess supporting electrolyte.[44−46] Diffusion coefficient values were calculated from the slope of the dependence of I_{ss} on microdisk radius (i.e., 5, 10, and 25 μm) or directly from the steady-state current according to eq 7. Table 1 summarizes the results obtained for both probes in various media ($T = 25$ °C). The diffusion coefficient values for 1,1′-ferrocenedimethanol in polyacrylate gels of various concentrations of the polymer neutralized with various concentrations of NaOH without added LiClO₄ are practically the same within experimental error, with an average value of 6.26×10^{-10} m²/s, except in 1.5% PAA gel. The diffusion coefficient in 1.5% PAA gel is 12% lower than the average value for other gels. In polyacrylate gels of various polymer concentration in the presence of 0.1 M LiClO₄, the diffusion coefficient of 1,1′-ferrocenedimethanol is the same within experimental error, with an average value of 5.91×10^{-10} m²/s. This value is within 6% of the value obtained in LiClO₄-free gels. This difference is probably due to the viscosity change after addition of 0.1 M LiClO₄. The diffusion coefficient of 1,1′-ferrocenedimethanol in 0.1 M aqueous solution of LiClO₄ was 7.33×10^{-10} m²/s. This value is 19% higher than that in polyacrylate gels with 0.1 M LiClO₄. Diffusion coefficient of 4-hydroxy-TEMPO determined in 1% PAA gel was the same within experimental error as that in an aqueous solution of

TABLE 1: Diffusion Coefficients of 1,1′-Ferrocenedimethanol and 4-Hydroxy-TEMPO in Various Media ($T = 25$ °C)

electroactive probe	medium	$(D \pm 3 \text{ std. dev.}) \times 10^{-10}$ [m²/s]
1,1′-ferrocenedimethanol	polyacrylate gels, no electrolyte	6.58 ± 0.31^a
		6.15 ± 0.27^b
		6.12 ± 0.28^c
		6.20 ± 0.28^d
		5.53 ± 0.27^e
	polyacrylate gels + 0.1 M LiClO$_4$	$6.10 \pm 0.25^{a,f}$
		5.90 ± 0.27^b
		5.61 ± 0.28^c
		6.03 ± 0.25^d
		5.91 ± 0.29^e
	0.1 M LiClO$_4$ aqueous solution	7.33 ± 0.36
4-hydroxy-TEMPO	polyacrylate gels, no electrolyte	6.42 ± 0.29^c
	polyacrylate gels + 0.1 M LiClO$_4$	6.36 ± 0.27^c
	0.1 M LiClO$_4$ solution	6.59 ± 0.30

^{a} 0.5% PAA + 49.4 mM NaOH (refers to part II of the conductometric titration curve). ^{b} 1% PAA + 16.7 mM NaOH (refers to part I of the conductometric titration curve). ^{c} 1% PAA + 89.1 mM NaOH (refers to part II of the conductometric titration curve). ^{d} 1% PAA + 157.5 mM NaOH (refers to part III of the conductometric titration curve). ^{e} 1.5% PAA + 127.6 mM NaOH (refers to part II of the conductometric titration curve). ^{f} Formation of gels strongly inhibited by excess LiClO$_4$.

LiClO$_4$. As one can see from Table 1, the differences observed between the values of diffusion coefficients in solutions and low concentrations of the polymers in the gels are practically negligible. Data presented in Table 1 also demonstrate that the addition of large amount of electrolyte, LiClO$_4$, does not significantly influence diffusivities of the electroactive species in gels. This is not surprising since the electroactive probes are uncharged and do not interact electrostatically with supporting ions or charged polymeric chains of the polyacrylate gel.

The diffusivity of species in an ideal solution is described by Stokes−Einstein equation

$$D = kT/(6\pi\eta a) \qquad (8)$$

where k is the Boltzmann constant, T is temperature, η is the viscosity of solution, and a is the radius of the diffusing species. According to this equation, diffusivity of species is inversely proportional to the viscosity of an ideal solution.

In our case, the macroscopically observed viscosity of polyacrylate gels differs significantly from that for aqueous solutions. For example, the viscosity of 1% aqueous solution of PAA with 0.1 M LiClO$_4$ is approximately 2.1 times larger than that of 0.1 M aqueous solution of LiClO$_4$, and the viscosity of a gel is much greater than that for PAA solution. However, as one can see from Table 1 those differences in macroscopic viscosity do not influence the diffusion coefficients of the uncharged electroactive probes. The same phenomenon was observed for low concentration of the polymer in biopolymeric gels of agarose and *iota*-carrageenan.[47] This is probably due to the existence of channels filled with the solution and trapped in the structure of the gel. This effect shows that diffusion of small molecules in PAA gels of low concentration of the polymer does not depend on the macroscopic viscosity of the system and is controlled by the local microscopic viscosity, which is close to that of the solvent of the solution immobilized in the gel network.

According to eq 8, the diffusivity of a species is proportional to the temperature of the system. We have examined the
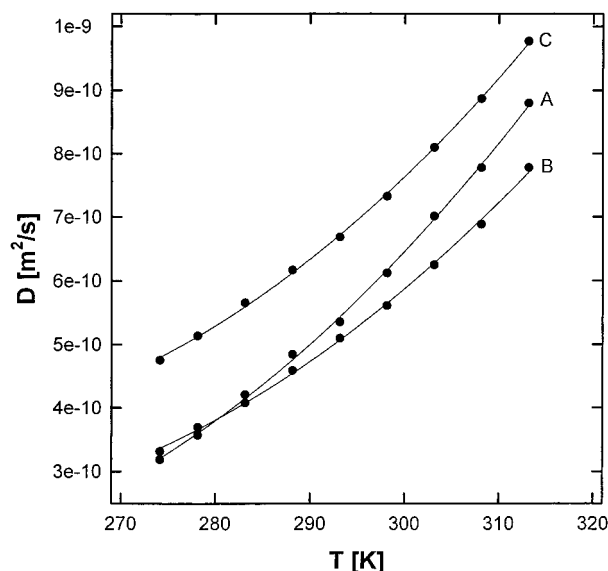
Figure 4. Temperature dependence of 1,1′-ferrocenedimethanol diffusion coefficient in various media: (A) salt-free sodium polyacrylate gel, (B) sodium polyacrylate gel with 0.1M LiClO$_4$, and (C) 0.1M aqueous solution of LiClO$_4$.

temperature dependence of 1,1′-ferrocenedimethanol in the 1% polyacrylate gel with and without added salt, and in aqueous solution. The results are presented in Figure 4. For the temperature range from 1 to 40 °C, all dependencies can be fitted by second order polynomial equations, i.e., $D = 1.27 \times 10^{-13}T^2 - 6.02 \times 10^{-11}T + 7.30 \times 10^{-9}$, $D = 1.08 \times 10^{-13}T^2 - 5.24 \times 10^{-11}T + 6.58 \times 10^{-9}$, and $D = 1.29 \times 10^{-13}T^2 - 6.30 \times 10^{-11}T + 8.07 \times 10^{-9}$ (D in m²/s, T in K) for salt-free polyacrylate gel (curve A), polyacrylate gel with 0.1 M LiClO$_4$ (curve B), and 0.1 M aqueous solution of LiClO$_4$ (curve C), respectively. The correlation coefficient departed from 1 by less than 0.001. The differences between diffusivities of the probe in 0.1 M aqueous solution of LiClO$_4$ (curve C) and the polyacrylate gel with 0.1 M LiClO$_4$ (curve B) are almost constant for the temperature range studied.

Thallium (I) Cations. To investigate electrostatic interactions in polyacrylate gels we selected Tl$^+$ cation as an electroactive charged probe. Since the polyacrylate network is negatively charged we expect strong attractive interactions with any cations in the system. Thallium (I) was used as a probe in sodium polyacrylate gels or as a native counterion in thallium polyacrylate gels. In a probe mode, a low concentration (2 mM) of TlNO$_3$ was added to the sodium polyacrylate gels and, in the native counterion mode, poly(acrylic acid) was neutralized with solution of TlOH. The diffusion coefficients of Tl$^+$ for both cases was determined from steady-state currents of thallium cation reduction at mercury film disk electrodes, according to eq 7.

Steady-state voltammograms of Tl$^+$ reduction in sodium polyacrylate gels were very well defined and reproducible, with coefficient of variation (calculated for five voltammograms) of less than 6%. Since the measurements were performed in systems of various conductances (various amounts of added NaOH or in other words various degree of PAA neutralization), we had to take into account the contribution of migration to reduction currents of Tl$^+$.[48] Assuming that the magnitude of the contribution of migrational flux of an electroactive probe to the measured current is identical in a gel and in aqueous solution, if the conductances of the two media are the same, the ratio of the diffusion coefficient of this probe in a gel D to that in a solution D^0 can be estimated using the following

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TABLE 2: Transport Properties of Tl$^+$ in Various Media (T = 25 °C)

electroactive probe	medium	D/D^0
Tl$^+$ (TlNO$_3$)	polyacrylate (Na$^+$) gels, no electrolyte	0.99[a]
		0.62[b]
		0.29[c]
		0.26[d]
		0.25[e]
Tl$^+$ (TlOH)	polyacrylate (Tl$^+$) gels, no electrolyte	0.29[f]
		0.30[g]
	polyacrylate (Tl$^+$) gels + 0.1 M LiClO$_4$	0.31[f,h]

[a] 1% PAA + 16.7 mM NaOH (refers to part I of the conductometric titration curve). [b] 1% PAA + 60.0 mM NaOH (refers to part II of the conductometric titration curve). [c] 1% PAA + 89.1 mM NaOH (refers to part II of the conductometric titration curve). [d] 1% PAA + 120.0 mM NaOH (refers to part III of the conductometric titration curve). [e] 1% PAA + 157.5 mM NaOH (refers to part III of the conductometric titration curve). [f] 1% PAA + 51.1 mM TlOH. [g] 1% PAA + 70.0 mM TlOH. [h] Formation of gels strongly inhibited by excess LiClO$_4$.

expression:

$$D/D° = (I_{ss}(gel)\, c_{Tl+}{}^b(aq))/(I_{ss}(aq)\, c_{Tl+}{}^b(gel)) \qquad (9)$$

where $I_{ss}(gel)$, $I_{ss}(aq)$, and $c_{Tl+}{}^b(gel)$, $c_{Tl+}{}^b(aq)$ are steady-state currents measured in the polyacrylate gel and aqueous solution of LiClO$_4$ at a given microdisk electrode and bulk concentrations of Tl$^+$ ions in the gel and aqueous solution of LiClO$_4$, respectively. To adjust the conductance of aqueous solutions to those of gels, appropriate amount of 1 M LiClO$_4$ was added to aqueous solutions of Tl$^+$.

Table 2 presents our experimental results for normalized diffusion coefficient of Tl$^+$ probe D/D^0 in sodium polyacrylate gels of various degree of neutralization of poly(acrylic acid) (various amount of added NaOH). Note, that diffusion coefficients determined voltammetrically, and listed in Table 2, are effectively observed diffusion coefficients. They result from mobilities of condensed and uncondensed counterions as well as from the mobility of large gel particles. As one can see, the transport of the Tl$^+$ probe depends strongly on the degree of neutralization of PAA, or in other words on the charge separation distance b in the polyion, see eqs 4–6. For low concentration of added NaOH (large values of charge separation distance), the diffusion coefficient of Tl$^+$ in sodium polyacrylate gels is very close to that observed in aqueous solutions without polymer. As the charge separation distance in polyacrylate units decreases due to the addition of NaOH, the diffusion coefficient of Tl$^+$ in the gel decreases. This illustrates stronger electrostatic interactions between negatively charged polymer network and probe cations.

We compared our experimental results for Tl$^+$ probe transport in sodium polyacrylate gels with the predictions of Manning's theory for polyelectrolytes.[39,40] However, since there is a dearth of models for three-dimensional networks of ionic polymers, we use the theoretical treatment for polyionic solutions. Comparison of experimental and theoretical results is presented in Figure 5. As one can see, according to Manning's theory there are three segments in the theoretical dependence (similarly to conductometric titration curves). For low concentration of added NaOH and consequently large values of b, the charge density of ionic polymer ξ is less than 1, and, according to Manning's theory, no condensation of counterions is expected (they are subject to Debye–Hückel interactions with polyions). In this region (equivalent to region I of a conductometric titration
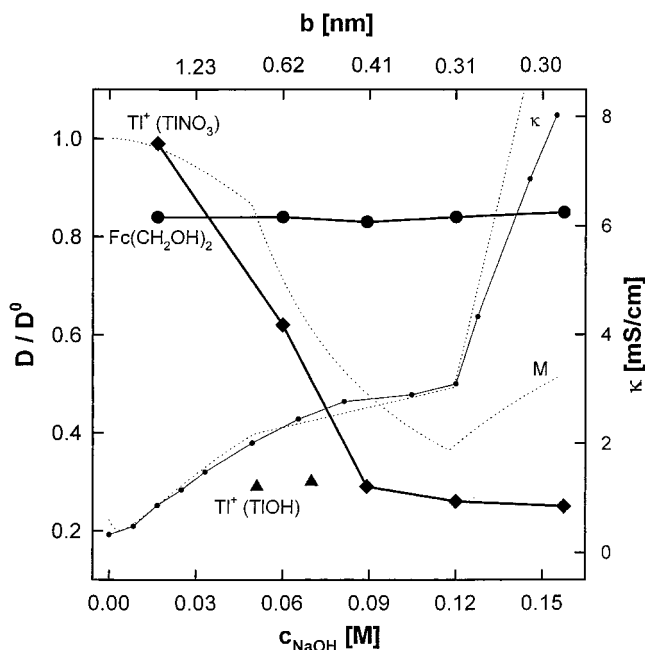

Figure 5. Dependencies of normalized diffusion coefficients determined voltammetrically (solid lines and symbols) for chosen electroactive probes in sodium polyacrylate gels with respect to concentration of added NaOH. The thinner solid line presents appropriate conductometric titration curve. The dotted lines refer to theoretical predictions according to (M) Manning's theory and calculated (κ) conductometric titration curve.

curve), the diffusion coefficient of counterions is described by eq 14 from the Appendix.

With an increase in NaOH concentration, the charge density of the polymer ξ becomes greater than 1, and counterions are assumed to condense on polyionic chains as required to avoid exceeding the critical charge density ξ_c, for monovalent counterions $\xi_c = 1$.[39,40] This region of NaOH concentration is equivalent to region II of a conductometric titration curve. When the degree of neutralization of PAA α reaches and exceeds 100%, the charge density of the polyion reaches a constant value. Therefore, any subsequent addition of NaOH acts as an addition of a neutral electrolyte (this is equivalent to region III of a conductometric titration curve).

As one can see from Figure 5, experimental results for the Tl$^+$ probe in sodium polyacrylate gels are very close to the theoretically predicted only for very low values of charge density (or in other words large values of b). As the charge density of polyion increases, significant differences between the postulated theoretical behavior of solutions of polymers and polymeric gels can be observed. The diffusion coefficient of Tl$^+$ in gels is smaller than that predicted theoretically for equivalent polyionic solutions; the electrostatic interactions in gels are apparently stronger that those in polyelectrolyte solutions. This is probably due to the three-dimensional structure of a gel and, consequently, larger charge density of the entire system than that for individual polyionic units.

To show the very important role of metal counterions from added base in the structure of polyacrylate gels, we have examined the voltammetric behavior (and consequently transport behavior, see eq 7) of Tl$^+$ cations in gels formed by neutralization of PAA solution with solution of TlOH. Steady-state voltammograms of Tl$^+$ reduction at mercury film disk microelectrodes in thallium polyacrylate gels were of the same quality as those from sodium polyacrylate gels, with coefficient of variation (calculated for five voltammograms) of less than 6%.

It should be pointed out here that the contribution of migration to the total reduction currents of Tl$^+$ in thallium polyacrylate gel (Tl$_x$(PA), $x \gg 1$) is negligible even without excess added salt.[48] The normalized diffusion coefficients of Tl$^+$ cations D/D^0 in thallium polyacrylate gels without and with LiClO$_4$ electrolyte are presented in Table 2 and Figure 5. However, as with sodium polyacrylate gels, it should be mentioned here that the large excess LiClO$_4$ inhibits formation of a solid gel structure and polymeric network becomes almost liquid. To determine D^0-values, the conductance of aqueous solutions was adjusted to that of the gels by addition of an appropriate amount of 1 M LiClO$_4$. As one can see, the diffusion coefficient of Tl$^+$ in salt-free thallium polyacrylate gels of low degree of neutralization (charge density ξ slightly greater than 1) is significantly lower than that in sodium polyacrylate gels, with Tl$^+$ as a probe. This illustrates how strongly transport properties of thallium cations depend on the source of those ions. It also shows how strongly those counterions are attracted by polyanions forming the thallium polyacrylate network. In the presence of large concentration of salt, LiClO$_4$, in polyacrylate solution neutralized with TlOH, a very small increase in Tl$^+$ diffusion coefficient is observed. This is probably due to the replacement of a fraction of Tl$^+$ cations by added Li$^+$ cations.

Concluding Remarks

We have shown that for low concentrations of polyacrylate in a gel, the diffusion of small uncharged molecules is mainly influenced by the composition of the solution immobilized in the gel network. Therefore, transport properties of uncharged molecules in such systems can be predicted based on the solution composition, mainly on its viscosity. However, transport properties of ions in polyacrylate gels depend strongly on the charge density of the polymer. Since the amount of a strong base added to PAA determines the charge separation distance and charge density of the polyanion, the strength of electrostatic interactions between simple ions and polyions in PAA gels depends on the degree of neutralization of the polyacid. We have shown that for very low degree of neutralization of PAA and, consequently, for very low charge density of that ionic polymer, the diffusion coefficient of the probe cation Tl$^+$ is identical to that in solution without polymeric network. As the charge density of polyacrylate network increases with addition of NaOH, the diffusion coefficient of thallium probe cation decreases due to electrostatic interactions with the polymeric network. While is has been shown previously that the low concentration of an ionic polymer in a gel does not significantly influence transport properties of uncharged molecules in that medium,[35,47] our experimental results for the probe cation Tl$^+$ show for the first time the dependence of transport properties of the probe cation on the wide range of charge densities of anionic gels. Since the experimental results suggest that transport properties of ions, both counter- and coions, in ionic polymeric gels can be modified by selection of appropriate charge density of the polymer, they might have significant practical consequences in gel-based separation techniques and in the development of gel-based sensors. Additionally, polyacrylate gels with their wide range of available charge densities can mimic behavior of other ionic gel systems, and can be used as simple and inexpensive models. Transport properties of ions in polyionic gels and their dependence on charge density of gels should also vary with the charge of the diffusing ions. Studies on diffusional behavior of multicharged cations in anionic polymeric gels are underway in our laboratory.

Figure 5 summarizes experimental and theoretical results for voltammetric and conductometric measurements by presenting the dependencies of normalized diffusion coefficients of uncharged and charged probes and the conductivity of gels on concentration of added base. The former empirical relation for the charged probe cation is compared with the theoretical predictions according to Manning's line charge theory for monovalent counterions in solutions of ionic polymers.

It has been shown for several examples of polyelectrolytes that Manning's line charge model predicts accurately diffusion of counterions in solutions of polyelectrolytes.[31,32] The relatively large differences between theoretical predictions and experimental results for polyacrylate gels observed for large concentrations of NaOH are probably due to stronger electrostatic interactions in three-dimensional networks of ionic gels than in polyelectrolyte solutions. Since there is a dearth of theoretical models for three-dimensional polyionic systems, we were not able to compare our experimental results with any other theory.

An interesting phenomenon has been observed in thallium polyacrylate gels from PAA neutralized (and gelled) by TlOH; the diffusion coefficient of thallium counterion was very low even for a low degree of neutralization of the polyion and its value was close to that of Tl$^+$ probe in high-charge-density sodium polyacrylate gels (see Figure 5). This result illustrates how strongly transport properties of thallium cations depend on their role in polymeric network (probe ions or native counterions) and it shows that polyacrylate gels can be treated as three-dimensional networks consisting of negatively charged polyacrylate chains linked by strongly immobilized metal counterions (Na$^+$ or Tl$^+$) of the strong base used for their neutralization and swollen by a solution (or solvent). To the best of our knowledge this is first direct experimental evidence of such a structure.

The new method proposed for calculation of the conductivity of polyacrylate gels, based on the summation of partial conductivities of all types of ions and coupled to chemical (acid–base) equilibrium is very general, and it can be applied for any analogous ionic polymer systems to predict their conductomeric properties for any degree of neutralization or any charge density of polyion. Additionally, this model can be applied not only for hydrogels but for gels based on mixed or nonaqueous solvents. Therefore, the method may be extremely useful to predict conductivities of nonaqueous polyionic gels for gel-based batteries or other power sources.

The theoretical predictions for conductivity of polyacrylate gels agree well with experimental measurements especially for nonzero values of counterions mobility along the polyions. Therefore, this approach can be used for the determination of diffusion coefficient of counterions condensed onto polyion chains (not only free to diffuse in solution).

Appendix

Concentration of ions, their diffusion coefficients, and conductivities of polyacrylate gels can be derived from eqs 1–6 for all three regions of titration described in the section Conductivity of Polyacrylate Gels.

Region I.

$$c_{H^+}^{u} = c_{H^+} \cong K_a \frac{1-\alpha}{\alpha} \qquad (10)$$

where α is given by eq 5

$$c_{M1^+}^u = c_{M1^+} = c_b \tag{11}$$

$$c_{M2^+}^u = c_{M2^+} = c_s \tag{12}$$

$$c_{A2^-}^u = c_{A2^-} = c_s \tag{13}$$

$$D_i^u = D_i^0 \left(1 - \frac{1}{3}A\left(\xi, \frac{c_{PE}}{c_s}\right)\right) \quad i = H^+, M1^+, M2^+, A2^- \tag{14}$$

where A is given by

$$A(x, y) = \sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty} {}_{(m,n)\neq(0,0)}[\pi x^{-1}(m^2 + n^2) + 1 + 2y^{-1}]^{-2} \tag{15}$$

and

$$c_{PE} = c_{H^+} + c_b \tag{16}$$

$$\kappa = \frac{F^2}{RT}(c_{H^+}^u D_{H^+}^u + c_{M1^+}^u D_{M1^+}^u + c_{M2^+}^u D_{M2^+}^u + c_{A2^-}^u D_{A2^-}^u) \tag{17}$$

Region II.

$$c_{H^+}^c = x_{H^+}\left(1 - \frac{1}{\xi}\right)c_{PE} \tag{18}$$

$$c_{M1^+}^c = x_b\left(1 - \frac{1}{\xi}\right)c_{PE} \tag{19}$$

$$c_{M2^+}^c = x_s\left(1 - \frac{1}{\xi}\right)c_{PE} \tag{20}$$

where c_{PE} is given by eq 16, $x_{H^+} = c_{H^+}/(c_{H^+} + c_b + c_s)$, $x_b = c_b/(c_{H^+} + c_b + c_s)$, $x_s = c_s/(c_{H^+} + c_b + c_s)$, and c_{H^+} is given by eq 10

$$c_{H^+}^u = c_{H^+} - c_{H^+}^c \tag{21}$$

$$c_{M1^+}^u = c_b - c_{M1^+}^c \tag{22}$$

$$c_{M2^+}^u = c_s - c_{M2^+}^c \tag{23}$$

$$c_{A2^-}^u = c_{A2^-} = c_s \tag{24}$$

$$D_i^u = D_i^0 \left(1 - \frac{1}{3}A\left(1, \frac{c_{PE}}{\xi c_s}\right)\right) \quad i = H^+, M1^+, M2^+, A2^- \tag{25}$$

$$D_i^c = kD_i^0$$
$$i = H^+, M1^+, M2^+, \text{ and } k \text{ is adjustable parameter } (k \geq 0) \tag{26}$$

$$\kappa = \frac{F^2}{RT}(c_{H^+}^u D_{H^+}^u + c_{M1^+}^u D_{M1^+}^u + c_{M2^+}^u D_{M2^+}^u + c_{A2^-}^u D_{A2^-}^u + c_{H^+}^c D_{H^+}^c + c_{M1^+}^c D_{M1^+}^c + c_{M2^+}^c D_{M2^+}^c) \tag{27}$$

Region III.

$$c_{M1^+}^c = x_b\left(1 - \frac{1}{\xi}\right)c_{PE} \tag{28}$$

$$c_{M2^+}^c = x_s\left(1 - \frac{1}{\xi}\right)c_{PE} \tag{29}$$

where

$$c_{PE} = N_{tot}c_{PAA}^0 - \tilde{c}_{OH^-} \tag{30}$$

$$\tilde{c}_{OH^-} \cong \sqrt{\frac{K_w}{K_a}N_{tot}c_{PAA}^0} \tag{31}$$

and

$$x_b = c_b/(c_s + c_b), \, x_s = c_s/(c_s + c_b)$$

$$c_{M1^+}^u = c_b - c_{M1^+}^c \tag{32}$$

$$c_{M2^+}^u = c_s - c_{M2^+}^c \tag{33}$$

$$c_{OH^-}^u = c_b - c_{PAA}^0 N_{tot} + \tilde{c}_{OH^-} \tag{34}$$

$$c_{A2^-}^u = c_s \tag{35}$$

$$D_i^u = D_i^0 \left(1 - \frac{1}{3}A\left(1, \frac{c_{PE}}{\xi(c_s + c_{OH^-}^u)}\right)\right)$$
$$i = M1^+, M2^+, OH^-, A2^- \tag{36}$$

$$D_i^c = kD_i^0$$
$$i = M1^+, M2^+, \text{ and } k \text{ is adjustable parameter } (k \geq 0) \tag{37}$$

$$\kappa = \frac{F^2}{RT}(c_{M1^+}^u D_{M1^+}^u + c_{M2^+}^u D_{M2^+}^u + c_{OH^-}^u D_{OH^-}^u + c_{A2^-}^u D_{A2^-}^u + c_{M1^+}^c D_{M1^+}^c + c_{M2^+}^c D_{M2^+}^c) \tag{38}$$

Subscripts $M1^+$, $M2^+$, and $A2^-$, denote counterion 1 (from the strong base, here Na^+), counterion 2 (from added electrolyte, here Li^+), and coion 2 (here ClO_4^-), respectively, superscripts c and u denote condensed and uncondensed species, K_a is a dissociation constant of PAA (2.51×10^{-5}),[49] K_w is the ionic product of water, D_i^0 is diffusion coefficient of infinitely diluted ith ionic species in water, c_{PE} is equivalent concentration of polyion (i.e., molar concentration of polyion times number of ionized groups per polyion), $\tilde{c}_{OH^-}$ is concentration of OH^- ions from hydrolysis of polyacrylate, and x_{H^+}, x_b, and x_s refer to molar fractions of hydrogen ions, added base, and neutral electrolyte, respectively. It has been assumed that the initial volume of PAA solution is significantly larger than the total volume of the added base.

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