Determination of Li$^+$ Self-Diffusion Coefficients in an Aqueous Suspension of Sulfonated Polystyrene Latex by Pulsed-Field-Gradient, Spin-Echo NMR

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The self-diffusion coefficients of ^{7}Li$^+$ in a suspension of sulfonated polystyrene latex particles is determined by pulsed-field-gradient, spin-echo NMR over a wide range of electrolyte concentrations. The self-diffusion coefficient of the Li$^+$ counterion in the suspension without electrolyte is significantly less than that found in a solution of LiClO$_4$ at the same bulk concentration. This suggests that a large fraction of the Li$^+$ counterions are electrostatically bound to the large latex particles. The effective charge on the particles is inferred from this measurement. The self-diffusion coefficient of Li$^+$ increases upon the addition of NaClO$_4$ to the deionized suspension. Measuring selectively the dependence of Li$^+$ diffusion on the amount of added electrolyte characterizes the ion-exchange behavior of the latex suspension. The self-diffusion coefficients determined by NMR agree with prediction of the nonlinear Poisson−Boltzmann equation and gradient-diffusion coefficients of hydrogen counterion determined in the same latex by steady-state voltammetry.

Introduction

Solutions of polyelectrolytes and charge-stabilized suspensions of colloidal particles are an important class of natural and synthetic materials.[1−9] A few examples of these systems are latex paint, milk, liposomes, micelles, globular proteins, ion-exchange resins used to purify water, DNA, humic acids found in soils, chondroitin sulfate found in mammalian connective tissues, polyelectrolytes used as thickeners in foods, colloidal clays found in natural waters, eukaryotic cells, and various liquid crystals. A property common to all of these materials is the large asymmetry with respect to size and charge of the electrolyte ions (or aggregates). For example, the model system used in this study contains monodisperse latex spheres, suspended in water, having a radius of 44 nm and approximately 12 000 negative charges on each particle, arising from sulfonate moieties, and Li$^+$ counterions in solution. This gives rise to asymmetries of approximately 12 000:1 and 360:1 with respect to charge and radius, respectively, between the negatively and positively charged species. The larger, more highly charged entity is termed a macroion.

An important consequence of this asymmetry is that, even in dilute solutions or suspensions, the small counterions accumulate near the surface of the macroion, thus depleting the concentration of counterions far from the macroion.[10,11] This distinguishes macroionic systems from more symmetric electrolytes such as LiClO$_4$, in which ion-pairing occurs only at much higher concentrations of electrolyte.[12] This ability of the macroion to bind counterions can be understood in terms of either a specific, site-binding model[13] or a nonspecific, purely electrostatic interaction, which can be described quantitatively by the nonlinear Poisson−Boltzmann equation[14] or by Monte Carlo simulations.[5,15]

Regardless of the mechanism of ion binding, the consequence is that the electrostatic repulsion between neighboring macroions is screened by the intervening counterions, which partially

neutralize the charge on the macroion. This effect has been quantified recently for a variety of spherical macroions over a wide range of experimentally accessible parameters.[11] Counterion binding not only regulates interactions between macroions; it diminishes the diffusion coefficient of the counterion, since, due to the large asymmetry with respect to size, the macroion is static on the time scale of motion of the counterion.[16−20]

The most pronounced suppression of counterion diffusion occurs in deionized macroionic solutions or suspensions, in which the only ions present are the macroion and its accompanying counterion. The main effect of adding additional electrolyte is ion exchange of the bound counterion with added ion of the same charge, which increases the diffusion coefficient of the counterion in proportion to the mole fraction of bound counterion released. Values of the diffusion coefficient of the counterion in a macroionic system without added electrolyte can be used to predict the ion-exchange behavior of the system over a wide range of concentration of added electrolyte.[18,20] Furthermore, the diffusion coefficient value of the counterion in the absence of added electrolyte can be used to infer the effective charge responsible for interactions between macroions. Definition and measurement of the effective charge have been the subject of a large body of theoretical and experimental work for almost 50 years.[5]

We have recently carried out an investigation of the diffusion behavior of hydrogen ion in the presence of polystyrene latex particles using voltammetry at a microelectrode. The experimental results agree with the predictions of the nonlinear Poisson−Boltzmann equation and a simple, semiempirical model over a wide range of concentration of added electrolyte.[20]

The purpose of this study is to show the equivalence of the gradient- and self-diffusion coefficients determined by the electrochemical and NMR methods, respectively. This work parallels closely a previous comparative study of the voltammetric and NMR methods that reported the diffusion behavior

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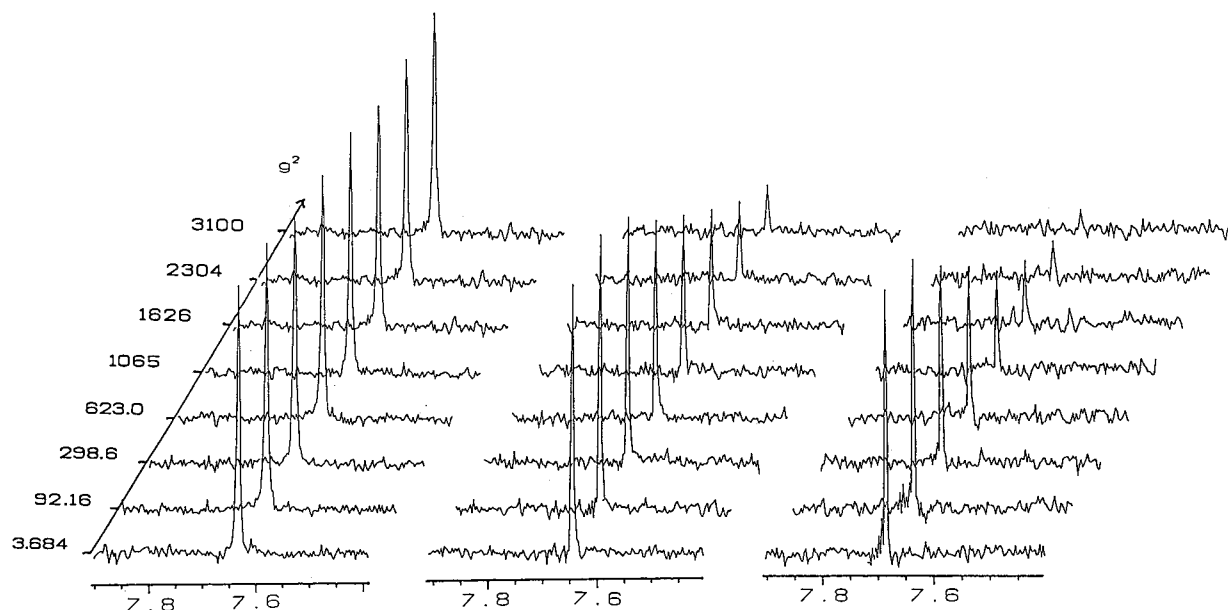
Figure 1. Experimental PFGSE-NMR spectra for $^7Li^+$ as counterion to the latex particles. The influence of added electrolyte, $[NaClO_4]/mM$, on the spin−echo amplitude, A, as a function of g^2 (G^2 cm^{-2}): (a) 0.012; (b) 2.132; (c) 213.2.

of Tl^+ in the presence of a linear polyelectrolyte, poly-(styrenesulfonic acid).[18]

Experimental Methods

Latex Preparation. The synthesis and characterization of the latex suspension have been discussed in detail.[20] All of the water used to prepare solutions had a resistance of 18 MΩ (Milli-Q, Millipore). Latex volume fractions, ϕ, were determined gravimetrically using a value for polystyrene density of 1.05 g/cm^3. The particles are monodisperse spheres with radii, a, of 44 nm.

For this study, the surface charge density on the particles was -8.00 $\mu C/cm^2$ (12 150 elementary charges), as determined by two conductometric titrations of the acid form of the latex with NaOH. Conductivity measurements were carried out using a dip cell conductivity probe (Fisher). We prepared the latex with Li^+ as counterion by adding a freshly prepared aqueous solution of 0.01 M LiOH to the acid form of the latex ($\phi = 1.92\%$). Approximately 10% excess LiOH was added to ensure complete replacement of hydrogen counterion with Li^+. At this point, iridescent crystals formed, but only upon resting for several minutes (i.e., it was close to the order−disorder transition).[21] The sample was then centrifuged and resuspended with ultrapure water three times, after which the conductivity of the supernatant was only 1.3 $\mu S/cm$. This procedure produced a latex suspension with Li^+ as counterion to the particles. The mean concentration of the Li^+ counterion in each sample was determined from

$$[counterion] = 3\sigma\phi/Fa(1 - \phi) \qquad (1)$$

where σ is the surface charge density on the particle corresponding to Li^+ (-8.00 $\mu C/cm^2$, determined from the titration) and F is Faraday's constant (96 485 C/(mol e)).[2] The deionized sample was prepared immediately before the experiment. The concentration of adventitious electrolyte in this sample was estimated to be 12 μM, as determined from the measured conductivity of 1.5 $\mu S/cm$ in the supernatant.

NMR Experiments. All of the pulsed-field-gradient, spin−echo (PFGSE) NMR experiments were carried out at 25 °C using a Bruker AVANCE 500 MHz spectrometer (1996) with

an Oxford narrow bore magnet (1989), SGI INDY host workstation, and XWINNMR software. The instrument is equipped with a three-channel gradient control unit (GRASP III), variable-temperature unit, precooling and temperature stabilization unit, and three frequency channels with waveform memory and amplitude shaping unit. A 5-mm i.d. $^1H/BB$ (^{109}-Ag−^{31}P) triple-axis gradient probe (ID500−5EB, Nalorac Cryogenic Corp.) was used for all ^7Li diffusion measurements.

^7Li is a quadrupolar nucleus (spin of $^3/_2$) with a natural abundance of 92.58% and gyromagnetic ratio of 1.04×10^8 $rad \cdot s^{-1} \cdot T^{-1}$ (relatively low compared to ^1H).[22] Despite this, it gave a very sharp line ((1 Hz fwhm) with a large signal intensity, using a sweep width of 4664 Hz. The NMR probe was tuned to the ^7Li frequency (194.37 MHz in the 500 MHz spectrometer (^1H frequency, 500.13 MHz)). The probe is equipped with actively shielded gradient coils and was calibrated against a 2.23 mM solution of $LiClO_4$, using g as an adjustable parameter in eq 2 to fit the known diffusion coefficient of Li^+ (1.02×10^5 cm^2/s, calculated from eq 3 and the diffusion coefficient at infinite dilution).[23] The maximum gradient strength was about 64 G/cm for the y axis.

The longitudinal eddy current (LED) pulse sequence was used in all PFGSE-NMR diffusion experiments.[24,25] This pulse sequence was used since relaxation occurs largely via T_1 rather than the faster T_2, and a settling time, T_e, can be used to minimize residual eddy currents from the gradient pulse. The gradient pulse interval, Δ, and gradient duration, δ, were 350 and 5 ms, respectively. The settling time was 10 ms and the relaxation delay was 1 s. Typically, 2048 scans were collected for individual spectra. The pulsed-field gradient was applied in the y direction for the latex samples and in both the y and z directions for $LiClO_4$ solutions used for calibration. The gradient strength in a series of ^7Li experiments was incremented from 1.9 G/cm to about 56 G/cm in 10 increments. The signal decayed approximately 1 decade and 10% for the samples with the largest and smallest diffusion coefficients, respectively (see Figure 1). Accurate diffusion coefficients were obtained for seven samples from the slopes of ln (A/A_0) vs g^2, determined by least-squares regression. Quality of the linear regression is expressed in terms of uncertainty in D in Table 1. The actual instrument time for one measurement of diffusion coefficient

Li$^+$ Self-Diffusion Coefficients

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TABLE 1: Self-Diffusion Coefficients of Li$^+$ in the Presence of the Latex Particles Determined by PFGSE-NMR

ϕ^a (%)	[Na$^+$] (nM)	log X^c	D^d ($\times 10^5$ cm^2 s^{-1})	δD^e	$D/D^{\circ\,f}$
3.68	0.012	−2.26	0.064	0.030	0.062
3.60	0.070	−1.48	0.141	0.027	0.136
3.60	0.702	−0.48	0.375	0.038	0.363
3.23	2.132	0.05	0.599	0.051	0.583
3.60	7.037	0.52	0.859	0.084	0.844
3.23	213.2	2.05	0.831	0.092	0.906

^{a} Measured gravimetrically. ^{b} Known amount of added NaClO$_4$. ^{c} Calculated from $X = $ [Na$^+$]/[Li$^+$] where [Li$^+$] is determined from eq 1; $\sigma = -8.00\ \mu$C/cm^2. ^{d} Measured from slope of ln (A/A_0) vs g^2, eq 2. ^{e} Estimated from $\delta D/D = \delta D_s/D_s + \delta D_r/D_r$ where s refers to sample and r to the reference value; δD_s and δD_r are the confidence intervals at 95% confidence, eight degrees of freedom, of the slopes of semilogarithmic plots of eq 2 expressed in units of D. ^{f} Calculated from D and eq 3.

by NMR was 12 h. The voltammetric technique required about 3 min per measurement.

Results and Discussion

Pulsed-Field-Gradient, Spin-Echo (PFGSE) NMR. The investigation of counterion binding in macroionic solutions or suspensions using NMR can be carried out by chemical shift,[13] quadrupolar relaxation, or PFGSE studies.[16,26] In this study we use the PFGSE method to measure the self-diffusion coefficient of ^{7}Li$^+$ as the counterion to a highly charged latex particle. The influence of added NaClO$_4$ on the diffusion coefficient of Li$^+$ is determined. The reference system is an aqueous solution of LiClO$_4$. The results of this experiment allow a direct comparison with predictions of the Poisson−Boltzmann equation and with the gradient-diffusion coefficient of hydrogen ion determined previously in the same latex by voltammetry at a microelectrode.[20] Lithium is a favorable nucleus because it has a high relative receptivity compared with other univalent cations and a narrow line width due to its relatively small electric quadrupole moment (i.e., slow T_2 relaxation for a spin $^3/_2$ nucleus).[22,27] In addition, the sample is easily prepared by neutralization of the acid form of the latex with LiOH.

In addition to the usual static magnetic field, the basic PFGSE experiment applies a linear gradient in the magnetic field strength, g, across the sample in two square pulses of brief duration, δ. In the LED experiment, there is a 90° (pulse immediately before and after the first gradient pulse and one immediately before the second gradient pulse. The second gradient pulse begins at time Δ after the beginning of the first gradient pulse. The experiment concludes with two further 90° pulses to allow the last gradient pulse to settle.

The first gradient pulse endows the spins in different regions of the sample with different precession frequencies, depending on the local field strength. This dephases the magnetization in the rotating xy frame during the gradient pulse, labeling the position of the spins with the degree of dephasing, and causing a loss of transverse magnetization.[16,27]

In the absence of diffusive motion during the gradient pulse interval, Δ, the spins are refocused completely, except for relaxation decays, giving maximum recovery of the spin-echo amplitude at the conclusion of the sequence. If, however, the translational motion of spins due to self-diffusion is significant in the direction of the field gradient during Δ, then, upon refocusing, some of the magnetization is lost. This gives rise to an attenuated spin-echo signal, A, described by

TABLE 2: Gradient-Diffusion Coefficients of H$_3$O$^+$ in the Presence of Latex Particles Determined by Voltammetry

ϕ^a (%)	[Li$^+$]^b (mM)	log X^c	D^d ($\times 10^5$ cm^2 s^{-1})	$D/D^{\circ\,e}$
0.710	0.001	−2.59	0.223	0.024
0.592	0.001	−2.51	0.270	0.029
0.474	0.001	−2.42	0.372	0.040
0.356	0.001	−2.29	0.428	0.046
0.237	0.001	−2.11	0.372	0.040
0.710	0.009	−1.65	0.613	0.066
0.592	0.015	−1.35	1.21	0.130
0.356	0.011	−1.25	1.12	0.121
0.710	0.028	−1.15	1.28	0.138
0.237	0.013	−1.00	1.02	0.110
0.592	0.046	−0.85	1.73	0.186
0.356	0.035	−0.75	2.54	0.274
0.710	0.087	−0.65	2.30	0.248
0.237	0.042	−0.49	2.60	0.280
0.474	0.101	−0.41	2.97	0.320
0.592	0.145	−0.35	3.44	0.371
0.356	0.110	−0.25	4.01	0.432
0.710	0.277	−0.15	4.16	0.449
0.474	0.260	0.00	4.91	0.530
0.237	0.130	0.00	5.01	0.540
0.592	0.460	0.15	5.79	0.626
0.356	0.339	0.24	6.23	0.673
0.710	0.874	0.35	6.51	0.705
0.237	0.410	0.50	7.22	0.780
0.474	0.861	0.52	7.29	0.790
0.592	1.453	0.65	7.66	0.832
0.356	1.072	0.74	8.20	0.889
0.710	2.765	0.85	8.12	0.885
0.474	2.484	0.98	8.63	0.940
0.237	1.298	1.00	8.66	0.940
0.592	4.595	1.15	8.75	0.958
0.356	3.391	1.24	8.82	0.963
0.710	8.745	1.35	8.81	0.971
0.237	4.104	1.50	9.24	1.010
0.474	8.418	1.51	8.99	0.990
0.592	14.531	1.65	8.37	0.929
0.356	10.725	1.74	8.47	0.936
0.710	27.653	1.85	7.63	0.857
0.237	12.977	2.00	9.30	1.030
0.474	26.621	2.01	8.20	0.920

^{a} Measured gravimetrically. ^{b} Known amount of added LiClO$_4$. ^{c} Calculated from $X = $ [Li$^+$]/[H$_3$O$^+$], where [H$_3$O$^+$] is determined from eq 1; $\sigma = -7.73\ \mu$C/cm^2. ^{e} Calculated from D and eq 3.

the expression[28]

$$A/A_0 = \exp\{-\gamma^2 g^2 \delta^2 (\Delta - \delta/3)D\} \tag{2}$$

In eq 2, A_0 is the spin-echo amplitude in the absence of the gradient pulses, γ is the gyromagnetic ratio of ^{7}Li, and D is the self-diffusion coefficient of Li$^+$.

Inspection of eq 2 shows that, for a given strength of the field gradient, the recovered spin-echo amplitude decreases exponentially with the self-diffusion coefficient of Li$^+$. The value of the self-diffusion coefficient of Li$^+$ is found from the slope of a plot of ln (A/A_0) vs g^2. Figure 1 shows typical spectra for ^{7}Li as a function of g^2 for three latex samples, each with a different concentration of NaClO$_4$. Clearly, the self-diffusion coefficient of Li$^+$ in the presence of the latex particles decreases as electrolyte is removed from the suspension.

Table 1 shows the self-diffusion coefficients of Li$^+$ in the latex suspension at various concentrations of NaClO$_4$. Table 2 gives the complementary data for the gradient-diffusion coefficients of H$_3$O$^+$ determined voltammetrically in the acid form of the latex at various concentrations of LiClO$_4$.[20]

The effects of the latex particles on the diffusion behavior of each ion are compared by normalizing to the value unperturbed by the macroion. The diffusion coefficient of the ion in the

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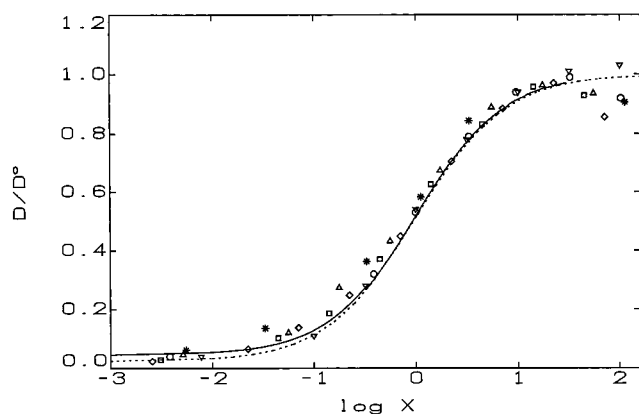
Figure 2. Normalized self-diffusion coefficient ratios of Li$^+$ in the latex suspension (*) determined by PFGSE-NMR and gradient-diffusion coefficients of H$_3$O$^+$ in the same suspension at volume fractions, ϕ/% of: ($\triangledown$) 0.237; ($\triangle$) 0.356; ($\bigcirc$) 0.474; ($\square$) 0.592; ($\diamondsuit$) 0.710. The amount of added electrolyte is expressed as $X = $ [Na$^+$]/[Li$^+$] and $X = $ [Li$^+$]/[H$_3$O$^+$] for the NMR and voltammetric data, respectively. See Tables 1 and 2. Theoretical models: (—) nonlinear Poisson−Boltzmann equation; (- - -) semiempirical equation.

presence of the latex is denoted by D. The symbol $D°$ is the diffusion coefficient of the ion in an aqueous solution of 1:1 electrolyte, without the latex. This diffusion coefficient value is corrected for effects of activity by using the Debye−Hückel relation[12]

$$D° = D^\infty(1 - 0.256I^{1/2}) \qquad (3)$$

where I is the molar ionic strength of 1:1 electrolyte and D^∞ is the value of the diffusion coefficient at infinite dilution (9.3 × 10^{-5} and 1.03 × 10^{-5} cm^2/s for H$_3$O$^+$ and Li$^+$, respectively).[23] Viscosity does not change enough over the experimental range to influence the D values of counterions, as shown by the negligible change in the D value of a neutral molecule in the latex with added electrolyte.[20] The ratio $D/D°$ indicates the degree of suppression of the diffusion coefficient of the ion due to electrostatic interactions with the particle and its accompanying counterions. A $D/D°$ value of unity means that the diffusion coefficient of the counterion is unaffected by the presence of the particles. A $D/D°$ value of zero corresponds to the situation in which all of the counterions are bound to the latex particles. The influence of added electrolyte on $D/D°$ values is shown in Figure 2. The symbol X in Figure 2 is the concentration ratio of added electrolyte to accompanying counterion ([Li$^+$]/[H$_3$O$^+$] or [Na$^+$]/[Li$^+$]). The numerical values for these data are also given in Tables 1 and 2.

The agreement of the normalized diffusion coefficients for Li$^+$ and H$_3$O$^+$, determined by NMR and voltammetry, respectively, is very good. The scatter in the data at high concentrations of electrolyte (log $X \approx 2$) is probably due to flocculation of the latex. The solid line in Figure 2 is the prediction of the nonlinear Poisson−Boltzmann equation, coupled with a theoretical model of diffusion within the framework of the cell model.[20] The dashed line is the fit by a semiempirical equation

$$D/D° = (\alpha + X)/(X + 1) \qquad (4)$$

where α is the $D/D°$ value in the deionized suspension, determined voltammetrically. Equation 4 has no adjustable parameters; a single measurement of $D/D°$ in the deionized macroionic system is sufficient to predict $D/D°$ values over the entire range of added electrolyte. These two curves agree remarkably well with each other and with the data. The positive

deviation of the data from the predictions around log $X = -1$ has been observed in a wide range of macroionic systems; it possibly reflects a fundamental flaw in the theories.[11,29]

The α value, the value of $D/D°$ at $X = 0$, can be used to infer the effective charge on the latex particles. The basic idea is that the bound counterions neutralize an equivalent number of anionic sites on the surface of the particle; only the "free" counterions contribute to diffusion. Within this model, the effective charge has the value, $Z* = \alpha Z$. The effective charges determined by voltammetry and PFGSE-NMR are 291 and 753, respectively (see Tables 1 and 2). Although these effective charges are significantly different, both are much less than the intrinsic charge, Z. The values of $Z*/Z$ are within experimental error for latex suspensions of this kind.[11]

Conclusions

The self-diffusion coefficients of Li$^+$ in the presence of highly charged latex particles were determined by pulsed-field-gradient, spin-echo NMR. Diffusion coefficient values measured over a wide range of added electrolyte characterize the effective charge on the particles and the ion-exchange properties of the particles. The diffusion coefficient values agree with the Poisson−Boltzmann theory, a semiempirical theory, and previous data from voltammetric experiments for the gradient-diffusion coefficients of H$_3$O$^+$ in the same latex. The good agreement between the NMR and voltammetry suggests that either method is useful for investigating counterion binding in macroionic systems. Exploiting both the spin and electroactive properties of ions increases the number of counterions available for this kind of study. The much greater speed of the voltammetric technique makes it especially advantageous when large numbers of measurements are required.

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