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Molecular and Ionic Transport in Polymeric Systems: Electroanalytical Studies

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Molecular and Ionic Transport in Polymeric Systems: Electroanalytical Studies

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ABSTRACT

Transport of simple ions and molecules in polymeric systems such as solutions, colloidal suspensions and polymeric gels is of interest for the description of many biological and synthetic systems, such as cellular membranes, biological matrices, ion-exchangers, new materials for power sources, and gel-based sensors. The transport of ions in ionic polymeric media is suppressed due to long range electrostatic interactions between polyions and counterions or coions. This paper presents an overview of recent developments in transport studies in polymeric systems using electroanalytical methods. Two systems with important applications, polymeric gels and solutions of ionic polymers, are discussed. Appropriate theoretical models and experimental results for synthetic and biological systems are presented.

INTRODUCTION

Transport of simple ions and molecules in polymeric systems such as solutions, colloidal suspensions and polymeric gels is of interest for the description of many biological and synthetic systems, such as cellular membranes, biological matrices, ion-exchangers, new materials for power sources, and gel-based sensors [1,2]. The transport of ions in ionic polymeric media is suppressed due to long range electrostatic interactions between polyions and counterions or coions. Changes in transport behavior are most noticeable in solutions of low ionic strength, because at higher ionic strength the overall charge of the polyion is shielded by the electrical double layer formed by the ions of the supporting electrolyte. The inference of ionic interactions

from transport data requires measurements over a wide range of concentration, extending to solutions nominally without added electrolyte. Effectiveness of electroanalytical techniques, such as steady-state voltammetry and chronoamperometry at microelectrodes for this purpose has been demonstrated for polymeric solutions [3-12], colloidal suspensions [13-16], and polymeric gels [17-24].

This review discusses transport in two systems with important applications: solutions of ionic polymers and polymeric gels. Appropriate theoretical models and experimental results for biological and synthetic systems are presented.

EXPERIMENTAL TECHNIQUES

Studies of ionic interactions in polymeric systems require measurements of transport of ions and molecules over a wide range of concentrations, extending to solutions of very low ionic strength, nominally without added electrolyte. Many techniques have been used for determination of diffusion coefficients of simple ions in solutions of ionic polymers (polyelectrolytes), including radioactive tracer [25-29] and PFGSE NMR [30-34]. Recently, the effectiveness of electroanalytical methods, such as steady-state voltammetry and chronoamperometry with microelectrodes, and conductance measurements has been demonstrated [3-24].

Since the steady-state current, i_s , at microelectrodes is proportional to the flux of reactant, the voltammetric signal is very sensitive to changes in the value of the diffusion coefficient, D . The value of D can be calculated directly from the steady-state current at a disk microelectrode according to the following equation [35-37]:

$$D = \frac{i_s}{4nFCr_d} \quad (1)$$

where C is the concentration of electroactive species, r_d is the radius of the microelectrode, n is the number of electrons transferred, and F is the Faraday constant. This method has advantages of simplicity, low cost, and very high throughput in comparison with other methods (NMR, radioactive tracer method) used to study these systems.

Chronoamperometry with microelectrodes can be used to determine the diffusion coefficient of ions or molecules when their concentration is not known [38,39]. For a microdisk electrode of a radius r_d , if the pulse time t satisfies $\frac{Dt}{r_d^2} \leq 10^{-4}$, the normalized current, i/i_s , is given by [38]:

$$i/i_s = [1 + (2r_d / \pi \sqrt{\pi Dt})] \quad (2)$$

where i is the current at the time t .

THEORETICAL MODELS

The electrostatic interactions between small ions and macroions in solutions influence the transport of small ions, with the most pronounced effect observed for counterions [1,2]. According to Manning's theory with line charge model [40-42] the counterion self-diffusion coefficient depends on the dimensionless charge density, λ . Manning's theory treats polyions as infinitely long line charges. Counterions are assumed to condense onto the polyion chain as required to avoid exceeding the critical charge density, λ_c (for monovalent counterions $\lambda_c = 1$). These

condensed counterions are inside the hydration layer; therefore their mobility is that of the polyion, usually negligible in comparison with the mobility of free counterions. Uncondensed counterions and coions are subject to Debye-Hückel interactions with the polyions. Depending on the charge density of the polyion, the ratio of the diffusion coefficient of the counterion in the polyelectrolyte solution to that in solution without polyelectrolyte is [41]:

$$D_{PE}/D_0 = 1 - 1/3 \times A(\lambda; X) \quad \text{for } \lambda < 1 \quad (3)$$

$$D_{PE}/D_0 = 1 - 1/3 \times A(1; \lambda^{-1} X) \quad \text{for } \lambda > 1 \quad (4)$$

where

$$\lambda = \frac{e_0^2}{4\pi\epsilon\epsilon^0 b k T} \quad (5)$$

e_0 is the elementary charge, ϵ is the dielectric constant of the solvent, ϵ^0 is the permittivity of vacuum, b is the length of the polyion per ionized group (charge spacing), k is the Boltzmann constant, and T the absolute temperature. D_{PE} and D_0 are diffusion coefficients of counterions in solutions with and without polyelectrolyte, respectively, X is the ratio of the concentration of polyelectrolyte to the concentration of added univalent salt, $X = C_{PE} / C_{SE}$, and $A(\lambda; X)$ is given by:

$$A(\lambda; X) = \sum_{\substack{m_1=-\infty \\ (m_1, m_2) \neq (0,0)}}^{\infty} \sum_{m_2=-\infty}^{\infty} [\pi\lambda^{-1}(m_1^2 + m_2^2) + 1 + 2X^{-1}]^{-2} \quad (6)$$

where m_1 and m_2 are integers.

In salt-free solution, $X \rightarrow \infty$,

$$D_{PE}/D_0 = 1 - 1/3 \times A(\lambda; \infty) \\ \text{for } \lambda < 1 \quad (7)$$

$$D_{PE}/D_0 = \lambda^{-1} \times [1 - 1/3 \times A(1; \infty)] \\ \text{for } \lambda > 1 \quad (8)$$

where $A(\lambda; \infty)$ can be obtained from eq. 6 by setting $X^{-1} = 0$. Numerical evaluation of the series results gives $A(1; \infty) = 0.40$, and therefore:

$$D_{PE}/D_0 = \lambda^{-1} [1 - 1/3 \times 0.40] = 0.867 \times \lambda^{-1} \\ \text{for } \lambda > 1 \quad (9)$$

As one can see from eqs. 3-9, measurements of counterion diffusion coefficients yield the charge spacing, b , of the polymer and thus could be used for structural characterization.

The Poisson-Boltzmann equation has been used extensively to describe properties of polyelectrolyte systems with different geometries [1,2,43-45]:

$$\nabla^2 \psi = - \left(\frac{1}{\epsilon^o \epsilon} \right) \sum_i z_i e n_i \exp(-z_i e \psi / kT) \\ (10)$$

where ψ denotes the average potential, n_i and z_i are the number concentration at the cell boundary and the valence of ion species i , and the other symbols have their usual meaning. Equation 10 can be used to calculate the quantity $1 - f$, the number fraction of counterions in the deionized solution that have an energy of attractive electrostatic interaction with the macroion greater than kT . These counterions are considered to neutralize the anionic sites of the macroion, and their transport is limited by the diffusion of the macroion, which has a diffusion coefficient 2

orders of magnitude less than that of the free counterion. The fraction of ions f is free to diffuse. The value of f is identified with the D/D_0 -value in Manning's theory and with the experimentally determined transport ratio in deionized solution.

SOLUTIONS

We have shown that the transport rate of the singly charged cations of hydrogen and thallium, in solutions of the synthetic polymer poly(styrenesulfonic acid), PSSA, without supporting electrolyte, is only one-third that in solution without polyelectrolyte [3-5]. This result agrees well with the predictions of the two major theories for polyelectrolytes, described in the previous section. A phenomenological equation for describing the results of measurements of diffusion coefficients in polyelectrolyte systems has been developed [4]. Over the entire range of ionic strengths, the diffusion coefficient of a counterion in polyelectrolyte solution, D , normalized by the diffusion coefficient of the same ion in solution without polymer, D_0 , should follow:

$$\frac{D}{D_0} = \frac{(\alpha/\gamma + 1)}{1/\gamma} \quad (11)$$

where γ is a ratio of the concentration of an univalent salt to the equivalent concentration of the ionic polymer ($\gamma = C_{SE}/C_{PE}$), and α is an empirical factor equivalent to the ratio of the diffusion coefficient of a counterion in polyelectrolyte solution to its value in the absence of polyelectrolyte, both in solution without any electrolyte. The parameter α can be determined empirically, by simple calibration curves in the presence and absence

of polyelectrolyte [4]. Equation 11 permits prediction of an influence of added electrolyte on diffusion of small counterions in a solution of ionic polymer. Experimental results for transport of hydrogen cation in solutions of four concentrations of PSSA have been compared with predictions of that phenomenological equation, Figure 1, and they were identical within an experimental error.

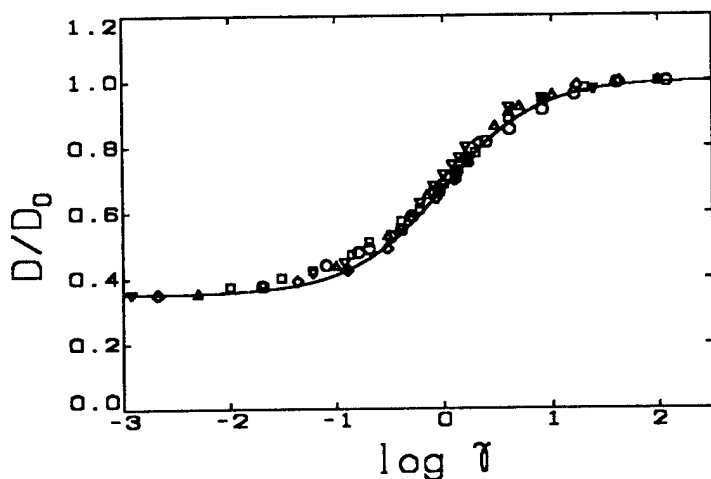


Figure 1. Calculated (solid line) and experimental transport ratio, D/D_0 , for various ratios of electrolyte (LiClO_4) to hydrogen ion concentration ($\gamma = C_{\text{SE}} / C_{\text{H}}$) for reduction of hydrogen ion in: (O) 0.05, () 0.1, (Δ) 0.2, (\diamond) 0.47, (∇) 1.05 mM PSSA solution. (Reprinted with permission from ref. 4. Copyright 1994 American Chemical Society.)

No specific influence of the anion of the supporting electrolyte on transport of counterions in PSSA solutions has been found. From a group of several cations (Li^+ , Na^+ , K^+ , Cs^+ , TMA^+ (tetramethylammonium), and TEA^+ (tetraethylammonium)), only TEA^+ shows preferentially strong interactions with PSSA. Strong influence of a charge of a cation of supporting electrolyte on transport properties of counterions in polyelectrolyte solutions has been demonstrated [4]. The dependence of the normalized diffusion coefficient of hydrogen counterion on concentration of electrolytes with

various cation charges (+1, +2, and +3) indicates the stronger interactions of polyion with more highly charged cations than with monovalent cations. Very similar phenomenon has been found for multicharged counterions. It has been shown for metal cations such as Pb^{2+} and Cd^{2+} that their interactions with ionic polymers are much stronger than for monovalent cations such as H^+ and Tl^+ [5], see Figure 2.

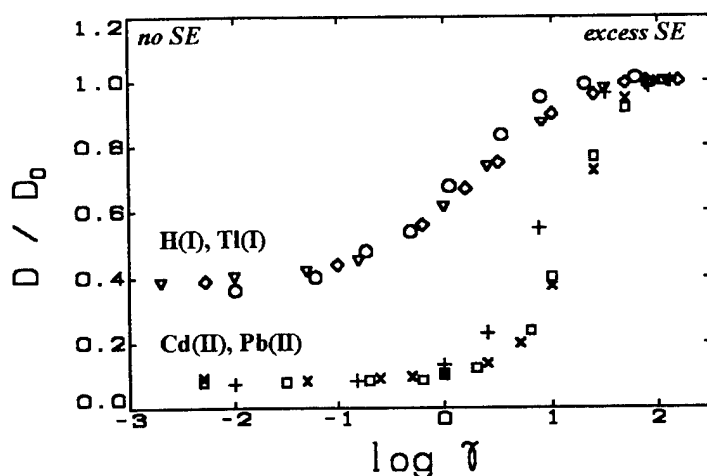


Figure 2. Transport ratio, D/D_0 , of H^+ , Tl^+ , Cd^{2+} and Pb^{2+} counterions in PSSA solutions. (O) 0.1 mM H^+ , 2 mM PSSA, (∇) 0.1 mM H^+ , 20 mM PSSA, (\diamond) 0.1 mM Tl^+ , 20 mM PSSA, (\square) 0.1 mM Cd^{2+} , 20 mM PSSA, (\times) 0.05 mM Cd^{2+} , 2 mM PSSA, (+) 0.1 mM Pb^{2+} , 20 mM PSSA; $\gamma = C_{\text{SE}}/C_{\text{PSSA}}$, SE - LiClO_4 .

Group of anionic biological polyelectrolytes that have a range of charge separation distances, and hence of charge densities have been studied [7,9] to test the predictive power of Manning's theory. Transport of monovalent cations was investigated in solutions of the sodium (or potassium) salts of anionic polysaccharides iota- (ι -), kappa- (κ -), lambda-carrageenan (λ -car), dextran sulfate and chondroitin sulfate (with the charge separation distance, b , of 0.47, 1.01, 0.48, 0.25, and 0.58 nm, respectively), by steady-state voltammetric reduction of the

probe ions Tl^+ and H^+ at mercury film and platinum disc microelectrodes, respectively.

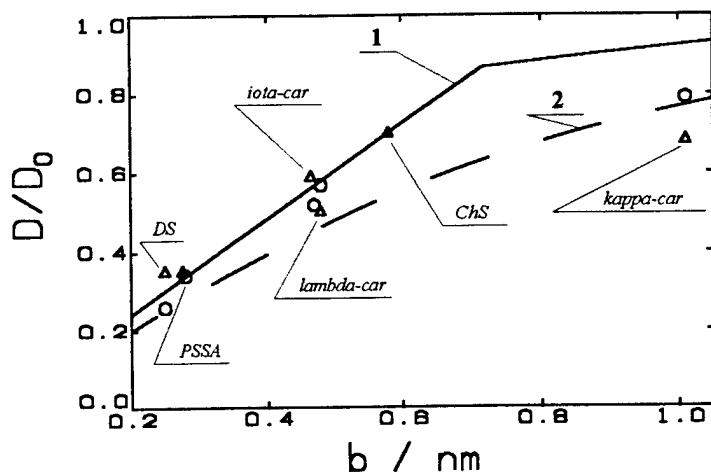


Figure 3. Transport ratio, D/D_0 , as a function of the charge separation distance, b , according to Manning's (1) and the Poisson-Boltzmann (2) model, together with experimental D/D_0 -values for Tl^+ (Δ) and H^+ (O) in polyelectrolyte solutions without electrolyte. (Reprinted with permission from ref. 9. Copyright 1998 American Chemical Society.).

Figure 3 presents experimental transport ratio, D/D_0 , as a function of the charge separation distance together with values calculated according to Manning's theory (eqs. 3-9) and the Poisson-Boltzmann model (eq. 10). The results generally agree better with Manning's theory for $\lambda > 1$, whereas the single result for polyion with $\lambda < 1$ (κ -car) appears to lie closer to the prediction of the Poisson-Boltzmann model [9].

We have shown that steady-state voltammetry with microelectrodes can be used successfully for the study of transport of counterions in mixed solvent solutions of polyelectrolytes [8]. The interactions between poly(styrenesulfonate) ion and thallium(I) counterion in solutions without added electrolyte were found to depend on the bulk dielectric constant of the solvent, see Figure 4.

This dependence was observed for ethanol-, methanol- and 1,4-dioxane-water mixtures. For example, in a solution of ethanol-water mixture of dielectric constant $\epsilon = 25$, the diffusion coefficient of Tl(I) in PSSA was found to be one-tenth the value in simple acid solution, which means that the transport of Tl(I) in PSSA was 10 times slower than in *p*-TSA.

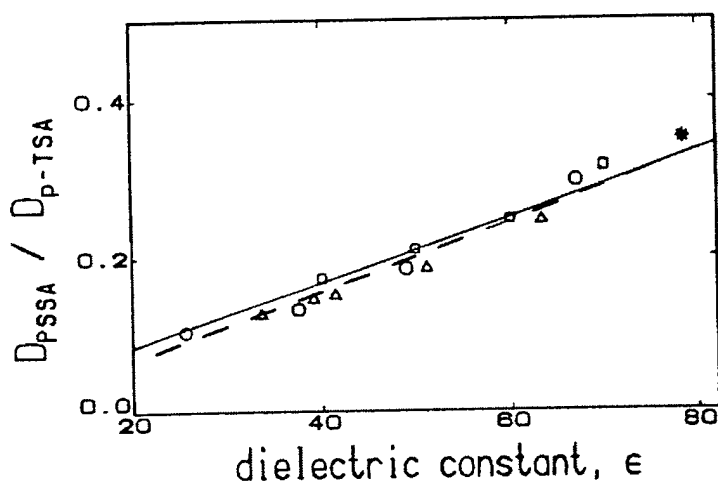


Figure 4. Dependence of the ratio $\alpha = D_{Tl(I), PSSA} / D_{Tl(I), p-TSA}$, with no supporting electrolyte solutions, on the dielectric constant of organic solvent-water mixtures: (O) ethanol-water; (Δ) methanol-water; () 1,4-dioxane-water; (*) water, 0.16 mM Tl(I), 10 mM PSSA (or *p*-TSA). The solid curve was calculated according to eqs 3-9, and the dashed curve was calculated as an average dependence for all solvents. (Reprinted with permission from ref. 8. Copyright 1996 American Chemical Society.)

This is much lower than the value of 0.35 obtained in aqueous solution, $\epsilon = 79$, for the same system [8]. Similar changes in transport properties of counterions in polyelectrolyte solutions with changes in dielectric constant of solvent are predicted by Manning's theory, see eqs. 3-9. Although these results were obtained for only one kind of counterion, Tl(I), this methodology can be used to study the transport properties of other electroactive mono- and multivalent counterions under variety of

experimental conditions, in solutions of various solvents and polyelectrolytes, including naturally occurring, biological polyelectrolytes.

As shown by Manning's theory, measurements of counterion diffusion coefficients yield the charge spacing, b , of the polymer and thus should reveal the conformation of a polyion such as the coil, helix or multiple helix. Conformation of polyions, both naturally occurring and synthetic, critically influences their properties, including chemical reactivity [10].

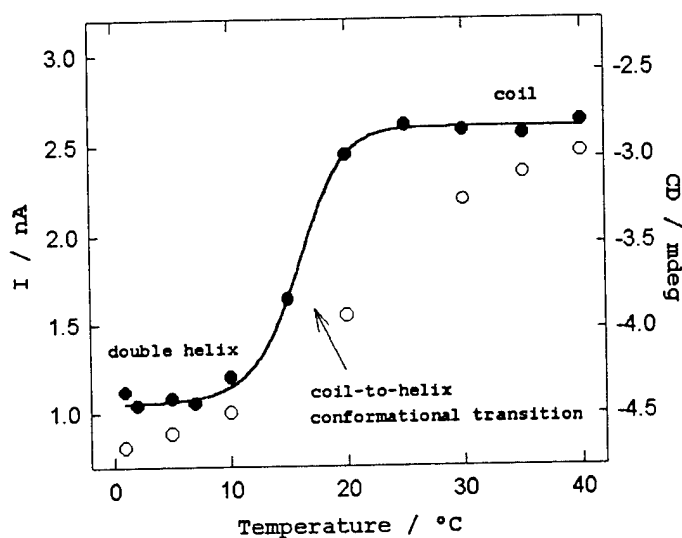


Figure 5. Dependence of the normalized (*versus* the limiting diffusional current at 20 °C) reduction current of 0.3 mM Ti^+ (●) and circular dichroism response at 300 nm (O) on temperature of 20 mM κ -carrageenan solution. (—) Best fit of voltammetric results. (Reprinted with permission from ref. 41. Copyright 2000 American Chemical Society.)

It has been shown that voltammetric measurements of diffusion coefficient of counterions can be used together with Manning's theory to obtain values of charge spacing for an anionic polymer to identify the

coil-to-helix transition [10,12]. The experimental example was the transformation from coil to double helix of κ -carrageenan (κ -*car*) induced by a decrease in temperature. Figure 5 shows dependence of transport properties of electroactive probe ion, Tl^+ , on a conformational form of κ -*car*, and comparison of voltammetric and circular dichroism results for the same system.

It has been also shown [11] that very simple conductance experiments can reveal coil-to-helix transition of an anionic polymer, that those results are identical to voltammetric data [12], and they can be used for determination of the charge spacing in conformers.

GELS

Topological definition of a polymeric gel is a three-dimensional network constituted of basic elements connected in some way (usually crosslinked) and swollen by a solvent, a major component of the system (in some cases a gel can contain up to 99% solvent). A gel possesses the unique property of incorporating and retaining a proportion of liquid molecules outweighing by far the proportion of the basic, added component. This is a rather unusual way in which large amounts of liquid can be maintained "solid", and therefore, gels possess many advantages characteristic of both the liquid and solid state of matter [46-49]. It has been shown that electroanalytical techniques including voltammetry (see eq. 1) and chronoamperometry (see eq. 2) with microelectrodes can be used effectively in transport studies in polymeric gels [17-24, 50-52].

We have demonstrated for polyacrylate gels [18] that 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. For a 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 the thallium probe cation decreases due to electrostatic interactions with the polymeric network. While it 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 [17], the 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.

Figure 6 summarizes experimental and theoretical results, based on a new model [18], 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.

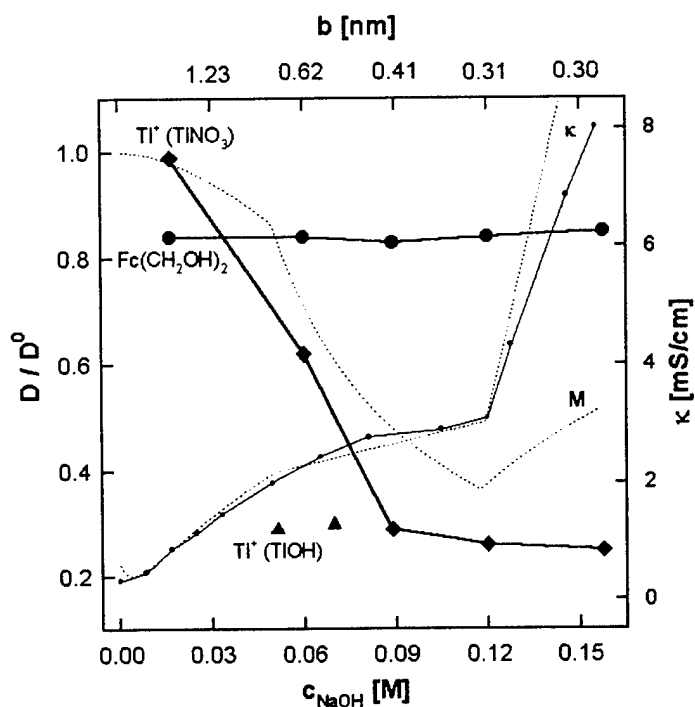


Figure 6. Dependencies of normalized diffusion coefficients determined voltammetrically (solid lines and symbols) for chosen electroactive probes in sodium polyacrylate gels with respect to concentration of added NaOH. The thinner solid line presents appropriate conductometric titration curve. The dotted lines refer to theoretical predictions according to Manning's theory (M) and calculated conductometric titration curve (κ). (Reprinted with permission from ref. 18. Copyright 1999 American Chemical Society.)

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 6) [18]. 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). This is the first direct experimental evidence of such a structure.

Some polymeric gels undergo discontinuous volume phase transitions as a function of environmental variables such as pH or temperature [53,54] with a significant change of volume. The phase transition of a polymer gel results from a competitive balance between a repulsive force that acts to expand the polymer network and an attractive force that acts to shrink the network. Since polymeric gels exhibit such dramatic changes in their structure by responding to environmental changes, they have been studied for applications such as drug delivery [55-57], separation media [58], and sensors [59-61]. In such applications, the knowledge of diffusion coefficients of ions and molecules as a fundamental measure of molecular mobility and electrostatic interactions is of great importance.

We have shown that electroanalytical techniques can be used successfully to monitor transport of ions and molecules in polymeric gels undergoing discontinuous volume phase transitions [20-24]. Transport of ions and molecules has been studied in temperature responsive gels of poly(N-isopropylacrylamide), NIPA [24], and poly(N-isopropylacrylamide-*co*-acrylic acid), NIPA-AA [20-23]. The NIPA hydrogels undergo a discontinuous volume phase transition at 32 °C; this transition results in a release of approximately 93% of the

solution mass from the gel phase [24], while the NIPA-AA hydrogels undergo this transition at 45 °C; and it results in a release of approximately 40% of the solution from the gel phase [21]. Diffusion coefficients of electroactive probes in gels under a wide range of experimental conditions have been determined from steady-state voltammograms, according to eq. 1, or using normalized chronoamperometry with microelectrodes, eq. 2. Similar diffusion coefficients for 1,1'-ferrocenedimethanol, $\text{Fc}(\text{MeOH})_2$, in NIPA-AA gels were obtained by either electroanalytical technique at temperatures lower than 20 °C [21]. The uncertainty in the $\text{Fc}(\text{MeOH})_2$ concentration in the gels, resulting from the discontinuous volume change transition, necessitated the use of concentration independent chronoamperometric data, eq. 2, to obtain reliable diffusion coefficient values for $\text{Fc}(\text{MeOH})_2$. As indicated by results of Figure 6, for temperatures above the volume phase transition, changes of concentration of $\text{Fc}(\text{MeOH})_2$ are detected in a copolymeric collapsed phase.

The enormous macroscopic viscosity of NIPA-AA hydrogels had no significant effect on transport of small probe molecules [21]. For example, in a 4% (w/w) NIPA-AA gel, the viscosity is approximately six orders of magnitude greater than the viscosity of aqueous solution. However, the diffusion coefficient of $\text{Fc}(\text{MeOH})_2$ has only decreased by a factor of two compared to the diffusion coefficient of $\text{Fc}(\text{MeOH})_2$ in aqueous solution, while for an ideal system, according to the Stokes-Einstein equation, the diffusion coefficient should be inversely proportional to the viscosity of that system. This difference illustrates the distinction between macroscopic and microscopic viscosity; a heterogeneous

environment exists in these gels, which allows a solute to easily diffuse within a solution encapsulated in the pores of a swollen and semi-rigid polymer network. The observation that there is only slight resistance to the diffusion of $\text{Fc}(\text{MeOH})_2$ through the polymer network indicates the potential of these gels to be used as semi-rigid electrolytes for electrochemical applications.

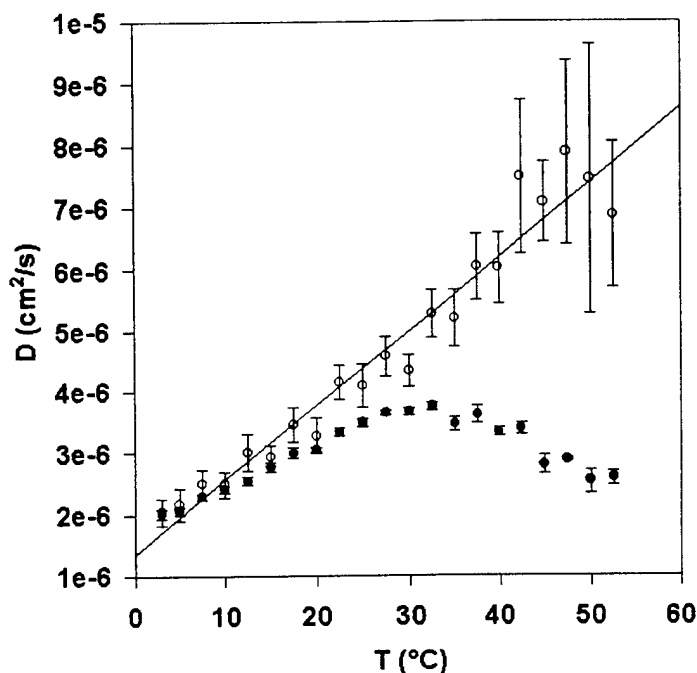


Figure 6. Temperature dependence of the $\text{Fc}(\text{MeOH})_2$ diffusion coefficient in a 5% (w/v) NIPA-AA gel as determined by normalized chronoamperometry (O) and steady-state voltammetry (●). The line on the graph represents the best fit of the chronoamperometric data by linear regression. (Reprinted with permission from ref. 21. Copyright 2000 American Chemical Society.)

A new model for description of transport in polymeric gels in their swollen state has been proposed [22]. The modified equation taking into account the "obstruction effect" and "hydration effect" was proposed, and this

equation successfully predicated the diffusion coefficient of TEMPO in the NIPA-AA gels.

Poly(N-isopropylacrylamide-*co*-acrylic acid) can be swollen by organic solvents [20]. The electrooxidation of methanol at platinum microelectrodes in NIPA-AA gels has been studied as a function of temperature. Diffusion coefficients of methanol in NIPA-AA gels of various copolymer concentrations were determined from the steady-state voltammetric currents over the temperature range 5 - 55 °C. Transport parameters (diffusion coefficients and activation energies of diffusion) were compared to those for undiluted methanol, and related to the transport properties of uncharged probe molecules of $\text{Fc}(\text{MeOH})_2$ in both liquid and gel media. Diffusion of uncharged species, methanol and $\text{Fc}(\text{MeOH})_2$, in the gels was as fast as in liquid media. Activation energies of diffusion for methanol and $\text{Fc}(\text{MeOH})_2$ in the gels were smaller than those observed in liquid media, they did not depend on the copolymer concentration in the range 1.3 – 2.5 %. The smaller values of obtained for gels may suggest a slight decrease in local viscosity in this medium compared to undiluted methanol resulting from the condensation of positively charged species (Li^+ and product of the electrode process) on the ionized carboxylic groups of acrylic acid incorporated in the polymeric chains, even if the environment is not very ionic [20].

SUMMARY

This paper demonstrates the power of electroanalytical techniques, mainly voltammetry and chronoamperometry with microelectrodes as employed to measure transport of specific species of ions and molecules in solutions and gels of ionic

polymers over wide variation of concentration and identity of ionic polymers, electrolytes, solvents, and wide range of temperatures. Transport of counterions in solutions of polyelectrolytes reported for variety of charges of counterions and charge densities of ionic polymers can be used as an indicator of electrostatic interactions in those systems. Experimental results are compared with two theoretical models, Manning's line charge approach and the Poisson-Boltzmann equation. Diffusion of ions and molecules is reported for biological and synthetic polymeric gels. Effects of the discontinuous volume phase transitions of temperature-sensitive gels on transport properties are presented. Macroscopic and microscopic viscosity of gels and the influence on transport of ions and molecules is discussed.

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