

Diffusion of Uncharged Probe Reveals Structural Changes in Polyacids Initiated by Their Neutralization: Poly(Acrylic Acids)

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The diffusion studies of the uncharged probe (1,1'-ferrocenedimethanol) have been successfully applied for the evaluation of the changes in the three-dimensional structure of poly(acrylic acids) of various molecular weights (ranging from 2000 to 4 000 000 g/mol) during their neutralization with a strong base. The qualitative picture of the macromolecule arrangement during the titration of the polyacids has been obtained from the conductometric measurements. The characteristic changes in the poly(acrylic acid) conductivity are practically the same for all polyacids examined and are in a very good agreement with the predictions of our theoretical model of the polyelectrolyte conductance. The transformation of the polyelectrolyte solution into the gel-like or gel phase has been investigated more quantitatively by tracing the changes in the diffusion coefficient of the uncharged probe redox system. The probe diffusivities, D , were determined using steady-state voltammetry at microelectrodes for a wide range of neutralization degree, α , of the polyacids tested. The dependencies of D versus α are of similar shape for all poly(acrylic acids). The first parts of the dependencies reflect a rapid increase in D (up to neutralization degree of either 45% for the lowest molecular-weight poly(acrylic acid) or 75–80% for other polyacids). They are followed by the parts of a slight drop in the diffusion coefficient. The changes in the probe diffusivity become stronger as the molecular weight of poly(acrylic acid) increases. The maximum probe diffusion coefficients are greater than the initial values in the pure polyacid solutions by 14, 24, 19, 30, and 28% for poly(acrylic acid) of molecular weights of 2000, 450 000, 1 250 000, 3 000 000, and 4 000 000 g/mol, respectively. The variation in the probe diffusion coefficient qualitatively follows the line of the changes in the macroscopic viscosity of the polyelectrolyte system. This is in contrast to the predictions of the Stokes–Einstein relation and, therefore, suggests that the changes in the probe diffusion rate are mainly due to the structural changes in the polyacrylate medium and the macromolecular rearrangements induced by the chemical, acid–base reaction. By adapting the obstruction model for diffusion in homogeneous gels, the transport characteristics of the probe were converted into the structural characteristics of the polyelectrolytic systems. It has been found that the most ordered structure of the polyelectrolyte, or in other words the most permeable structure, is obtained when poly(acrylic acid) is neutralized at 75–80%.

Introduction

In recent years much attention has been paid to the studies of various physicochemical aspects of polymeric gels made by the free-radical copolymerization.¹ The crucial point in the synthesis of such the polymer materials is the chemical incorporation of specific units, called cross-linkers, into the macromolecular structure. These molecular units modify the unique features of the polymeric gels and make them structure ordered and three-dimensional.^{2–4} An alternative method of gel formation may include common chemical reactions involving polymers. Good examples of this type of gels are polyacrylates obtained as a result of neutralization of poly(acrylic acid) (PAA) with strong base.⁵ In this case charged polymeric chains are “linked” electrostatically by small cationic counterions. This interesting class of gels has not been explored extensively yet.

Recently, we have shown that using an appropriate proportion of a strong base and solution of PAA of large molecular weight one can obtain a polyacrylate gel characterized by a unique charge separation distance, and, consequently, by a unique and

well-defined charge density of the polymeric chain.⁶ 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. Our studies revealed to what extent the electrostatic interactions between polyacrylate networks and counterions (or any probe ions of the opposite charge) affect the transport of these ions in gels. The significant drop in the mobility of the cationic species may serve as a proof of electrostatic nature of “cross-linkage” in the polyacrylate gels.⁶

The magnitude of the counterion diffusivity is also correlated with the concentration of the polyelectrolyte and its molecular weight, as shown for tetramethylammonium (TMA) salt of fully neutralized PAA of various nominal molecular weights ranging from 2000 to 230 000 g/mol.⁷ The counterion (TMA⁺) diffusion coefficient was found to be roughly independent of polyelectrolyte concentration down to about 10^{−2} M, followed by a rapid increase in TMA⁺ diffusivity for the polyelectrolyte concentration interval 10^{−2} to 10^{−3} M. The results were interpreted in terms of a modified cell model of polyelectrolyte solution where the finite length and the shape of polyions were taken into account.

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In the characterization of the polyionic gels that are obtained as, e.g., products of an acid–base reaction, it is vital to distinguish between the polyelectrolyte solution and polyelectrolyte gel. In other words, it would be very useful to determine the diagnostic criteria which allow one to detect the transformation of the polyelectrolyte solution into the gel medium.

The aim of this work is to study the process of PAA gelation and the transport properties of the resulting polyelectrolyte as a function of the amount of added strong base and the molecular weight of the PAA employed. It is obvious that the transformation of the PAA solution into the more ordered polyacrylate gel phase changes both the charge density of polychains and the three-dimensional structure of the polymeric system. Consequently, these changes affect diffusivity of probe molecules. To eliminate the influence of the electrostatic interactions on the species transport, the probe system should bear no net charge. Therefore, by tracing the changes in the diffusion coefficient of an uncharged species, one is able to monitor only the structural changes in the polymeric system. The transport characteristics of the uncharged probe system can be obtained from the steady-state voltammetry at microelectrodes. By adapting an obstruction model for diffusion in homogeneous gels, we are able to convert the transport parameters into the structural characteristics of the polyelectrolytes examined. The results are correlated with the measurements of conductivity and macroscopic viscosity. The conductometric data are compared with the predictions of the theoretical model developed in our previous work⁶ and based on Manning's formalism.^{8,9}

Experimental Section

Chemicals. Poly(acrylic acids) of average nominal molecular weights of 2000, 450 000, 1 250 000, 3 000 000, and 4 000 000 g/mol (approximately 0.1% cross-linked), and sodium hydroxide (NaOH) were purchased from Aldrich. The molecular weight of the smallest polyacid was determined from the gel permeation chromatography measurements, while the higher molecular weights were determined from the polyacid viscosities. The molecular weight distribution was not available from the manufacturer. Cross-linking was estimated as ca. 0.1% and was not done on purpose; it was a result of a side radical reaction. 1,1'-Ferrocenedimethanol ($\text{Fc}(\text{CH}_2\text{OH})_2$, 98%) was purchased from Fluka. A NaOH solution was standardized with potassium hydrogen phthalate (Aldrich), which was dried at 110 °C for 2 h before use, and other chemicals were used as received. Ultrapure water (Milli-Q, Millipore Corporation) of a conductivity of about 0.056 $\mu\text{S}/\text{cm}$ was used in all experiments.

Polyelectrolyte Preparation. Sodium salts of poly(acrylic acids) were prepared by neutralization of 1.5% (w/w) aqueous solutions of PAA with the appropriate amount of 3.53 M NaOH. The higher molecular weight poly(acrylic acids) are more difficult to dissolve due to the lower entropy of mixing compared to the smaller polymers. Thus, their solubility in water is limited, and the concentration of the polymer greater than 1.5% resulted in obtaining nonhomogeneous samples. Electroactive probe, 1,1'-ferrocenedimethanol (~2 mM), was added to the 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 Scientific; its value was $(0.663 \pm 0.013)/\text{cm}$.

Voltammetry. Electrochemical measurements were performed using an AMETEK PARC model 283A potentiostat,

controlled via software by a PC computer. All experiments were carried out in the three-electrode system. Two platinum electrodes served as the counter and the quasi-reference electrodes. This setup eliminated a possible leak of electrolyte from the salt bridge. A 5 μm in radius platinum disk microelectrode (nLab, Poland) was used as the working electrode. The cell was water-jacketed. The temperature in the cell was controlled using a refrigerated circulator (Isotemp 1016P Fisher Scientific). Before each experiment, the microelectrode was polished with aluminum oxide powder of various sizes (down to 0.05 μm) on a wet pad, rinsed with water, and then dried with ethanol. The surface of the microelectrode was inspected optically with a Nikon, model Epiphot 200, inverted microscope for reflected light.

Five replicates of voltammograms were taken after each addition of NaOH. All measurements were performed at 25 °C.

Viscosity Measurements. Measurements of polyelectrolyte viscosity were performed at constant temperature of 25 °C using a Brookfield digital viscometer (model HADV-E) with a HA/HB spindle set. Prior to the measurements the instrument was calibrated with a Brookfield viscosity standard of 5080 mPa s at 25 °C. The set of disk-type spindles used in the experiments allowed the measurement of apparent viscosity. Spindle no. 1 was selected for the measurements of poly(acrylic acids) of 2000 and 450 000 g/mol molecular weight, while spindles no. 6 and 7 were used for higher molecular weight polyacids. The rotational speed of the spindles was in the range 0.3–100 rpm.

The measurements were performed at different rotational rates in a 600 mL beaker (83 mm in diameter) filled with a partially or totally neutralized PAA. Several available rotational speeds starting from its minimum value were selected. Depending on the rotational speed, the time needed to achieve a constant reading at a given rate varied from 30 s for 100 rpm to about 15 min for 0.3 rpm.

We believe the measurements done at high shear did not cause any chain scission, since the measurements done again at low shear gave results very similar to the initial ones.

It has been found that the logarithm of the viscosity of the poly(acrylic acids) employed in the studies linearly decreased with the increase in the logarithm of shear rate. The correlation coefficient for this linear dependence was better than 0.99.

Results and Discussion

The physical properties and the structure of a polyacrylate system strongly depend on the charge density of the polyanionic chains. This quantity can be easily controlled by the titration of PAA with a concentrated strong base.⁶ Each consecutive addition of the strong base increases the number of ionized carboxylic groups and, in consequence, changes the charge density of the polyacrylate chain. According to Manning's concept^{8,9} and our recent model,⁶ an increase in the charge density of polymeric chains changes the way the mobile counterions interact with the polyionic chains. These effects can be investigated conductometrically, and the results are shown in Figure 1. In this Figure the conductometric curves obtained during the titration of salt-free 1.5% (w/w) poly(acrylic acids) of various nominal molecular weights with NaOH(aq) are presented. Each curve can be formally divided into three parts which reflect different mechanisms of the electrostatic interactions between the cationic counterions and the polyacrylate anions. The first part of the curves (up to 0.09 M of NaOH) corresponds to the long-range attractive interactions and, therefore, the Debye–Hückel linear screening approximation is valid here. For larger concentrations of NaOH (or, in other

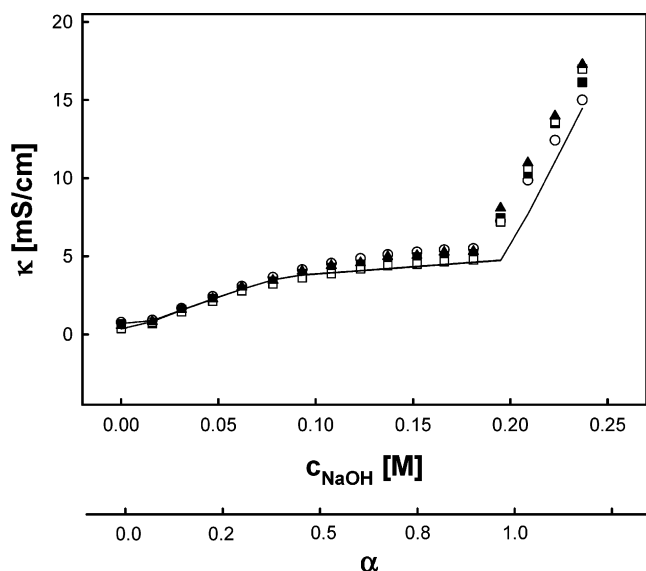


Figure 1. Conductometric titration curves for 1.5% (w/w) salt-free poly(acrylic acids) of various nominal molecular weights: 450 000 (○), 1 250 000 (■), 3 000 000 (□), and 4 000 000 g/mol (▲). The second horizontal axis corresponds to neutralization degree. Solid line represents theoretical curve. $T = 25\text{ }^{\circ}\text{C}$.

words, when the effective charge density parameter of the polyanion starts to exceed unity) the titration curves reach a plateau-like region. An almost constant conductivity of the polyelectrolyte system, seen at this stage of the titration, is due to the condensation of the counterions on the polyionic chains. Each new portion of the Na^+ counterions is trapped by the polyanion. Thus, their mobility is significantly reduced and, as a consequence, they contribute less to the total conductance of the system. Finally, when the point of complete neutralization is passed, a substantial increase in the conductivity is observed due to the presence of excess, very mobile, OH^- ions accompanied by the cationic counterions.

It is worth noting that the progress in the formation of polyacrylates of various molecular weights is accompanied by a strong reduction in the fluidity of the polymeric system and a change in the color from milky, for PAA aqueous solutions, to transparent for polyacrylate medium. The only exception is the lowest molecular weight PAA where no visible changes have been observed.

The experimental data have been compared to the theoretical predictions of our model of polyelectrolyte conductance.⁶ According to this model, conductivity of a polyelectrolyte system is calculated as a sum of independent contributions of all ionic species. Their specific transport behavior and concentrations are, in turn, determined by the quantity related to the charge density of the linear polyion and given by

$$\xi = \frac{F^2}{4\pi\epsilon\epsilon_0 N_A R T l} \alpha = \xi_0 \alpha \quad (1)$$

where ϵ and ϵ_0 are the relative permittivity of the solvent and the permittivity of vacuum, respectively, l denotes the length of the monomer (0.3 nm for acrylic acid), N_A is the Avogadro constant, R is the gas constant, T denotes temperature, and α is the neutralization degree expressed by

$$\alpha = \frac{N}{N_{\text{tot}}} = \frac{c_{\text{H}^+} + c_{\text{b}}}{N_{\text{tot}} c_{\text{PAA}}^0} \cong \frac{c_{\text{b}}}{N_{\text{tot}} c_{\text{PAA}}^0} \quad (2)$$

where N , N_{tot} , c_{PAA}^0 , c_{b} , and c_{H^+} are the number of ionized groups in the polymeric chain, the total number of monomers in the polymeric chain, the initial concentration of PAA, the concentration of the added base, and the concentration of the H^+ ions from the dissociation of PAA or partially neutralized PAA, respectively.

Figure 1 reveals that the changes in the conductivity of all poly(acrylic acids) examined but the one of molecular weight of 2000 g/mol are practically identical and are in a very good agreement with the theoretical predictions. According to the calculations done, the shift of the conductometric curve observed for the lowest molecular weight PAA may be a result of overestimation of the number of monomer units for this particular polyacid. Therefore, the corresponding data were not included in Figure 1.

The conductance measurements, although very valuable for the investigation of the electrostatic interactions in the polymeric structure, give little information on the structural changes and macromolecular arrangements during the transformation of the polyelectrolyte solution into the gel medium.

The structure of a forming homogeneous gel, or in general a three-dimensional network of polymeric chains, can be studied more quantitatively by tracing a diffusing molecule through the polymeric environment. Diffusion of an uncharged solute in such a system may be treated as a random walk of molecules through a series of openings (channels) between the polymer chains. The radius of the openings must be greater than the hydrodynamic radius of the solute. Thus, a reduction in the diffusivity may be attributed to the polymer chain obstacles encountered by the solute. According to the obstruction model for diffusion in homogeneous hydrogels,^{10,11} the drop in diffusion coefficient of a species in a gel medium, D_{g} , with respect to that in water, D_0 , can be expressed in terms of the probability of encountering a series of these openings

$$\frac{D_{\text{g}}}{D_0} = \int_{r^*}^{\infty} g(r) dr \quad (3)$$

where r^* is the limiting radius required to permit solute passage and $g(r)$ is the distribution function describing the distribution of the radii of openings between polymer chains, expressed by¹²

$$g(r) = \frac{\pi r}{2\rho^2} \exp\left[-\frac{\pi(r)^2}{4\rho^2}\right] \quad (4)$$

where ρ is the mean radius of this distribution.

By carrying out the integration of eq 3 and by taking into account a finite thickness of the polymer chain, one gets

$$\frac{D_{\text{g}}}{D_0} = \exp\left[-\frac{\pi(r_s + r_p)^2}{4(r_o + r_p)^2}\right] \quad (5)$$

where r_o is the average radius of the openings between the polymer chains, and r_p and r_s are radii of the polymer chain and the solute, respectively.

The polymer chain radius can be estimated using the following formula:¹³

$$r_p = \sqrt{\frac{M_m v}{\pi l N_A}} \quad (6)$$

while the hydrodynamic radius of a diffusing species can be

estimated from the Stokes–Einstein relation:

$$r_s = \frac{RT}{6\pi N_A \eta D_0} \quad (7)$$

in which M_m is the molecular weight of the monomer, v is the specific volume of the polymer (for PAA of molecular weight of 1 100 000 g/mol $v = 0.73 \text{ cm}^3/\text{g}$),¹⁴ η is the viscosity of the solution, and T is the temperature at which D_0 and η were determined.

The left-hand side of eq 5 can be easily determined for electroactive probes using the steady-state voltammetry at microelectrodes.^{6,15–20} The steady-state diffusion-limited current at disk microelectrodes, I_{ss} , is directly proportional to the diffusion coefficient of the redox species, D , via the following relation

$$D = \frac{I_{ss}}{4nFc^b r_e} \quad (8)$$

where n is the number of electrons exchanged per molecule, F is Faraday's constant, c^b denotes the bulk concentration of the electrode process substrate, and r_e is the radius of the microdisk.

The redox system chosen for the examination was 1,1'-ferrocenedimethanol. This probe species is stable in aqueous solutions in a wide range of pH, gives one-electron diffusion-limited anodic response at Pt microelectrodes, and bears no net charge. Its transport is, therefore, not affected by the electrostatic interactions with both polyions and electric field present within the electrode system. The voltammograms of the 1,1'-ferrocenedimethanol oxidation recorded for the selected points of poly(acrylic acid) titration curves were well defined and well reproducible with the coefficient of variation of the wave heights less than 2.5%. The exemplary sets of voltammograms for two selected poly(acrylic acids) (2000 and 4 000 000 g/mol) at some stages of neutralization are shown in Figure 2. The limiting currents, determined from the voltammetric waves, and eq 8 allow one to obtain the transport characteristics of the probe at different stages of sodium polyacrylate formation (or, in other words, for various charge densities of the polyacrylate chains). The probe diffusivities found, D , were normalized with respect to the corresponding value in the aqueous solution, D_0 , and are presented in Figure 3 as a function of the concentration of NaOH added and the neutralization degree parameter for five poly(acrylic acids) of various molecular weights. The average value of 1,1'-ferrocenedimethanol diffusivity, D_0 , determined voltammetrically in the aqueous solutions of similar pH and ionic strength (adjusted by additions of appropriate amount of KCl to the buffered solutions) to these of poly(acrylic acids) treated with NaOH was $(6.67 \pm 0.17) \times 10^{-10} \text{ m}^2/\text{s}$.

An inspection of the data presented in Figure 3 reveals three important facts. First, all dependencies are of similar shape. The part of a rapid increase in D (up to the neutralization degree of either 45% for the lowest molecular weight PAA or 75–80% for other polyacids) is followed by a slight drop in the diffusion coefficient. The maximum values of D are as follows: $(6.54 \pm 0.10) \times 10^{-10}$, $(6.10 \pm 0.09) \times 10^{-10}$, $(5.75 \pm 0.06) \times 10^{-10}$, $(6.62 \pm 0.12) \times 10^{-10}$, and $(6.23 \pm 0.08) \times 10^{-10} \text{ m}^2/\text{s}$ for PAA of molecular weights of 2000, 450 000, 1 250 000, 3 000 000, and 4 000 000 g/mol, respectively. Second, the changes in the probe diffusivity become stronger as the molecular weight of PAA increases. The maximum probe diffusion coefficients are greater than the initial values in the pure polyacid solutions by 14, 24, 19, 30, and 28% for PAA of

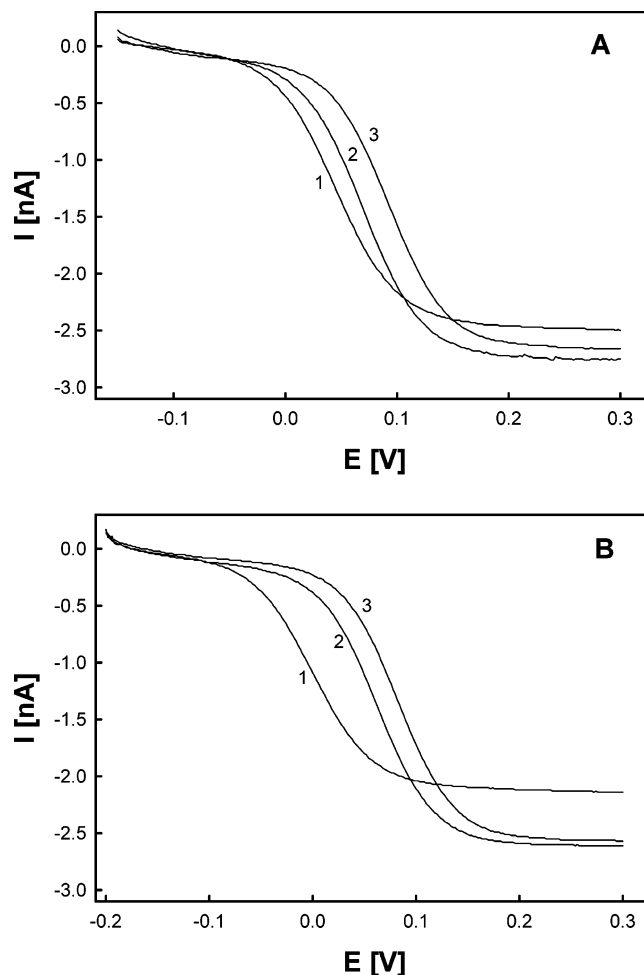


Figure 2. Voltammetric responses of Pt, 5 μm in radius, microdisk for the oxidation of 2 mM 1,1'-ferrocenedimethanol in two selected 1.5% aqueous solutions of poly(acrylic acids): 2000 g/mol (graph A) and 4 000 000 g/mol (graph B). Each graph consists of voltammograms recorded at 0% (1), 50% (2), and 100% (3) neutralization degree. $T = 25^\circ\text{C}$. Scan rate: 10 mV/s.

molecular weights of 2000, 450 000, 1 250 000, 3 000 000, and 4 000 000 g/mol, respectively. Although a rising tendency can be noticed in the set of the numbers obtained, no monotonicity is observed. Inhomogeneity in the polymer molecular weight and an uncertainty in its determination as well as specific conformational differences may contribute to this scattered dependence. The numbers obtained can be interpreted as the maximum enhancement of the diffusion rate for 1,1'-ferrocenedimethanol driven by the structural changes in the polyacrylate system. Finally, it is worth noting that the diffusion of probe molecules in the poly(acrylic acid)/polyacrylate is almost as fast as in aqueous solution. The smallest diffusivities of the probe, observed for aqueous solutions of the poly(acrylic acids), depart from the D_0 value by no more than 27%.

The introduction of a certain portion of the strong base into the PAA solution results in the change in the chemical nature of the polyacid (the polysalt is formed) and in the physical transformation of the polyacid solution into the much more viscous gel-like medium. The detailed studies on the changes in intrinsic viscosity of the polyacrylate systems of the molecular weights smaller than 800 000 g/mol in the presence of a salt were done by Noda et al.²¹ Their investigation was limited to the region where no excess of OH^- ions was present. According to this work the intrinsic viscosity of the polyelectrolytes studied increases with the increasing ionization degree. This is consistent

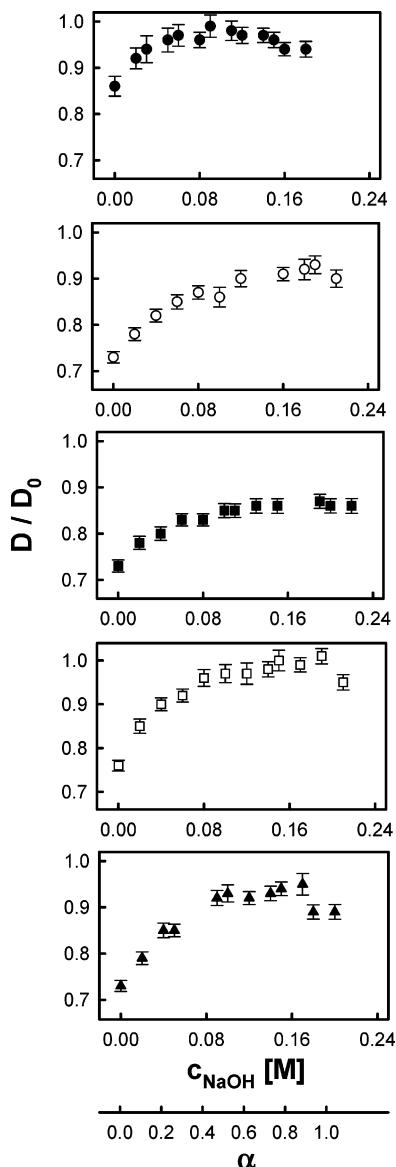


Figure 3. 1,1'-Ferrocenedimethanol diffusion coefficient versus concentration of added NaOH and neutralization degree of poly(acrylic acids) of various nominal molecular weights: 2000 (●), 450 000 (○), 1 250 000 (■), 3 000 000 (□), and 4 000 000 g/mol (▲). The probe diffusivity was normalized with respect to that obtained in aqueous solution, D_0 . The results are accompanied by their standard deviations. $T = 25\text{ }^{\circ}\text{C}$.

with our results obtained for salt-free poly(acrylic acid) of molecular weight of 450 000 g/mol. However, for the higher molecular weight poly(acrylic acids), a little different behavior is observed: the increase in viscosity up to the neutralization degree of 80% is followed by a very slight decrease up to 100%, which is then followed by a rapid drop for an excess of NaOH added. This behavior is observed for salt-free systems and occurs for the polyelectrolytes that form gels. The nature of this effect requires further research.

Interestingly, the variation in the probe diffusion coefficient qualitatively follows the line of the changes in the macroscopic viscosity of the polyelectrolyte system, as illustrated in Figure 4. The initial increase (and then the slight decrease) in the probe diffusivity accompanied by the increase (and then the slower decrease) in macroscopic viscosity of the polymeric system is in contrast to the predictions of the Stokes–Einstein relation (see eq 7). This conclusion confirms our expectation that the changes in the probe diffusion rate, measured by the diffusion

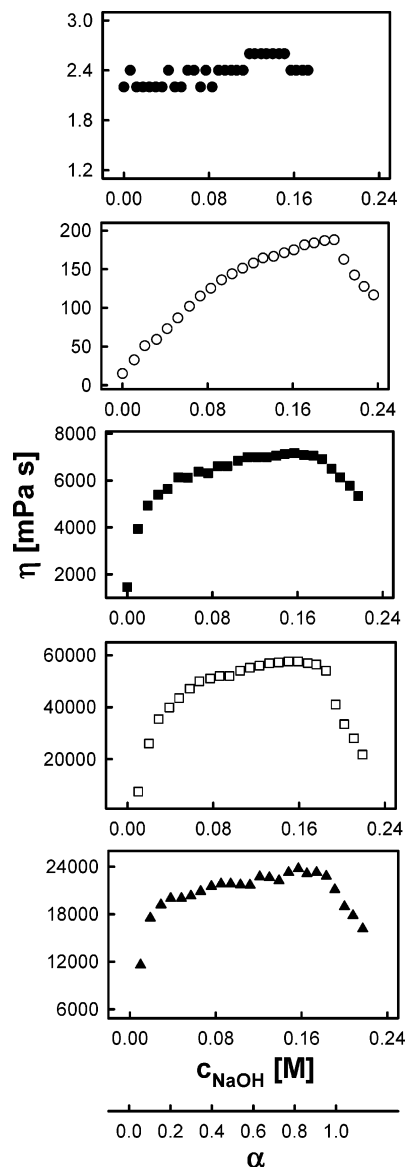


Figure 4. Changes in macroscopic viscosity during the titration of poly(acrylic acids) of various nominal molecular weights: 2000 (●), 450 000 (○), 1 250 000 (■), 3 000 000 (□), and 4 000 000 g/mol (▲). $T = 25\text{ }^{\circ}\text{C}$.

coefficient, are mainly due to the structural changes in the polyacrylate medium and the macromolecular rearrangements induced by the chemical reaction. Quantitatively, such a behavior can be described by the obstruction model of diffusion developed for the homogeneous gels and presented earlier in this section. The key parameter in this approach, whose magnitude may quantify arrangement of polychains in the macromolecule system, is the radius of the openings between the polymeric chains, r_o (see eq 5).

Having determined the D values for different stages of the poly(acrylic acid) neutralization as well as the corresponding value in the aqueous solution, D_0 , one is able to determine the r_o parameter using eqs 5–7. The r_s and r_p parameters were estimated to be 0.37 and 0.30 nm, respectively.

The variation of the r_o quantity versus the neutralization degree of poly(acrylic acids) studied is shown in Figure 5. Since r_o is directly proportional to the D/D_0 ratio, it is not surprising that the shape of the dependencies obtained is similar to that for D vs α relation. As the titration advances the consecutively increasing polychain charge density, which strengthens the

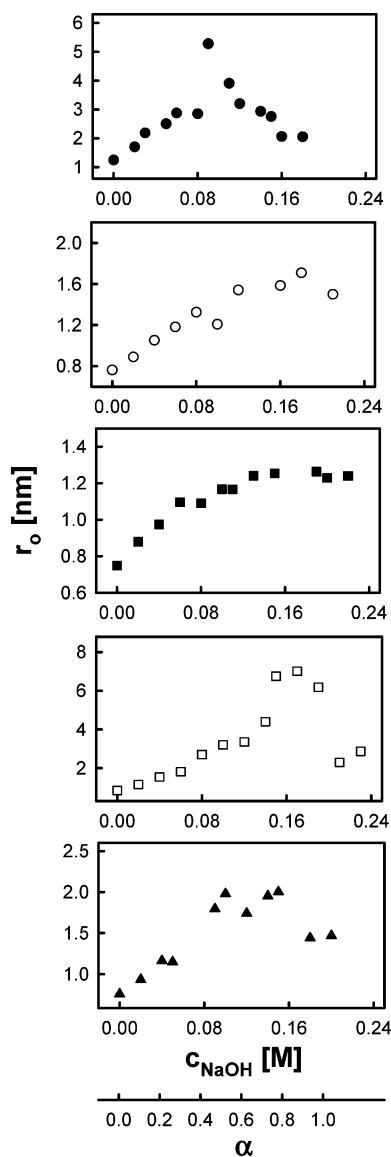


Figure 5. Calculated average radii of openings between polyacrylate chains versus concentration of added NaOH and neutralization degree of poly(acrylic acids) of various nominal molecular weights: 2000 (●), 450 000 (○), 1 250 000 (■), 3 000 000 (□), and 4 000 000 g/mol (▲). $T = 25\text{ }^{\circ}\text{C}$.

magnitude of the repulsive interactions between negatively charged polyions, causes an increase in the distances between the polychains. This process resembles the swelling behavior of the cross-linked polymeric gels. At a certain stage of the PAA neutralization, the presence of the excessive amount of Na^+ ions weakens these interactions, due to the screening of the polyionic charge, and, additionally, increases slightly the local, microscopic, viscosity of the solution inside the polymeric structure. The latter lowers the probe diffusivity and consequently results in the apparent decrease in the determined opening radii. Similarly to the changes in the probe diffusivity, the size of openings between polyacrylate chains becomes the largest for poly(acrylic acids) neutralized on average at 80% (or 45% for the lowest molecular weight PAA). The maximum numbers found for r_o are as follows: 5.3 ± 1.2 , 1.6 ± 0.2 , 1.3 ± 0.1 , 6.8 ± 2.8 , and 2.0 ± 0.3 nm for PAA of molecular weights of 2000, 450 000, 1 250 000, 3 000 000, and 4 000 000 g/mol, respectively. It is seen that the maximum r_o decreases in a series of polyacids of molecular weights from 2000 to 1 250 000 g/mol, and then significantly increases for polyacids

of 3 000 000 and 4 000 000 g/mol in molecular weight. This increase for the highest molecular weight poly(acrylic acids) examined is a result of the formation of highly ordered three-dimensional structure of the swollen polyacrylate gels.

Concluding Remarks

It has been shown that the diffusion studies of the uncharged probe system provide quantitative information on the changes in the structure of a polymeric system during its transformation from the solution into the gel-like or gel phase. The transport characteristics of the probe can be conveniently obtained from the voltammetric experiments at microelectrodes and then converted into the structure characteristics of the polymeric system according to the obstruction model of diffusion in gels. The results presented reveal that the most ordered structure of the polyelectrolyte, or in other words the most permeable structure, is obtained when PAA is neutralized at 75–80%. At this stage of polyacrylate formation the diffusion rate is the largest, as is the macroscopic viscosity (for the highest molecular weight polyacids), and its magnitude is very close to that determined for the aqueous solution. The above effect can be used for the detection of the gelation process.

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