

# Zeta Potential of Nafion Molecules in Isopropanol-Water Mixture Solvent

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**ABSTRACT:** Structure of Nafion in isopropanol/water mixture solvent has been investigated using zeta potential. It was found that zeta potential of Nafion strongly depends on the concentration. When the concentration of Nafion varied from 0.5 to 1 wt %, zeta potential increased significantly from about 0 to  $-12$  mV, corresponding to the change of structure of Nafion molecules from true solution to dispersion of aggregates. While the concentration is above 5 wt %,

micelle-like structure of Nafion aggregates was proposed. The dependence of zeta potential of Nafion on pH value at concentration of 5 wt % shows a nonmonotonic function and isoelectric point of Nafion-Na of 8.0 was observed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3306–3309, 2008

**Key words:** ionomer; Nafion; polymer electrolyte membrane; zeta potential

## INTRODUCTION

Nafion, a perfluorosulfonated ionomer produced by Du Pont, has been extensively used as proton exchange membranes for the applications of fuel cells because of its chemical/electrochemical stability and its excellent ionic conductivity in the hydrated state.<sup>1–3</sup> The general technique for the preparation of Nafion films is to evaporate the solvent from a Nafion solution, known as recast process. However, to have a better understanding of the nature and structure of the formed membrane, detailed information of solution properties is a prerequisite.

Nafion solutions in different solvents have recently attracted increasing attention. Studies on the self-assembling of Nafion chains in different solvents using small angle neutron or X-ray scattering<sup>4,5</sup> and electron spin resonance<sup>6,7</sup> have revealed that Nafion solutions contain large particles. Rod-like structure of Nafion chains, in which the perfluoro backbone constitutes the solvophobic core of the rod, the pendant chains are located at the periphery of the rods, and the ionic groups are at the rod-solvent interface, has been proposed. Viscometric study of diluted solutions of Nafion showed an increase in the reduced viscosity at low concentration, which was attributed to an increase in the polymer extension, resulting from the decrease of charge screening by other adjacent chains.<sup>8</sup> Dynamic

light scattering experiments<sup>9–11</sup> have also been carried out in both aqueous solutions and organic solutions. Different sizes of Nafion aggregates were found in all aqueous solutions and most of organic solutions. These aggregates were attributed to the hydrophobic interaction of fluorocarbon backbone and the electrostatic interaction through the ion pairs on side chains.

It is becoming clear that many properties of polyelectrolyte, such as molecular dimensions and molecular interactions, rely on the electrical potential of polyelectrolyte molecules. Since the dimensional size of a polymer molecule in solution is typically in the same range with colloidal particles, zeta potential which is initially used to describe the surface charge density of colloidal particles has been introduced to polyelectrolyte system by Strauss et al.<sup>12</sup> Recently, Liu and coworkers have investigated the interaction of an anionic polyelectrolyte sodium polyacrylate with oppositely charged surfactant using zeta potential. It has been demonstrated that at certain conditions (addition of salt), the polymer chains can wrap around discrete micelle-like structure.<sup>13</sup>

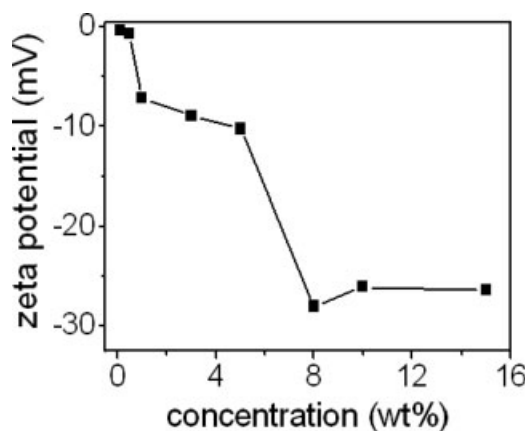
The often used commercially available Nafion solutions are dissolved in isopropanol (IPA)/water mixture solvent. In this present work, we reported that zeta potential can be used to describe the structure of Nafion in IPA/water mixture solvents, which may affect the properties of membrane formed from these solutions or dispersions.

## EXPERIMENTAL

Nafion solution (DE-520, EW1100) was purchased from DuPont, which contains 5 wt % of perfluorosul-

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**Figure 1** Zeta potential of Nafion as a function of concentration in isopropanol/water solutions at 25°C with a pH value of 3.0. Solid line is a guide to eyes.

fonate resin ( $H^+$  form) and 95 wt % of IPA/water mixture (10 : 9 weight ratio). Water was deionized through a Milli-Q system (Barnsted Nanopore, resistivity =  $18.0M \Omega \text{ cm}^{-1}$ ). All the other solvents and chemicals were reagent grade and were used as received.

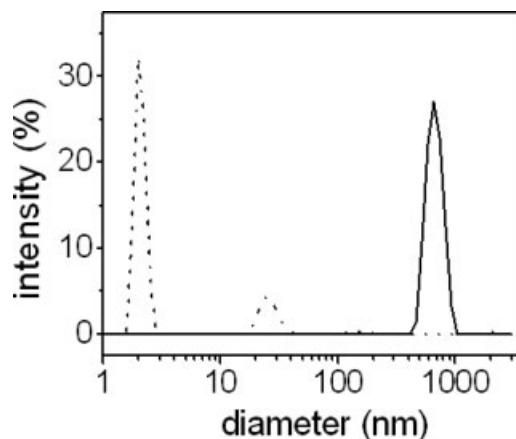
Nafion solutions with concentrations above 5 wt % were prepared by diluting concentrated Nafion aqueous solution, which was obtained by solvent evaporation of the purchased Nafion solution at 100°C, using desired amount of IPA/water mixture. Nafion solutions with concentrations below 5 wt % were prepared by diluting the received Nafion solution with IPA/water mixture (10 : 9 weight ratio). The pH values of all Nafion solutions were adjusted using 1M  $H_2SO_4$  solution or saturated NaOH isopropanol solution.

Zeta potential measurements were carried out on Zetasizer Nano-ZS (Malvern, UK) using laser Doppler velocimetry and phase analysis light scattering. The temperature of the scattering cell was 25°C and the data were analyzed with the software from supplier. Dynamic light scattering measurements were carried out with Malvern HPPS Laser Particle Size Analyzer (Malvern, UK) with scattering angle of 90° at 25°C using He-Ne laser (633 nm).

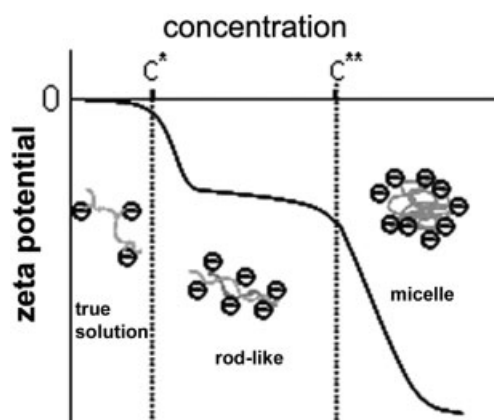
## RESULTS AND DISCUSSION

Zeta potential of Nafion molecules in IPA/water mixture solvent with fixed pH value of 3.0 as a function of concentration was first measured at 25°C, as shown in Figure 1. Two critical concentrations where zeta potential changed significantly were clearly observed at 0.5 and 5 wt %, respectively. When the concentration of Nafion is below 0.5 wt %, zeta potential in this regime is close to zero, suggesting that the charge density along the polymer chains is

relatively low. Since the  $pK_a$  value of sulfonate end-groups of Nafion is around  $-6$ ,<sup>14</sup> the sulfonic acid end-groups are fully dissociated. Thus, the possible explanation for the observed zero zeta potential in this regime is the molecular dissolution of Nafion which leads to an extension of polymer chains and accordingly a low charge density along polymer chains. While the concentration of Nafion increased to 1 wt %, zeta potential dramatically increases to about  $-8.5$  mV, indicating that relatively high local charge density along Nafion chains exists. This result is understandable. When the concentration of Nafion is above a critical concentration (0.5 wt % in this case), hydrophobic interaction between PTFE backbones dominates the conformational structure of Nafion molecules. Rod-like structure of Nafion chains caused by primary aggregation may be formed, resulting in high local charge density and consequently larger zeta potential. When the concentration varied from 1 to 5 wt %, zeta potential increased slightly, from  $-8.5$  to  $-12.2$  mV. This probably results from the stronger electrostatic repulsion and higher charge screening effect from other Nafion aggregates at higher concentration, which make the size of aggregates smaller, resulting in a higher local charge density at the polymer-solvent interface. Accordingly, higher negative zeta potential was observed. This hypothesis was further proved by dynamic light scattering measurements, shown in Figure 2. It can be clearly seen that the particle size is about 30 nm in 0.5 wt % solution, corresponding to single molecular distribution of Nafion molecules, and it is about 800 nm in 5 wt % solution, corresponding to entanglement of Nafion molecules in solution respectively. This behavior has also been investigated in a very similar system using dynamic light scattering measurements by Lee et al.<sup>11</sup> With further increasing the concentration,



**Figure 2** Distribution of scattering intensity of Nafion molecules at different concentrations: 5 wt % (solid line) and 0.5 wt % (dot line).



**Figure 3** Diagram of state of zeta potential of Nafion in solutions in the coordinate of polymer concentration.

zeta potential of Nafion reaches the maximum, around  $-28$  mV at 8 wt %, and a plateau has been observed after that concentration. We believe that above a certain concentration (second critical concentration, 5 wt % in this case), more and more chains are entangled each other through PTFE backbone and micelle-like structure of Nafion molecules may appear to minimize the polymer-solvent interfacial energy. This leads to a maximum local charge density at solvent-polymer interface and accordingly a highest zeta potential of Nafion molecules. In this regime, further increase in concentration leads to an increase of number of aggregates. However, the local charge density of those aggregates does not change, resulting in a plateau of zeta potential at relatively high concentration.

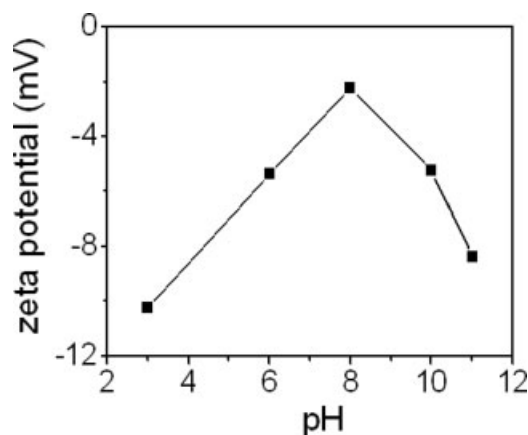
Since the chemical structure of Nafion composes hydrophobic poly(tetrafluoro ethylene) (PTFE) backbone and hydrophilic sulfonated fluorovinyl ether side chains, it is not surprising that different structures of Nafion chains exist in solutions. The diagram of zeta potential of Nafion molecules as a function of concentration has been illustrated in Figure 3. The result that two aggregation processes of Nafion exist in IPA/water mixture solvent is qualitatively consistent with observations in methanol/water mixture solvent using dynamic light scattering technique described in literature.<sup>11</sup> The critical concentration observed in methanol/water mixture solvent is about 10 times lower than that in this study. This difference probably comes from the solubility of the PTFE backbone of Nafion in different solvent. Compared to methanol, isopropanol is a better solvent for PTFE backbone. Therefore, the aggregation of Nafion in isopropanol/water mixture occurs at a relatively high concentration.

The dependence of zeta potential of Nafion molecules in IPA/water mixture on pH value of solutions was investigated at  $25^{\circ}\text{C}$  with a Nafion concentration of 5% in weight.  $1.0\text{M}$   $\text{H}_2\text{SO}_4$  or saturated NaOH iso-

propanol solution was used for adjusting the pH of Nafion solution to a desired value. Since the amount of added acid or base is quite small, the influence of the added acid or base on the concentration of Nafion was neglected.

It can be clearly seen from Figure 4 that zeta potential of Nafion in measured pH range is negative, indicating that Nafion molecules are negatively charged. Interestingly, zeta potential of Nafion molecules in IPA/water as a function of pH value shows a nonmonotonic behavior. Zeta potential of Nafion decreases initially with the increase of pH value; however, it increases after passing a minimum. The initial decrease of zeta potential is probably attributed to the increased amount of sodium ions diffused to the polymer-solvent interface which leads to higher screening of the charges on the side chain of Nafion molecules. Accordingly, zeta potential of Nafion decreases with pH value in this regime. At pH around 8.0, all the protons in the initial form of Nafion were replaced by sodium ions and the screening effect of charges on the side chain of Nafion reached a maximum. As a result, zeta potential of Nafion reaches minimum, about  $-2.23$  mV. At this pH value, the Nafion solution in IPA/water mixture even becomes turbid, as can be observed even by eyes. This result indicates that Nafion molecules in sodium ion form reach the isoelectric point and the polymer has the tendency to precipitate from the solution. With further increase of pH value of the solution, negatively charged  $\text{OH}^-$  ions start to adsorb onto the Stern layer and accordingly the diffusive layer becomes broader. Therefore, zeta potential of Nafion increases with the pH value in this regime.

To learn how the solvent affects the structure of Nafion molecules, zeta potential in water at  $25^{\circ}\text{C}$  with a concentration of 5% in weight and a pH of 3.0 was also measured. The value is  $-72.96$  mV



**Figure 4** Zeta potential of Nafion as a function of pH value in isopropanol/water solutions at  $25^{\circ}\text{C}$  with a concentration of 5% in weight. Solid line is a guide to eyes.

which is much larger than that in IPA/water mixture solution (about  $-10$  mV). It has shown in the literature that propanol has a better solubility with the fluorocarbon backbone of Nafion while water has a better solubility with Nafion ionic cluster part.<sup>11</sup> It is evident, that Nafion molecules in IPA/water mixture have less aggregation due to the solvation of the fluorocarbon backbone by isopropanol whereas Nafion molecules in water strongly aggregate through the solvophobic interactions of perfluoro carbon backbone. Therefore, the local charge density of Nafion in water is larger than that in IPA/water mixture solvent, resulting in a higher negative zeta potential in water solution.

### CONCLUSIONS

In this communication, we have demonstrated that zeta potential can be used to describe the conformational structure of polyelectrolyte molecules in solution. Zeta potential of Nafion in IPA/water mixture solvents has been reported as a function of concentration as well as pH value. At relatively low concentration (less than 0.5 wt %), zeta potential of Nafion is close to zero, suggesting a true solution of Nafion in this regime. With further increasing concentration, two critical concentrations where zeta potential of Nafion varies significantly were observed, corresponding to different structures (rod-like and micelle-like structures) of Nafion aggregates in solution. The dependence of zeta potential of Nafion on pH of solutions at 5 wt % shows a non-monotonic behavior. It initially decreases due to the charge screening effect and later starts to increase

because of the adsorption of hydroxide ions at the polymer-solvent interface. Moreover, a much larger zeta potential of Nafion in water solution has also been observed compared to that in IPA/water solution, attributed to large aggregations in water solution.

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