CONFORMATION OF NAFION MOLECULES IN DILUTE ISOPROPYL ALCOHOL/WATER MIXTURE SOLUTIONS

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ABSTRACT

Nafion polymer is an ionomer for proton exchange membranes and catalyst ink solutions in PEM fuel cell. In this work, the conformations of Nafion molecules in dilute solutions of IPA (isopropyl alcohol)/ water mixture solvents with various contents of IPA are investigated using dynamic light scattering and transmission electron microscope. The results show that there are two modes of Nafion molecular conformations in the solutions, i.e. the small particles mode due to the Nafion single chain molecules or small aggregates and the large particles mode due to the aggregate clusters of Nafion small particles. The sizes of the small particles and of large clusters change with the composition of IPA/water mixture solvent and has a largest Nafion particle size and a smallest cluster aggregate at an IPA/water molar ratio of around 1/3.

Keywords: Nafion conformation; dilute solutions; transmission electron microscopy; dynamic light scattering.

INTRODUCTION

The chemical structure of the Nafion consists of a hydrophobic perfluorocarbon backbone and hydrophilic vinylether side chains terminated with sulfonic acid groups [1]. The two structures are incompatible and have dual solubility parameters δ, i.e. $\delta_1 = 9.7$ $(cal/cm^3)^{1/2}$ ascribed to the perfluorocarbon backbone and $\delta_2 = 17.3$ $(cal/cm^3)^{1/2}$ ascribed to the sulfonated vinylether side chains [2]. It is an indispensable part of the proton exchange membrane fuel cells (PEMFCs) [3-5]. Nafion solutions are usually used for casting proton exchange membranes (PEMs) and preparing catalyst ink solutions [6-8]. Alcohol/water mixture solvents, especially isopropyl alcohol (IPA) and water mixture, are the most common solvents for casting Nafion PEM and catalyst ink solutions. However, the physical properties of Nafion in alcohol/water mixture solutions as a function of the alcohol/water wt (or vol, or molar) ratio had rarely been observed and discussed, thus the optimum alcohol/water ratios for the solvents of the Nafion casting membrane solutions and the catalyst ink solutions are still not clear. In this paper, using dynamic light scattering (DLS) and transmission electron microscope (TEM), we report the conformation of Nafion molecules in the dilute IPA/water mixture solutions with various IPA/water molar ratios (or wt ratios). The behavior of Nafion molecules in IPA/water mixture solvents with various IPA/water molar ratios is discussed based on the inter-molecular hydrogen bonding, ε_s and δ_s of the solvents.

EXPERIMENTAL

(a) Viscosity of IPA/water mixture solvents─ The flow times of the IPA (reagent grade, J.T. Baker) / water mixture solutions with the IPA concentration varied from 0.0 wt% to 100.0 wt% were measured at 25^oC using an Ubbelohde viscometer. Using the viscosity of pure water (i.e., 0.890 cP at 25^oC) as a reference, the viscosity of each mixture solution was calculated from its flow time; (b) Density of IPA/water mixture solvents ─ A Digital Density Meter, Type DA-505 KEM has been used to measure the density of the IPA/water mixture solvents; (c) Nafion solutions preparations─ The solid Nafion resin (equivalent weight 1100, Du Pont) was then dissolved in IPA/water mixture solvents, in which the IPA content ranged from 20 wt% to 100 wt%, to prepare Nafion solutions. All the Nafion-IPA/water solutions had a Nafion concentration of 0.6 mg/mL; (d) The DLS measurements were

carried out with a 256-channel autocorrelator (Brookhaven Co, model BI9000). The laser was an Ar ion (514 nm, operated at 100 mW, Spectra Physics model). The experiments were carried out at 25°C with a scattering angle of 55°; (e) The morphology of Nafion molecules in dilute solutions was observed using a JEM-2100 (HR) TEM at an accelerating voltage of 80 kV. The Nafion solution sample was frozen dried on a copper grid with 200 mesh carbon film (CF200-Cu, Electron Microscopy Sciences, Inc., PA) sample holder to fix the morphology of Nafion molecules same as in dilute solutions. The copper grid was floated on the top of the surface of a drop of 0.6 mg/ml Nafion solution for 12 h. Thus a thin film of Nafion solution was covered on the surface of the copper grid. It was frozen immediately in a liquid nitrogen container at a temperature of approximately -190°C for 4 h. The solvent of the frozen Nafion thin film on the copper grid surface was dried under vacuum at -130°C for 5 h. The copper grid with a dried Nafion film on its surface was then immersed in 1M $Pb(NO_3)_2$ (Aldrich) aqueous solution for 10 min to stain the sulfonic acid groups of Nafion, and then dried at room temperature. The copper grid was then rinsed with deionized water and dried at room temperature.

RESULTS AND DISCUSSION

3.1 Viscosities and densities of IPA/water mixture solvents

Figs. 1 and 2 show the plots of the mixture solvent viscosity and density, respectively, versus the wt ratio of IPA/ [IPA + water] and the IPA/water molar ratio at 25°C. The viscosity and density of the solvent do not change linearly with both the IPA/ [IPA + water] wt ratio and the IPA/ water molar ratio. These data show a parabola curve with a maximum viscosity at a IPA/ [IPA + water] wt ratio of around ~ 55 wt%, which corresponds to a IPA/ water molar ratio of around 1/2.9. Similar viscosity and density behavior results from the binary mixture of water with alcohol had also been reported in literature [9-11]. The self-association and inter-association through hydrogen bonding between water and alcohol have a great influence on the viscosity and density of the mixture solution. These data suggest that there is a strong hydrogen bonding interaction between the IPA and water molecules, which causes a higher mixture solvent viscosity and density than the linear combination viscosity

and density of the pure IPA and pure water. The maximum number of water molecules bounded per IPA molecule is around 3, i.e., the IPA/water molar ratio is around 1/3 (Fig. 3). It has been suggested that the alcohol molecules form clusters inside the H-bond network of water molecules at a alcohol/water molar ratio lower than that of the maximum viscosity and density (i.e., IPA/water < 1/3 molar ratio) [9]. The alcohol content of the alcohol/water mixture solvent increased higher than that of the maximum viscosity and density (i.e., IPA/water > 1/3 molar ratio), alcohol clusters start to get together and break the water H-bond net-work structure, leading to a lower viscosity with higher alcohol fraction.

3.2. TEM and DLS studies of dilute Nafion IPA/water solutions

Fig. 4 is the TEM observation of the conformations of the Nafion molecules which were frozen from the dilute IPA/water mixture solutions with various mole ratios of IPA/water. It was found that there were Nafion clusters with each cluster consisting of around 10-100 small Nafion particles, and the sizes of the small particles were around 10-50 nm. The DLS hydrodynamic radius (i.e., R_h) distributions of Nafion particles in various dilute IPA/water mixture solutions are illustrated in Fig. 5, which also shows two modes of Nafion particle size distributions. The small particle DLS mode has particle size distributions of around $\leqq$ 100 nm, which corresponds to the small Nafion particles in TEM micrographs and increases as the IPA content of the IPA/water mixture solvents increases from 20 wt% to 55 wt% then decreases when the IPA content in IPA/water mixture solvent increases from 55 wt% to 100 wt% IPA. The DLS large particle mode has particle size distributions of around 100-500 nm, which corresponds to the Nafion clusters observed in TEM and decreases when the IPA concentration of the IPA/water mixture solvent increases from 20 wt% to 55 wt% then increases as the IPA concentration of the IPA/water mixture solvent increases from 55 wt% to 100 wt%.
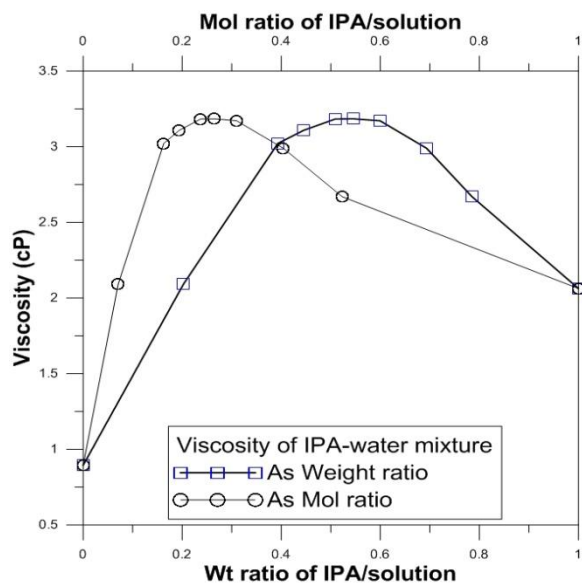
Fig. 1. Viscosity of the IPA/water solvent at 25^oC versus wt ratio of IPA/ [IPA + water] (□) and molar ratio of IPA/ water (○).
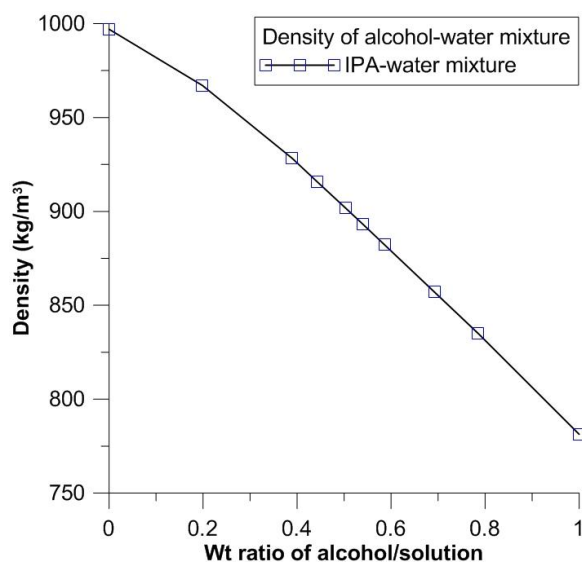

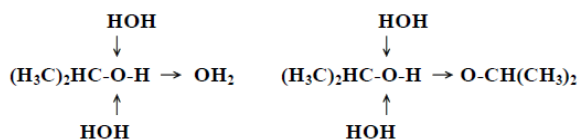*Fig. 2.* Density of the IPA/water mixture solvent at 25^oC versus the wt ratio of IPA/ [IPA + water]

Fig. 3. The hydrogen bonding interactions (i.e., the arrows in the graph) of water molecules with IPA molecule: IPA/water $\leq$ 1/3 mole ratio (left side) and IPA/water > 1/3 mole ratio (right side).

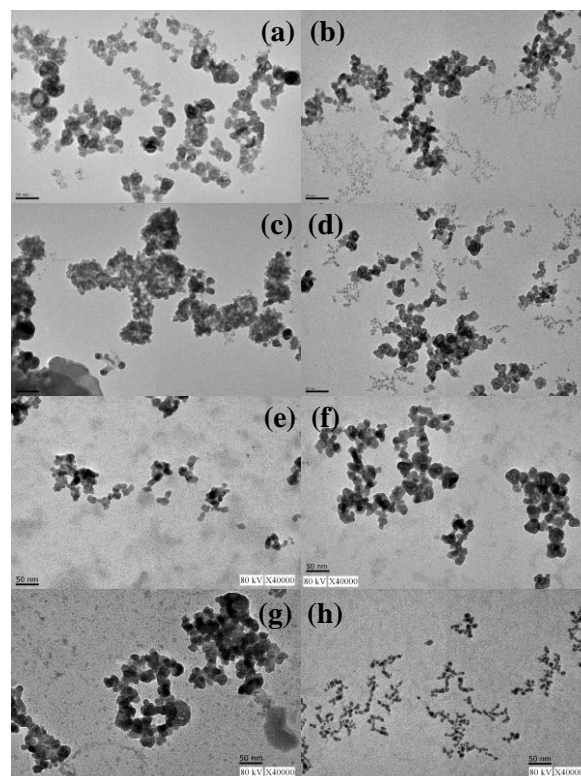3.2 TEM and DLS studies of the dilute Nafion-IPA/water mixture solutions

Fig. 4. TEM micrographs (×40000; scale bar 50 nm) of the polymer conformations of 0.6 mg/mL Nafion in IPA/water solutions. The concentrations of IPA in the mixture solvents from (a) to (h) are: 20, 45, 50, 55, 60, 70, 80, and 100 wt% respectively.
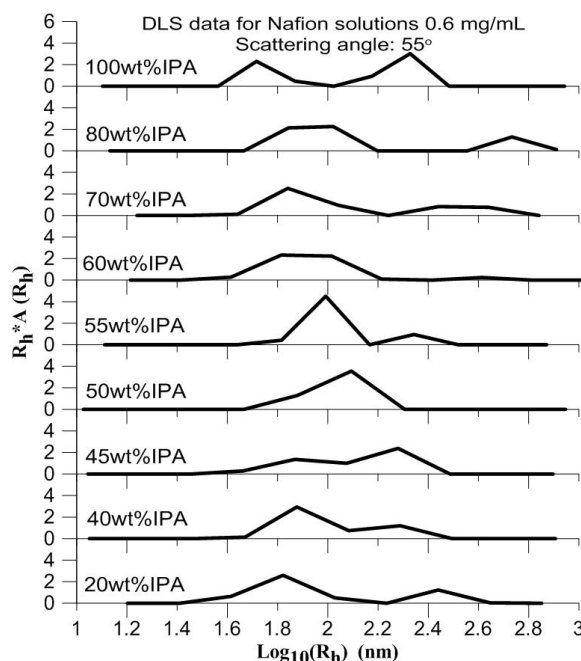

Fig. 5. DLS hydrodynamic radius (R_h) for 0.6 mg mL^{-1} Nafion solutions in IPA/water solvents. Tem=25^oC, scattering angle θ = 55°. The

number in the figure indicates wt% of IPA in the mixture solvent.

3.3. Discussions

In a Nafion IPA/water solution, the competition of the self-association and inter-molecular interactions among the Nafion, IPA, and water molecules determines the Nafion molecular conformation. We divide the IPA/water solvents into four regions: region-I (20-45 wt% IPA; 13.3-4.1 mol H_2O/mol IPA), region-II (50-60 wt% IPA; 3.3-2.2 mol H_2O/mol IPA), region-III (70-80 wt% IPA; 1.4-0.8 mol H_2O/mol IPA, and region-IV (100 wt% IPA). According to the density and viscosity data, inter-IPA/water molecular hydrogen bonding interactions occur in region-II with a maximum of 3 water molecules binding on an IPA (Fig. 3). Few self-hydrogen bonding interactions of water and IPA occur in this region. In region-I the mole ratio of H_2O/IPA is larger than 3 and contains "excess water molecules", which associate through self-hydrogen bonding. In region-III, the mole ratio of H_2O/mol is ~1.4-0.8. The $\delta = 11.8$ (cal/cm^3)$^{1/2}$ of IPA is close to that of the Nafion backbone and is compatible to Nafion backbone. Nafion can be dissolved in pure IPA. The $\delta = 23.40$ (cal/cm^3)$^{1/2}$ of water is much higher than those of both the backbone and vinyl ether side chains of Nafion. Nafion is not dissolved in pure water. In the IPA/water solutions, Nafion molecules are more likely to contact with IPA rather than with water. In solution region-I, each IPA molecule is isolated in a water cage and IPA molecules are separated from each other with a far distance. The Nafion molecules in the solutions should be in contact with the IPA. Since the Nafion concentration is very dilute, the Nafion molecules in contact with IPA are separated from each other and the particle sizes are small. As the IPA concentration in the IPA/water solvent is increased from region-I to region-II, the distance between the IPA molecules decreases. Thus the Nafion molecules in contact with IPA have more chance to interact with each other and form larger particles. The Nafion particle size increases as the IPA content in the solvent is increased from 20 wt% to 55 wt% and has a maximum particle size in region-II. As the IPA content in the IPA/water solvents increases from 55 to 100 wt% (region-III and region-IV), the IPA molecules break the water cage. More and more number of IPA molecules are for each Nafion polymer. The increase of binding IPA molecules per Nafion molecule results in a decrease of the number of Nafion molecules in a Nafion aggregated particle, thus the Nafion particle sizes decrease with increasing IPA concentration in region-III and region-IV.

CONCLUSION

Properties of various IPA/water mixture solvents and Nafion molecular conformations in dilute IPA/water solutions were investigated using DLS and TEM. We showed that the Nafion molecular conformations in dilute solutions were strongly influenced by the wt ratio of IPA/water. The maximum Nafion molecular aggregations attain at the solvents containing 40 wt%-55 wt% of IPA, wherein the inter-molecular hydrogen bonding interaction between the IPA and water molecules is in the highest degree.

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