Investigation of the equilibrium thermodynamic properties of the poly(vinylidene floride)/N-methyl-2-pyrrolidone/water ternary system: all-atom molecular dynamics simulation

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Abstract

One of the most common procedures for constructing polymer hallow fiber membrane is the non-solvent induced phase separation process. In this technique, solvents play a very important role in determining the membrane morphology. Since the filter performance of the material depends mainly on the morphology, understanding the thermodynamic phase equilibrium of the polymer/solvent/non-solvent mixture is important. To reveal the underlying physical nature of the solvent-polymer interactions and predicting the phase equilibrium of the ternary system, in this study, we investigate the miscibility of the PVDF/NMP/water ternary system, using a combination of molecular dynamics techniques and multicomponent Flory-Huggins theory. We quantify the affinity and association of PVDF as a function of NMP/water concentration by calculating, for example, the free energy of mixing and the scaling properties of PVDF.

Introduction

Poly(vinylidene floride), PVDF, hollow fiber membranes have been used to effectively remove suspended solids and micro-organisms during water treatment. Such polymer membranes are commonly constructed following the non-solvent induced phase separation process [1]. In this technique, solvents and non-solvents play a very important role in determining the membrane morphology. Since the performance of the material depends mainly on the morphology, a complete understanding of the thermodynamic phase equilibrium of the PVDF/solvent/non-solvent mixture is required.

Although PVDF/solvent/non-solvent systems have been used widely in industrial membrane applications, few experimental studies that construct the phase diagram of PVDF/solvent/non-solvent systems are present in literature [2,3]. Furthermore, to the best of our knowledge, there is only one molecular (or atomistic) level study that focus on such systems [2]. For this reason, in this present work, we investigate the miscibility of the PVDF/NMP/water ternary system using a combination of molecular dynamics (MD) techniques and multicomponent Flory-Huggins theory. Additionally, the effect of solvent/non-solvent concentration on the structural properties of PVDF is evaluated.

Methodology

All-atom MD simulations were carried out using the OPLS-AA force field for PVDF and NMP,[4][4] and the TIP4P/2005 water model [5]. Initial configurations were generated by arranging these molecules randomly in a cubic box. After equilibration simulations, a production MD run was carried out in the isothermal−isobaric (NPT) ensemble, maintaining the temperature at 298 K with a velocity rescaling thermostat and a coupling time of 0.1 ps. Isotropic pressure coupling was used for all the systems under investigation using a Parrinello–Rahman barostat with a reference pressure of 1 bar, coupling time of 1.0 ps, and compressibility of 4.5×10^{-5} bar^{-1}. A time-step of 2 fs was employed, and bonds were

constrained using the LINCS algorithm. Long range electrostatics were calculated using the particle mesh Ewald summation (PME) with a Fourier spacing of 0.12 nm and a fourth-order interpolation. The van der Waals and Coulomb cutoff was set to 1.2 nm. All simulations were performed using GROMACS 5.1.4 MD package.[6]
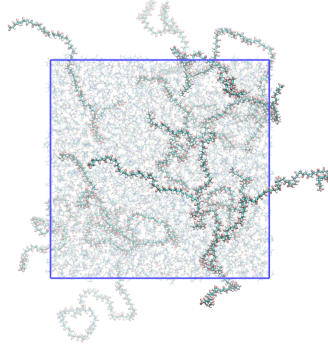

Figure 1: PVDF in water and NMP

Result and discussion

MD simulations has been carried out to quantify the miscibility of PVDF with NMP and water by calculating the composition dependent Flory-Huggins interaction parameter (χ), which is given by

$$\chi = \frac{V_{ref}\Delta H_m}{kT\, V_m\, \phi_A \phi_B}$$

where V_{ref} is the reference volume, which is taken as the volume of PVDF monomer and V_m is the total volume of the mixture. $\Delta H_m/V_m$ is the change in enthalpy upon mixing per unit volume.

χ can be either negative (favorable interaction) or positive value (phase separation) for polymer in good solvent and in a poor solvent, respectively. The results in figure 2 shows that PVDF and NMP are mutually soluble while PVDF and water are insoluble. In Literature, the solvent/polymer and non-solvent/polymer interaction parameters are normally taken as a constant. However, our result shows that there is a clear dependency on the composition of PVDF and it rapidly increase or decreases when $\phi > 0.6$. This information can then be used to calculate the Gibbs free energy of mixing of the 3 binary systems and predict the phase equilibrium of PVDF/NMP/water ternary system.
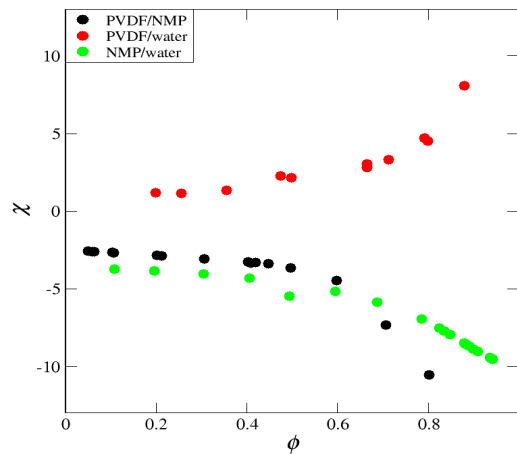
Figure 2: Flory-Huggins interaction parameter (χ) of NMP/PVDF and water/PVDF with increasing volume fraction (ϕ) of PVDF, and χ of NMP-water with increasing ϕ of NMP.

The structure of the PVDF is also quantitatively analyzed through the calculation of its radius of gyration (R_g). From MD simulations of PVDF with increasing number of monomers (N) in pure NMP and water, the scaling laws $R_g \sim N^\upsilon$ was obtained. The resulting Flory parameter υ of PVDF in NMP is comparable with existing polymer scaling theory for polymers in good solvent $\upsilon = 0.61$. However, υ achieved for PVDF in water is much lower than the theoretical value for polymer in poor solvent, $\upsilon = 0.13$. This is because PVDF is highly hydrophobic polymer and takes very ordered structure in water.

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