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Molecular dynamics simulation on evaporation of water and aqueous droplets in the presence of electric field

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ABSTRACT

The study on evaporation of water droplet with dissolved salt is important for the understanding of electrospinning and electrospray mass spectrometry experiments. In this work the dynamics of evaporation of water droplet and aqueous droplet with dissolved either LiCl, NaCl or KCl salt in the absence and presence of a homogeneous electric field are comparatively studied by molecular dynamics simulations. The results show that (1) the evaporations of water and aqueous droplets are all accelerated by applying an electric field; (2) the aqueous droplet evaporates slower than the water droplet at low electric field of 0.4 V nm^{-1}, however, its evaporation rate is enhanced significantly and exceeds the water droplet at high electric fields of 0.6 and 0.8 V nm^{-1}; (3) aqueous droplet with dissolved KCl molecules evaporates the fastest, and then followed by dissolved NaCl and LiCl molecules; (4) an optimal salt concentration is observed for the aqueous droplet, above which the evaporation rate is reduced significantly and may cause a electrospinning failure. The present results are qualitatively agree with the observations in the electrospinning experiment and are attributed to the fact that the electric field applied causes the droplet deformation, directional arrangement of water molecules along the electric field direction, acceleration of water molecules due to ions acceleration, as well as hydration effect.

1. Introduction

The evaporation of the droplet with dissolved salts in the presence of a high-voltage electric field has been applied in the electrospinning [1–10] and electrospray ionization process [11–15]. Electrospinning is a straightforward method to produce continuously polymer fibers. The standard setup for the electrospinning is composed of a syringe needle, connected to a high-voltage power supply, a syringe pump, and a grounded metal plate [16]. When a strong electrostatic force is applied to the syringe needle, the polymer solution is ejected from the syringe needle to form a thin spraying stream, finally, the polymer deposits and solidifies as a non-woven fibrous structure on the grounded metal plate after the solvent evaporates almost completely. Because the fibers prepared by the electrospinning has nanoscale diameter and a large surface-to-volume ratio, the fibers can be used as filter media, separation membranes, wound dressing materials, artificial blood vessels, sensors, composite reinforcements [17–20].

Many experimental investigations [1–10] have shown that the morphology of fibers prepared by the electrospinning is strongly related to the spinning conditions such as polymer concentration, needle-to-plate distance, applied electric field strength, and solvent evaporation. Some investigations [7–10] also demonstrated that adding the ionic salts into the spinning solution can improve the solution spinnability remarkably. Qin et al. [7] found no fibers were produced by electrospinning under the electric voltage of 5 kV when the Polyacrylonitrile (PAN) polymer solution did not dissolve salt, however, adding a small amount of LiCl salt into the solution increased the solution spinnability significantly due to enhancement of solution conductivity. Zong et al. [8] studied the effect of three kinds of salts (NaH_2PO_4, KH_2PO_4, NaCl) on electro spinning of biodegradable amorphous poly (D, L-lactide) (PDLA) membrane. They found that the smallest, moderate, and the largest average diameters of fibers were produced when 1 wt% NaCl, 1 wt% NaH_2PO_4, and 1 wt% KH_2PO_4 were respectively added into the 30 wt% PDLA solution as the spinning solutions. The dependence

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of fiber diameter on the salt type was attributed to the charge density carried by jet and the ion size. Qin et al. [9] investigated the internal structure of electrospinning polyacrylonitrile (PAN) nanofibers by adding different content of LiCl (1–4 wt%). The results showed that the added salts enhanced the PAN fiber spinnability, however, did not change the chemical composition of PAN, and showed that higher LiCl content reduced the diameter of PAN. Kim et al. [10] investigated the effect of adding the various concentrations of NaCl (0, 0.01, 0.1, and 1 M) on the morphology of Poly (acrylic acid) (PAA) nanofibers. The smallest diameter of the PAA nanofibers was prepared by PAA solution with 0.01 M NaCl, however, the nanofibers could not be produced when the concentration of NaCl increased to 1 M.

Though the evaporation of the solvent is only the concomitant for the electrospinning process, fast evaporation is essential to formation of ultrafine fibers with nanoscale diameters [16]. If the evaporation of the solvent is too slow, it will cause a failure of electrospinning because the polymer solution (not polymer fiber) is deposited on the metal plate [10]. Therefore, higher electric field strength and/or addition of the salt into the solution can improve the solution spinnability may be attributed to the enhanced evaporation rate of the solvent. Unfortunately, the responsible mechanisms for enhanced evaporation rate at thus conditions are not yet understood well.

Molecular dynamics attempts to simulate the real behavior of Nature by identifying each atom and following their motion in time through the basic laws of classical mechanics. Molecular dynamics simulating an evaporation process has no need of some assumptions made by computational fluid dynamics, so this method was adopted extensively to study the evaporation of liquid droplet [21–28] or thin liquid film [29–31] in the absence of an electric field. In the recent decade, molecular dynamics simulations were also used to investigate the behavior of water droplet with dissolved ions [11,12,14,15], macroions [13], or biological macromolecules [32] for understanding of electrospray mass spectrometry experiments. The main motivation for these investigations [11–15,32] is to analyze biological macromolecules with high accuracy and throughput. By the usage of electrospray ionization, nucleic acids, proteins, carbohydrates, and synthetic polymers have been extensively analyzed with ultrahigh accuracy [15]. These investigations just focused on how to produce completely desolvated macromolecules, but did not concern the effect of addition of ions on the droplet evaporation.

The objective of this work is to understand which parameters affect the solvent evaporation and how to accelerate the solvent evaporation in the electrospinning for fabricating high-quality nanoscale fibers. Because water has often been used as a solvent in the electrospinning, water droplet is selected in this work. The dynamic behavior and evaporation rate of water droplet (1120 water molecules) without or with dissolved LiCl, NaCl or KCl (20, 30, 40, 80, 100, 120 salt molecules) in the absence or presence of a homogeneous electric field (0.4, 0.6, 0.8 V nm^{-1} along x-direction) are comparatively studied by performing molecular dynamics simulations, which can give some insight into mechanism of enhanced evaporation rate. The droplet is heated in 600 K nitrogen gas atmosphere to activate its evaporation. Because there are only non-covalent bonds between water and most of macromolecular polymer used in the electrospinning [32], the macromolecular polymer has a small effect on the evaporation rate, and hence does not be included in the droplet.

2. Molecular dynamics simulations

2.1. Simulation cases

Molecular dynamics simulations are performed for evaporation of the water droplet and the aqueous droplet with dissolved either NaCl, LiCl or KCl in the absence or presence of a homogeneous electric field. The droplet is surrounded and heated by nitrogen gas during the evaporation. The initial configuration of the evaporation system is shown in Fig. 1. The droplet and nitrogen gas are placed in a cubic box with 12 nm side length. Ions, nitrogen molecules, and water molecules are distinguished with different colors. The radius of the initial droplets is 2 nm, and the number of water molecules in the droplet is 1120 for all simulation systems, which corresponds to the pure water density of 1 g cm^{-3}. The number of nitrogen molecules is 600 corresponding to 16.47 kg m^{-3} gaseous density. Three kinds of salts (120 NaCl, LiCl or KCl molecules) are respectively added into the droplet to analyze the effect of salt type on the droplet evaporation, and 20, 30, 40, 80, 100, and 120 LiCl molecules are respectively added into the droplet to analyze the effect of salt concentration on the droplet evaporation. A homogeneous electric field E along x-axis direction is applied to the box, so an additional force $F_i = q_iE$ is imposed on each charge q_i. Okuno et al. [16] estimated the electric field around the tip of syringe needle during the electrospinning and proposed that the value was in the range of about 0.7 to 100 V nm^{-1} for pure water as spinning solution. The electric field value of 0.4, 0.6, and 0.8 V nm^{-1} are adopted in the present work, two smaller values are selected in order to understand why the solution spinnability is worse for the electric field lower than the threshold value of 0.7 V nm^{-1}.

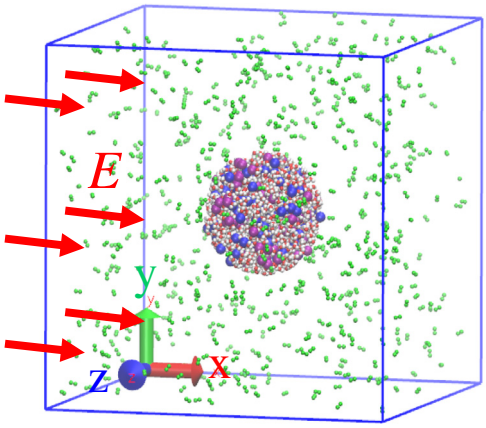

Fig. 1. Model of initial evaporation system: green ball is N, white ball is H, red ball is O, blue ball is positive ion, and purple ball is chloride ion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Potential function

In recent decade, some studies [33,34] have compared the properties of water and/or aqueous solution predicted by various water models. More recently, Vega and Abascal [35] conducted a comprehensive comparison between various water models. In their comparison, a certain number of points between zero (bad agreement) and ten (good agreement) was given for the predictions of each model and property. The results indicated that TIP3P, TIP5P, TIP4P, SPC/E and TIP4P/2005 obtained an average score of 2.7, 3.7, 4.7, 5.1, and 7.2, respectively. The SPC/E model for water molecules was originally proposed by Berendsen et al. [36], and the HO-distance and H–O–H angle for the SPC/E model are 0.1 nm and 109.47°, respectively. Using the SPC/E water model, Chowdhuri and Chandra [37] performed a series of molecular dynamics simulations of aqueous NaCl and KCl solutions. Their results of the concentration dependence of self-diffusion coefficients were found to be closer to the corresponding experimental values. The study objects of the present work are also aqueous droplets with dissolved salts, so that the SPC/E water model is chosen. Nitrogen