Molecular dynamics approach to the structural characterization and transport properties of poly(acrylonitrile)/N,N-dimethylformamide solutions

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A B S T R A C T

Poly(acrylonitrile) (PAN) in N,N-dimethylformamide (DMF) is a popular solution for producing large variety of polymer products. To precisely describe the behaviours of PAN and DMF in the synthesis processes, it is significant to call for more details about the structure, some thermodynamic and dynamical properties of PAN-DMF solutions. A PAN-DMF solution was simulated via molecular dynamics with an all-atom OPLS type potential in both the NPT and NVT ensembles. The simulation results were evaluated with quantum mechanical calculations (MP2/6-311++G(d,p) and counterpoise procedure) and were compared with available experimental results. The liquid structure was illustrated with pair correlation functions and transport and dynamics properties were calculated with the mean-square displacements MSD and the velocity autocorrelation functions. The strong H-bonds of C≡N···H—C═O, CH···O═C—H and CH2···O═C—H, with distances of 2.55 Å, 2.55 Å and 2.65 Å, respectively, were found. The largest interaction energy of −7.157 kcal/mol between DMF molecules and PAN molecules was found at 4.9 Å center-of-mass distance. A potential profile of intermolecular interaction of DMF with PAN along the interaction distance was presented, clearly showing an increase of DMF vaporisation heat when it getting close to PAN molecules. This provided very useful information to analyse the vaporisation behaviours of DMF at the microscopic level, which is essential to comprehensively understand molecular rearrangements towards the design of synthetic processes. The impact of the presence of the PAN on the DMF solution properties were also benchmarked with pure DMF solution.

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1. Introduction

Good mechanical properties and high thermal stability of poly(acrylonitrile) (PAN) make it one of the most popular polymers for producing large variety of products including textiles [1,2], carbon fiber precursors [3] and membranes [4,5]. One of the most extensively used solvent to dissolve PAN is N, N dimethylformamide (DMF) [6]. It has been reported PAN-DMF solutions exhibit very complicated behaviour [7,8], which determined the production processes and the properties of products. Most of the previous investigations have, however, been focused on solution preparation and processing conditions [9,10], for instance, the effect of solvent type on the morphology of resultant PAN fibers [10], without a sound theoretical understanding.

Recently, attempts have been made to understand the properties of the PAN-DMF solutions through both experiments at macro-level [7,11–13] and theoretical computations [14]. Eom and Kim [7]

investigated the dissolution process of PAN in DMF, the chain conformation of PAN in the dilute solutions, and the rheological properties of the concentrated PAN solutions. It was found that the physical properties were largely determined by polar terms. Bercea et al. [11] studied the gelation of PAN solutions in dimethylformamide through rheological measurements as the gelation was attributed to strong dipole–dipole forces between the macromolecules in PAN-DMF solution [14,15]. Brunchi et al. [12] investigated the dynamic behaviour, including viscoelastic parameters and gelation process, of PAN-DMF solutions with different polymer concentrations at different temperatures.

The calculations of the interaction of a PAN model monomer (PAN′) with DMF based on density functional theories (DFT) (at B3LYP/6-31+G(d,p) level) showed that PAN′ molecules interact with DMF through dipole−dipole interaction and binding energies for PAN′-DMF and DMF-DMF are −3.97 and −4.32 kcal/mol, respectively [14]. However, in these investigations only a few properties were identified at the microscopic level. Many properties still remain to be investigated and it essentially calls for more details about some thermodynamic and dynamical properties of PAN-DMF solutions. For instance, the evaporation process of DMF from jets during jet-spinning nanofiber production

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is critical for nanofiber formation and product features [16], especially for producing ultra-fine nanofibers. Accurately describing the process has been difficult due to the lack of fundamental data for evaporation heat relating to the microscopic behaviour of DMF in solution and wet fibers. Although there are various experimental methods for determining the enthalpy of vaporisation [17] and experimental vaporisation enthalpies for many liquids are available [18–20], they are for pure components or for homogeneous multicomponent systems. For most chemical processing and synthesis, the magnitude of this property does not remain constant because the environmental conditions and the molecular structure of the liquids and polymers change with the process of evaporation itself. The influence of molecular structure will be more significant, when the solvent reduces to a certain extent, due to the relationship between structure and energy [21]. For example, in the synthesis of nanofibers the evaporation heat of the solvent in the polymer solution jets varies during their traveling in the spatial area, due to the reduction of solvent monomers and the variation of intermolecular structure, where the solvent monomers generally tend to have stronger interaction with the polymer molecules. The evaporation heat is one of the most important factors in determining the evaporation rates. Therefore, understanding the variation of molecular structure and intermolecular forces with the environmental conditions is the basis for the design of chemical processes.

Molecular dynamics (MD) and Monte Carlo simulations have been extensively used to effectively investigate the various properties of liquids [22–24], since they can provide fine details of the motion of individual molecules as a function of time and the interaction between molecules. They can be utilized to quantify the properties of the liquids and the behaviours of the constituted components at a nanoscale level that is otherwise inaccessible. In the present study, the structure, thermodynamic and transport properties of a PAN-DMF solution were studied with MD simulations. The properties of pure DMF liquid were also calculated with MD simulation to study the solvent effects. Quantum mechanical (QM) calculations were performed to evaluate the interaction of PAN and DMF and the calculated binding energies from the MD simulations. The results are also compared with experiments and simulations performed by other authors.

2. Methodology

One of the basics in MD simulation is to have a sufficiently accurate interaction energy function or force field for the molecular system of interest. There are several force fields available for alkyl and alkyl nitrile groups, and DMF and other amides, including optimized potentials for liquid simulation (OPLS-UA (united atom) [25–28] and OPLS-AA (all-atom) [29], polarization models [30–37], test particle model (T-model) [38] and reactive force field [39]. The force fields for DMF have been discussed in previous publications [27,40]. Hydrogen bonding may be important in the PAN-DMF solutions and the intermolecular interactions determine the structure and properties of the liquid. Therefore, an all-atom force field is required. In this work OPLS-AA type potentials were used for PAN and DMF. The parameters for DMF and PAN are mainly from those modified by Lei et al. [41] and Jia et al. [42] and those in OPLS-AA [29] and summarized in Table 1.

Another important issue of the art of MD simulation is to build a molecular model and choose effective computational methods to approach the properties of interest, without significantly depending on the model and method. In practice, PAN polymers with a molecular weight (MW) of more than 1500 were used in producing nano-fibers and membranes. The concentration of the polymer in the solutions is from about 8–20 wt.%. So simplification of the system is unavoidable in order to possibly simulate the liquid mixture with such large macro-molecules. In the present work, a PAN molecule composed of 20 repeat units (PAN_{20}) was proposed and a molecular system containing 9.12 wt.% PAN_{20} was used.

Table 1
Parameters (the Lennard-Jones' ε and σ and partial charge q) of the intermolecular geometry of DMF and PAN.

	ε (kcal/mol)	σ (nm)	q (e)
DMF			
N	0.170	0.330	−0.46
O	0.210	0.303	−0.51
C(C═O)	0.110	0.370	0.51
H(C═O)	0.015	0.244	0.08
C(N─CH3)	0.080	0.367	−0.11
H(N─CH$_3$)	0.030	0.250	0.10
PAN			
NZ	0.17	0.320	−0.56
C(C≡NZ)	0.066	0.330	0.46
C1(>CH─)	0.066	0.350	0.04
H1(>CH─)	0.015	0.250	0.06
C2(─CH2─)	0.066	0.350	−0.12
H2(─CH2─)	0.030	0.250	−0.06

The molecular dynamics simulations were firstly run in the NPT ensemble with periodic boundary conditions at an average temperature of 300 K and 1 atm. Both the temperature and pressure were controlled by means of the Berendsen thermostat [43], whereas a coupling time of 0.1 ps was used for temperature and 1.0 ps for pressure. The initial configuration of the liquid phase was generated by a dynamics simulation of 2 ns. The obtained liquid phase has a density of 0.977 g/cm^3, which is comparable to the experimental data for 9.1 wt.% PAN-DMF solution (0.97 g/cm^3). Another dynamics simulation of 3 ns was performed to calculate the properties of the system and the results were dumped every 0.01 ps. The calculations showed that the simulation time is long enough to produce time-independent properties of the liquid.

The molecular dynamics simulations were performed with Tinker software [44]. Particle-mesh Ewald summation method [45,46] was used to treat the long-range electrostatic interactions with a real-space cut-off radius of 9.0 Å, a grid size of about 1 Å, and fifth-order B-splines. A cut-off distance of 12 Å was applied for the van der Waals (vdW) potential energy interactions. The motion equations are integrated using the well-known Velocity Verlet algorithm [47] with a 1.0 fs time step.

The PAN-DMF molecular structure and intermolecular interaction are also calculated by using the quantum mechanics (QM) in the present work. The ab initio calculations are at Second-order Møller-Plesset perturbation theory (MP2) level with the 6-311++G(d,p) basis set and by correcting the BSSE (Basis Set Superposition Error) via the counterpoise procedure (CP). 3-cyanopentane was used to present the residue of PAN. The calculation was performed for one DMF monomer and a 3-cyanopentane monomer (DMF-PAN) with Gaussian 09 [48], so that all intramolecular interactions were included in the calculations.

3. Results and discussion

3.1. Liquid structure

The intermolecular structure of the liquid has been investigated in terms of the pair correlation functions, $g_{ab}(r)$, which represents the probability of finding an atom of molecule b at a distance r from an atom of molecule a. The calculation is performed for all pair combinations of PAN nitrogen atom (NZ) with atoms in DMF to present the interaction of the nitrile groups of PAN with DMF with a correlation distance of 12 Å and a resolution of 0.1 Å (Fig. 1). The pair correlation functions shown in Fig. 2 exhibit the structure of molecules around the backbone of PAN molecules.

High possibility was found for pairs of H1—O, C1—O and C2—O, while a moderate one for H2—O (Fig. 2). Moreover, it was observed the positions of the first peaks of C1—N and C2—N are at 5.45 Å and 5.55 Å, respectively, and their distance to the position of C1—O and C2—O peaks (at 3.35 Å and 3.45 Å, respectively) is about 2.1 Å,