Journal of Molecular Liquids 192 (2014) 114–117

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Nanostructures of ionic liquids do not break up under shear: A molecular dynamics study

Simon N. Butler, Florian Müller-Plathe *

Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany

ARTICLE INFO

Available online 5 November 2013

Keywords:
Ionic liquids
Nanostructure
RNEMD
Shear
Simulation

ABSTRACT

Coarse-grained molecular dynamics simulations of a nanostructure-forming ionic liquid are performed. The reverse non-equilibrium molecular dynamics (RNEMD) technique is used to investigate the stability of the nanostructure under shear conditions. The calculations indicate that even extreme shear cannot break up these structures or alter them significantly. Thus, they are unlikely to be an impediment to shear and a cause for high viscosities.

1. Introduction

Ionic liquids (ILs) are room-temperature molten salts with promising applications in a number of areas [1–3]. One of the most oft-cited of these applications is as green solvents, thanks to their almost non-existent vapour pressure [4]. Further, thanks to the wide variety of possible ion-pair combinations, they have come to be termed *designer* solvents in recent years [5], the idea being that specific ion combinations could be chosen on an application-specific basis.

Such liquids were thought to be homogeneously organised until the work of Schröder et al. [6] in which the existence of a 'nanostructure' was suggested to account for deviations from the Stokes–Einstein relation. That such aggregation of polar and non-polar regions into a domain structure is possible was subsequently demonstrated in simulation studies by Lopes and Pádua using an all-atom model of 1-alkyl-3-methylimidazolium hexafluorophosphate ([$C_n$mim] [PF_6]) [7]. Initial experimental confirmation was provided at the same time via X-ray diffraction measurements by Triolo et al. [8] which showed that [$C_n$mim] [BF_4] liquids developed an intensity peak at low wave vectors for chain lengths above $n = 4$. This aggregation of ions into polar and non-polar domains has been advanced as the origin of the "trend shift" seen in properties, such as viscosity, conductivity, or vaporisation enthalpy [9], in which the rate of change of these properties with the length of the aklyl chain exhibits a discontinuity.

The existence, or otherwise, of such structures naturally has implications for the solvation properties of ionic liquids but the stability and robustness of this nanostructure has not, as yet, been investigated. That is, it has not been demonstrated how easily it might be disrupted and whether its existence may be taken for granted in non-equilibrium situations, such as during flow or in industrial processes like mixing, or whether the existence of nanostructures impedes shear flow and contributes to the high viscosity.

This question is addressed by the present work, in which shear is applied to a nanostructure-forming IL system and the effects examined. Nanostructural organisation was demonstrated for the liquid investigated herein [C_{10}mim] [PF_6], in an earlier work from this group [10], in which a coarse-grained (CG) force field was developed for [$C_n$mim] [PF_6] ionic liquids. Following recent improvements to the performance and parallelisation capabilities of our CG simulation package, IBIsCO [11], it is now possible for us to simulate bigger systems on longer time scales than those investigated during the force-field development and thus to investigate the stability of the nanostructure. This is achieved by use of the reverse non-equilibrium molecular dynamics (RNEMD) method developed by Müller-Plathe and coworkers, [12], which is built into IBIsCO. A comparable study has previously been performed by Raju et al. [13] but using the SLLOD algorithm [14] to generate shear, rather than RNEMD, and for significantly shorter simulation times. A comparison of different methods for obtaining the shear-rate-dependent viscosity via simulation may be found in [15] and [16]. Here, we prefer RNEMD for its ability both to access the low-shear-rate regime before the onset of shear thinning and to exceed those rates typically accessed by experiment.

2. Methodology

Molecular dynamics (MD) simulations were performed of coarse-grained models of [C_{10}mim] [PF_6] using parameters developed in an

* Corresponding author.
E-mail address: f.mueller-plathe@theo.chemie.tu-darmstadt.de (F. Müller-Plathe).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.10.021

earlier study [10]. The mapping scheme for the cation and anion, with labels, is shown in Fig. 1. The development of the force field parameters is described in detail in Ref. [10] but it is worth restating that as the non-bonded potentials are obtained via iterative Boltzmann inversion (IBI) from a reference all-atom model, there are no explicit charges on any of the super atoms. Instead, the Coulombic potential is implicitly accounted for in the tabulated non-bonded potential. We thus identify the 'polar' groups as atoms A, B, and PF (labelled in blue) and the 'non-polar' ones as atoms C and AP (labelled in red). The colours of the labels correspond to those used in the snapshots in Section 3.

The simulation systems contained 10,125 ion pairs in a $12 \times 12 \times 36$ nm^3 box. This was generated by duplicating a system with 3375 ion pairs three times in the z direction. This thus represents a three-fold system-size increase over [13]. The resulting configuration was then equilibrated for 50 ns, at which point aggregation of polar and non-polar domains could be observed. This system was then used as the starting configuration for the RNEMD simulations.

All simulations were performed in the NpT ensemble at 300 K and atmospheric pressure. The time step was 4 fs, in common with our prior investigation. The thermostat and barostat coupling times were 0.3 and 5.0 ps, respectively. The cut-off distance was 1.5 nm, which is significantly beyond the screening distance of 0.7 nm determined from atomistic simulations. RNEMD simulations were performed for between 20 and 80 ns for swap intervals of 1 to 200 steps and configurations were stored every nanosecond. Thanks to a combination of increased computational power and the parallelisation of IbisCo, these simulations are thus significantly longer than the 0.4 ns of Raju et al. and we can be confident that the systems are both fully equilibrated and that a steady state was reached after the application of shear. These long simulations also enable the motion of the system to be visually examined, as described in the video referenced in the following section.

The RNEMD method has been extensively described and reviewed. For a schematic picture of the method, see for example Fig. 1 of Ref. [17]. In brief, the system is divided into slabs along the z axis and momentum is exchanged between the central and outermost slabs at regular intervals throughout the simulation. The long-term effect of this process is to establish a velocity gradient along the z-axis, as illustrated by the green arrows in Fig. 2. In this manner, the conventional cause-and-effect relationship in shear experiments is reversed, thus allowing the easy-to-measure velocity gradient to be used to estimate the shear-rate-dependent viscosity according to

$$j_z(p_x) = -\eta(\dot{\gamma})\frac{\partial v_x}{\partial z}, \tag{1}$$

where j_z is the applied momentum flux in the z direction, $\eta(\dot{\gamma})$ is the apparent shear-rate-dependent viscosity at shear rate $\dot{\gamma}$ and the derivative is the velocity gradient along the z direction, as obtained using the mean molecular velocity in each slab.

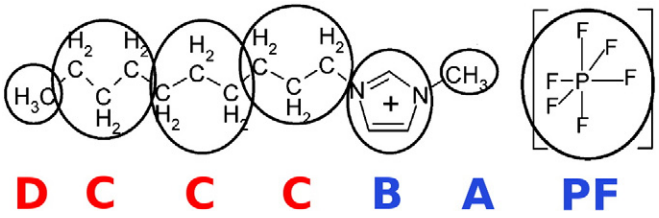

Fig. 1. Mapping scheme for the coarse-grained model of C10mim PF6. Groups of atoms in the cation are modelled as single-site "super atoms", labelled A, B, C, and D. The entire anion is represented as a single super atom, labelled PF.

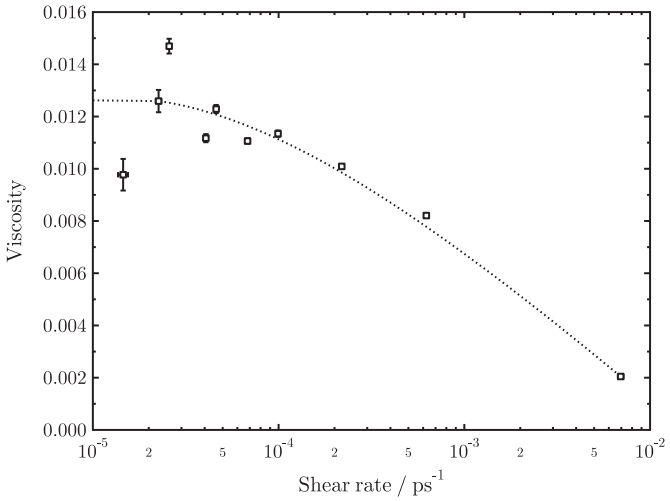

Fig. 2. Shear response of the C_{10}mim PF_6 system as measured via RNEMD simulations. Viscosity is plotted as a function of shear rate, as calculated using Eq. (1). A trend line is drawn as an aid to the eye. It can be seen that the shear thinning regime is accessed at shear rates above 10^{-4} ps^{-1} and that the highest shear rate investigated (corresponding to momentum swaps at every time step) corresponds to a viscosity of around 10–20% of that at zero shear.

3. Results and discussion

The shear response of the system is shown in Fig. 2. Viscosity is plotted as a function of shear rate for all swap intervals investigated. The zero-shear plateau is difficult to identify precisely as the simulation time required to converge the low-shear-rate simulations increases significantly but it is clear to see that the shear-thinning regime is accessed at above $\approx 10^{-4}$ ps^{-1} (c.f., a range of 10^{-2}–10^{0} ps^{-1} in [13]). The highest shear rate is obtained with momentum being swapped at every time step; that is, it the strongest perturbation possible using this implementation of RNEMD. The shear rates investigated are several orders of magnitude higher than those typically accessed via experiment ($\approx 10^{-8}$ ps^{-1}) [18–20], thus this represents a severe test of the stability of the system. This is further demonstrated by the velocity profiles, which indicate non-linear behaviour at high shear. They are included for reference in Fig. 5, which is discussed in detail below.

The aggregation of polar and non-polar domains can be clearly seen in the visualisations shown in Fig. 3. Polar and non-polar groups are coloured blue and red, respectively, as per the labels in Fig. 1. Fig. 3a shows snapshots of the unsheared system at 10-ns intervals, from which it can be seen that the nanostructure is mobile over the timescale of the simulation. The corresponding snapshots in Fig. 3b show that the nanostructure is intact even at the highest shear rate investigated and that the domains are not disrupted or otherwise broken up. Indeed, the two cases look qualitatively the same.

A video of the two systems is included in the Supporting Information. Separate simulation runs were performed with configurations stored more frequently in order to generate the video. The mobility of the domains can be clearly observed in the zero shear case and the influence of the shear field can be seen in the other system by looking at the opposing directions of flow in the centre and at the 'edges' of the system (i.e., in the exchange slabs). The domains appear intact during this process, rather than accelerated disruption and reformation rates being present.

Quantitative measurements of the effect on the liquid structure was obtained by calculating radial distribution functions (RDFs, $g(r)$), which are shown in Fig. 4. RDFs are shown for three systems corresponding to zero shear, "high shear" (swap interval of 10 steps; $\dot{\gamma} \approx 6 \times 10^{-4}$ ps^{-1}), and "very high shear" (swap interval of 1 step; $\dot{\gamma} \approx 7 \times 10^{-3}$ ps^{-1}) and for three representative combinations of atom types: B–PF, C–AP, and