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Dissipative particle dynamics simulation of the micellization–demicellization process and micellar shuttle of a diblock copolymer in a biphasic system (water/ionic-liquid)

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We simulated the thermoreversible micellization–demicellization process and micellar shuttle of a poly (*N*-isopropylacrylamide-*block*-ethylene-oxide) (PNIPAM–PEO) diblock copolymer in a water/ionic-liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6]) system by means of dissipative particle dynamics (DPD). The evolution of diblock copolymer chains (micellization–transfer–demicellization) in both water and the ionic liquid phase by the temperature effect reveals that it is a physical phenomenon, dependent on the solubility and interaction parameters of all chemical species involved in the multicomponent system. With the aid of a Monte Carlo simulation we calculated the Flory–Huggins interaction parameters χ of all the species. At room temperature the PNIPAM–PEO copolymer chains are miscible in the aqueous phase. At a higher temperature of $T = 303$ K the diblock copolymer shows the formation of micelles (micellization process). The micellar transfer to the ionic liquid phase was observed at $T = 333$ K. A further increase in temperature provokes the demicellization at $T = 346$ K. The process is reversible: reversing the temperature now to 333 K, shows the formation of the micelles. A further decrease in temperature makes the micelles go back to the water phase. All the simulation outcomes are qualitatively consistent with the experimental results, demonstrating that the DPD methodology may provide a tool for the investigation and analysis of the micellar transfer process in immiscible environments.

1. Introduction

The transfer of polymeric micelles between two immiscible phases has been termed the micellar shuttle.[1–4] This is an interesting phenomenon with a great potential for industrial and pharmaceutical applications.[5–8] The micellar shuttle is a quantitative reversible process with strong temperature dependence. Yiyong He *et al.*[1] have reported the micellar shuttle of poly(1,2-butadiene-*block*-ethylene oxide) micelles between water and an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6]). In this multicomponent system the diblock copolymer micelles move from one phase to another as an intact entity without changes in their conformation. Recently, Zhifeng Bai *et al.*[9] have reported the micellar shuttle of a poly(*N*-iso-propylacrylamide-*block*-ethylene oxide) diblock copolymer between water and the same hydrophobic ionic liquid; they have observed a micellization–demicellization process in both water

and the ionic liquid. More complex behavior of block copolymer micelles in different biphasic systems (water/ionic-liquid) has been reported by Guerrero-Sanchez *et al.*[10] (reversible transfer of poly(2-ethyl-2-oxazoline)-*block*-poly(2-nonyl-2-oxazoline) micelles comprising encapsulated dyes) and Z. Bai *et al.*[11] who observed the formation of micelle-concentrated droplets of the PB–PEO copolymer in the initial phase, sedimentation/creaming of the droplets to the interface, and diffusion of the micelles to the destination phase. Schubert and coworkers have also observed the formation of micelle-concentrated droplets in the system poly(oxazoline)/ionic liquid/water.[12] The experimental evidence suggests that the behavior exhibited by the polymeric micelles before and after the micellar shuttle is governed by the physical nature of the monomers that integrate the diblock copolymer chains, besides the solubility and interaction parameters of all chemical species involved play an important role. The micellization–demicellization process and micellar shuttle in a biphasic environment can be investigated in more detail through mesoscopic simulations than through experimentation. Mesoscopic simulations are efficient methods to investigate the physical processes of soft matter and their interactions with chemical environments.[13–15] They offer a particularly useful way of exploring the process of mass transfer and can help in understanding complex processes such as the micellar shuttle. In

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the mesoscopic simulations the atoms of each molecule are not directly represented, but they are grouped together into beads (coarse-grained models). This substantially reduces the number of particles to be simulated.

Thermally responsive polymers such as poly(N-isopropylacrylamide) (PNIPAM) have a wide range of applications in biotechnology and medicine. PNIPAM, in particular, is insoluble and undergoes a conformational change above its lower critical solution temperature (LCST) of 32 °C. Below the LCST, the polymer chains swell in water. Above the LCST, the solvent quality changes and the polymer segments are thought to become more hydrophobic. There is a transition for PNIPAM–PEO-modified chains, in which each random coil chain collapses into a core–shell nanostructure with a hydrophobic PNIPAM core and a hydrophilic PEO shell.

In the present work, we use dissipative particle dynamics simulations and coarse-grained models to explore the micellization–demicellization process and micellar shuttle of PNIPAM–PEO copolymer chains in a biphasic system (water/ionic-liquid ([BMIM][PF$_6$])) as a function of temperature. DPD is a meso-scale modeling method for simulating the equilibrium and dynamical properties of polymers in solution. The method is a coarse graining technique where degrees of freedom are removed mapping a few atoms into a unique site, unlike molecular dynamics (MD) simulations using fully atomistic descriptions which are computationally very expensive and cannot access relevant length and time scales, DPD still retains sufficient physical detail to simulate cooperative and mesoscopic-scale phenomena of experimental and theoretical interest. The DPD method is capable of exploring from a mesoscopic point of view how the polymeric micelles conformation and internal structure are modified by solubility and interaction parameter effects.

2. Simulation methodology

2.1. The DPD method

The DPD method has been used for modeling complex multi-phase systems at the mesoscale (10–100 nm). It was designed to bridge the gap between atomistic simulations and large scale simulations. It is an intermediate technique between the atomistic and network connection scale of polymers. It was firstly introduced by Hoogerbrugge and Koelman[16,17] and recently improved by Groot et al.[18–20] In DPD simulation a polymer chain is represented by a set of beads connected by springs. Each bead represents a section of a polymer chain corresponding in size to the persistence length of the polymer. Thus, a simple model for a linear block copolymer is formed by joining polymers of different beads together by springs. In this set of interacting particles or beads, all particles comply with Newton's equations of motion. The force acting on a particle is given by:

$$f_i = \sum_{j \neq i} F_{ij}^C + F_{ij}^D + F_{ij}^R \qquad (1)$$

where the conservative force (F_{ij}^C) is a soft repulsive force that acts between particles i and j. The dissipative force (F_{ij}^D) corresponds to a frictional force that depends both on the position and relative velocities of the particles. The random force (F_{ij}^R) is a random interaction between a bead i and its neighboring bead j.

All forces vanish beyond a cutoff radius r_c, which is usually chosen as the reduced unit of length, $r_c \equiv 1$. The conservative forces act to distribute the beads in space, the dissipative force acts to reduce velocity differences between the beads and finally, the stochastic force represents the degrees of freedom that have been eliminated in the coarse graining process.

The F_{ij}^C, F_{ij}^D and F_{ij}^R forces have the form

$$F_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij}) \, \hat{r}_{ij} & (r_{ij} < 1) \\ 0, & (r_{ij} \geq 1) \end{cases} \qquad (2)$$

$$F_{ij}^D = -\gamma \omega^D(r_{ij})(v_{ij}\hat{r}_{ij})\hat{r}_{ij} \qquad (3)$$

$$F_{ij}^R = \sigma \omega^R(r_{ij})\hat{r}_{ij}\zeta \qquad (4)$$

where a_{ij} is the repulsive force between particle i and particle j, $\hat{r}_{ij}$ is a unit vector in the direction of r_{ij}, $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ are weight functions of F_{ij}^D and F_{ij}^R forces respectively and ζ is a Gaussian noise term. In order for the DPD system to have a well-defined equilibrium state obeying Boltzmann statistics, the equilibrium temperature is defined as $k_B T = \sigma^2/(2\gamma)$, where γ is the dissipation strength, σ is the noise strength, and k_B is the Boltzmann constant. This condition fixes the temperature of the system and relates it to the two DPD parameters γ and σ ($k_B T$ is usually chosen as the reduced unity of energy). The parameter a_{ij} (henceforth referred to as the bead–bead repulsion parameter or simply as the DPD interaction parameter) depends on the underlying atomistic interactions and is related with the Flory–Huggins parameter (χ) via eqn (5):[18]

$$a_{ij} = a_{ii} + \frac{k_B T \chi_{ij}(T)}{0.306} \qquad (5)$$

It was deduced by Groot and Warren[18] in a series of computer simulations and links the Flory–Huggins χ parameters for polymers with the repulsion DPD a_{ij} parameter. To be able to use eqn (5) one must specify χ. The way we calculate this parameter is explained below.

The parameter a_{ij} is given in terms of $k_B T$ (DPD reduced units). A value of $a_{ii} = 25$ gives the pure fluid a compressibility close to that of liquid water for $\rho = 3$.

In order to study the micellization–demicellization process and micellar shuttle at different temperatures with DPD simulations we take the temperature dependence $\chi_{ij}(T) = \chi(T)$, in this way the real temperature is introduced into the DPD simulation.[21] The interaction parameters for eqn (5) were evaluated from bulk atomistic simulations using the Fan et al. model[22] (Blends from Accelrys). In this way the parameter interaction was expressed as:

$$\chi(T) = \frac{\Delta G(T)}{RT}$$
$$= \frac{Z_{12}E_{12}(T) + Z_{21}E_{21}(T) - Z_{11}E_{11}(T) - Z_{22}E_{22}(T)}{2RT} \qquad (6)$$

where ΔG denotes the Gibbs free energy, χ is the interaction parameter, Z and ΔE_{12} are the coordination number and differential energy of interaction of an unlike pair respectively.

The Blends binding energy task allows efficient sampling of the energy of interaction between specified molecules. The sampling algorithm in Blends itself is independent of temperature but

temperature effects can be taken into account, however, by weighting the distribution with the Boltzmann factor, $\exp(-E_{ij}/RT)$. The average binding energy at temperature T is the average of the weighted distribution function. Blends calculate mixing properties using force fields which describe approximately the potential energy hypersurface on which the atomic nuclei move. The force fields commonly used for describing molecules employ a combination of *internal coordinates* and *terms* (bond distances, bond angles, torsions, *etc.*), to describe that part of the potential energy surface due to interactions between bonded atoms, and *non-bond terms* to describe the van der Waals, electrostatic, and other interactions between atoms. Resuming, with this methodology the parameter interaction between two molecules takes into account the chemical structure and configurations. For more details see ref. 22.

In the DPD simulation, the dynamic behavior of the micellization–demicellization process is followed by integration of the equations of motion of each species using a modified version of the velocity-Verlet algorithm:[23]

$$
\begin{aligned}
\boldsymbol{r}_i(t + \delta t) &= \boldsymbol{r}_i(t) + \delta t \boldsymbol{v}_i(t) + \frac{1}{2}\delta t^2 \boldsymbol{f}_i(t), \bar{\boldsymbol{v}}_i(t + \delta t) \\
&= \bar{\boldsymbol{v}}_i(t) + \lambda \delta t \boldsymbol{f}_i(t), \ \boldsymbol{f}_i(t + \delta t) \\
&= \boldsymbol{f}_i(\boldsymbol{r}_i(t + \delta t), \ \bar{\boldsymbol{v}}_i(t + \delta t)), \boldsymbol{v}_i(t + \delta t) \\
&= \boldsymbol{v}_i(t) + \frac{1}{2}\delta t(\boldsymbol{f}_i(t) + \boldsymbol{f}_i(t + \delta t)).
\end{aligned}
\tag{7}
$$

where $\bar{\boldsymbol{v}}(t + \delta t)$ is the prediction of the velocity of a particle at time $t + \Delta t$. Note that the force is still updated once per integration, thus there is virtually no increase in computational cost. The integration of the equations of motion for each particle generates a trajectory through the system's phase, from which thermodynamic observables may be constructed by suitable averaging. From this information, the polymeric micelles conformation by the interaction parameter effect during the micellar shuttle process can be monitored.

2.2. Models and simulation parameters used in DPD

In the DPD simulation it is necessary to specify the number of beads and this is done employing a statistical polymer model which is determined by using the molar mass of each block copolymer and the characteristic ratio of each polymeric system, (C_n).[24] The linear diblock copolymer is thus represented by a mechanical model constituted by $n + m$ spherical beads denoted by $[PNIPAM]_n - [PEO]_m$.

We choose to deal with a system composed of 6 beads of PNIPAM and 9 beads of PEO because the thermo-responsive effect of PNIPAM is enhanced with this composition. Lodge and coworkers[9] report experiments with a 12 kDa PNIPAM block and a 19 kDa PEO block, that is, 39% of PNIPAM and 61% of PEO. The mesoscopic model constituted by 15 spherical particles is sketched schematically in Fig. 1(a) and (b) and has a molecular weight of 8965 g mol⁻¹; the polymeric chain represents 40% PNIPAM and 60% PEO. If we take exact values for the molar mass it results that both polymers have the same mass per sphere, 597 g mol⁻¹, and in our simulation they are normalized.

In DPD even in a heterogeneous system consisting of several different species, the basic assumption is that all bead-types (each representing a single species) are of the same volume. This assumption is necessary in order to conform to the Flory–Huggins χ parameter theory.

The architecture of the coarse-grained model is maintained fixed throughout the simulation process because the beads are held together by spring forces. However, the distance between beads can change because of the relaxation due to interactions between the particles and water/ionic-liquid environment.

Now with respect to the water solvent: each solvent bead represents a small volume of bulk water consisting of several molecules. For example, with the mapping of three water molecules ($N_m = 3$) on one bead Groot and Rabone[25] created a model for a phospholipid. Using this mapping factor, one DPD bead represents a volume of 90 Å³. This volume also corresponds with the volume occupied by three methylene groups. The exact mapping from one bead to a number of molecules depends on the size of the molecules the bead is to represent. Each DPD particle is considered equivalent to three water molecules, Fig. 1(c) and (d), and this approximation is convenient to reproduce, for example, the interfacial tension of a watery environment.[26]

The ionic liquid ([BMIM][PF₆]) was represented by two beads: one bead representing the anion and one more for the cation,[13] Fig. 1(e) and (f). It is important to remind that the interaction parameter for this system with the others (water, polymer) was made using a Monte Carlo method (Blends) which calculates the van der Waals and Coulombic contributions.

All DPD simulations were carried out in a rectangular box of $(15\ r_c, 20\ r_c, 15\ r_c)$ size, containing a total of 1.4×10^4 representative particles, spring constant $C = 4$, and a density $\rho = 3$. The DPD length scale is set by the parameter r_c. In our case, $r_c = 1$ nm, and thus a typical simulation box of $15 \times 20 \times 15$ in DPD units would represent a rectangular box of real spatial dimensions of $15 \times 20 \times 15$ nm. According to ref. 18 and 20, for $\rho = 3$ an interaction parameter $a_{ij} = 25\ k_B T$ reproduces the compressibility of water. The interaction parameters between identical chemical species were then chosen as: $a_{PEO-PEO} = a_{PNIPAM-PNIPAM} = a_{[BMIM][PF6]-[BMIM][PF6]} = a_{W-W} = 25$. The coarse-grained number was maintained constant during the DPD simulation; each bead has a radius equal to 1. A total of 7.5×10^5 time steps with a step size of $\Delta = 0.05$ were employed in the whole DPD simulation that mimics the micellization–demicellization process and micellar shuttle of the PNIPAM–PEO copolymer in the biphasic system (water/[BMIM][PF₆]).

3. Results and discussion

3.1 Multicomponent mesostructure and mesoscopic description

First, a predefined multicomponent template was constructed; see Fig. 2(a). In this multicomponent template the water phase, ionic liquid phase and diblock copolymer chains were defined in accordance with a real biphasic system reported by Bai *et al.*[9] Fig. 2(b) shows the diblock copolymer chains in the water phase. The chemical and physical nature of each representative model in mesoscopic simulation is described by interaction parameters (χ_{ij}).

Fig. 3 shows the interaction parameters χ_{ij} of all combinations of species and their evolution with temperature. The tendencies that exhibit the interaction parameters on temperature are:
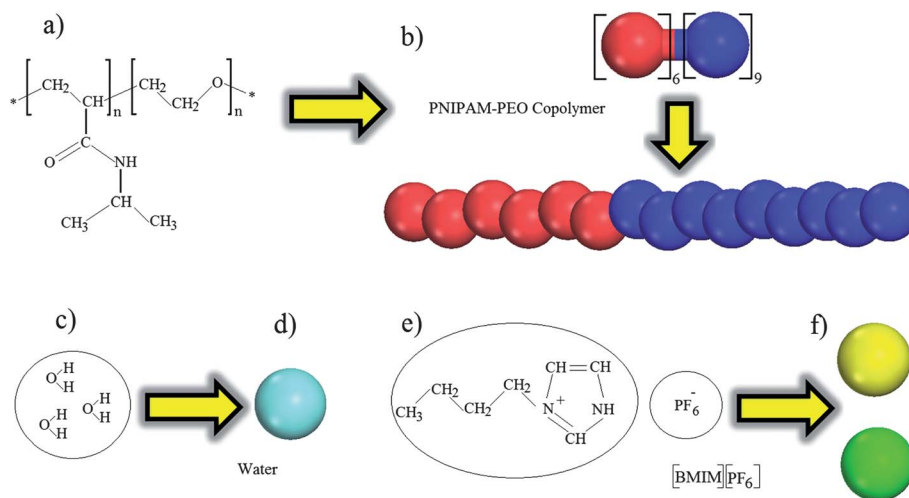
Fig. 1 Molecular structures and coarse-grained models employed in mesoscopic simulation: (a and b) diblock copolymer of PNIPAM–PEO, (c and d) water, and (e and f) ionic liquid ([BMIM][PF$_6$]).
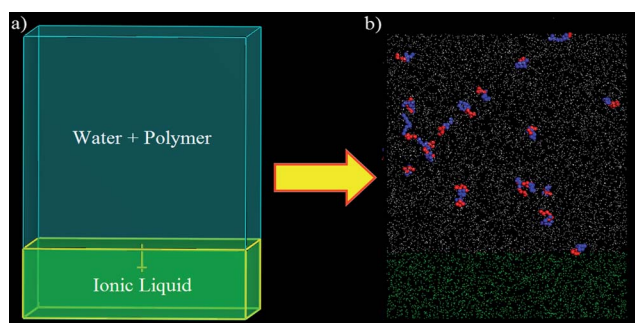

Fig. 2 Multicomponent mesostructure template employed to create a structured input for DPD simulation.

water–PNIPAM (line 3) and water–PEO (line 5) showing a breaking point around T = 303 K; water–ionic liquid (line 1) shows little variation; PEO–ionic liquid (line 2) shows a rapid decrease with temperature; PNIPAM–ionic liquid (line 4) shows
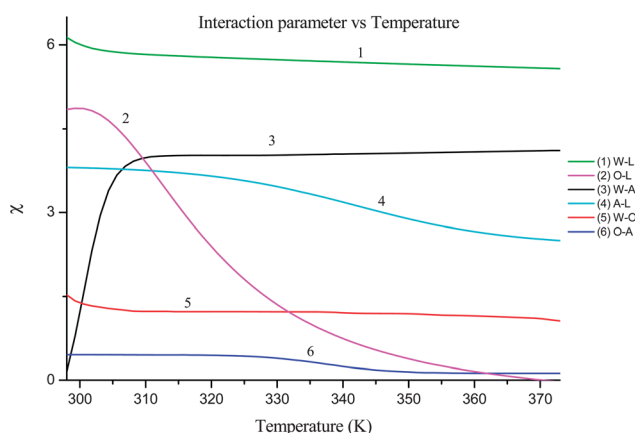

Fig. 3 Interaction parameters of all chemical species involved in the micellization–demicellization process in a water/ionic-liquid system obtained by a Monte Carlo molecular simulation: W = Water molecules, L = Ionic liquid, A = PNIPAM statistic segment, O = PEO statistic segment.

little variation until *T* is around 330 K; and PEO–PNIPAM (line 6) shows little variation until *T* is around 330 K.

3.2 Effect of solubility and interaction parameter in the micellization–transfer–demicellization process

PNIPAM is a polymer insoluble in water which undergoes a conformational change above its lower critical solution temperature (LCST) of 32 °C. Below the LCST, the polymer chains swell in water. Above the LCST, the solvent quality changes and the polymer segments are thought to become more hydrophobic. The PNIPAM–PEO copolymer is a water soluble thermo-responsive polymer; it contains water-soluble and temperature-responsive blocks which cause hydrophobic association at higher temperature. There is a transition for PNIPAM–PEO-modified chains, in which each random coil chain collapses into a core–shell nanostructure with a hydrophobic PNIPAM core and a hydrophilic PEO shell. The PEO block forms hydrophilic segments due to its excellent biocompatibility and water solubility and forms the shell of the polymeric micelle.[27–29]

Lodge *et al.*[9] have demonstrated a fully thermoreversible micellization–transfer–demicellization block copolymer micelle shuttle between water and hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]). They have interpreted that the reversible micelle transfer between the two media is based on the relative affinity of the two solvents to the corona chains and is triggered by the temperature change. They reported that at room temperature, PNIPAM–PEO block copolymers exist primarily as free chains in the aqueous phase. Upon heating above the micellization temperature ($T_m \approx 34$ °C), micelles are formed. Above the transfer temperature ($T_t \approx 68$ °C), the micelles transfer to the ionic liquid phase. Finally, above the demicellization temperature ($T_d \approx 81$ °C), they disintegrate to form free chains.

The micellization–demicellization process and micellar shuttle are thus controlled by the solubility and interaction parameters of all chemical species involved in the multicomponent system. So, at room temperature (298 K) the water and ionic-liquid phase

are immiscible due to a large difference between their solubility parameters (δ_{water} = 48.9 MPa$^{1/2}$ and $\delta_{[BMIM][PF6]}$ = 29.8 MPa$^{1/2}$)[30–34] or, equivalently, to the high value of their interaction parameters χ_{ij} ($\sim$6). According to our calculations this value is maintained in the analyzed temperature interval (298 K to 373 K), see Fig. 3. As the temperature is increased there is a change (decrease) in the solubility parameters of each species. There are not sufficient reported values of solubilities for the system PNIPAM–PEO/water/[BMIM][PF$_6$] as a function of temperature. But because there is a relationship between the parameters of interaction χ_{ij} of species and differences in solubilities (Hildebrand equation), in what follows, we interpret the reversible micelle transfer between the two media in terms of χ_{ij}.

The mesoscopic simulation started from a non-equilibrium state where the diblock copolymer chains and biphasic environment form a heterogeneous system, Fig. 2(b). Initially, 10^5 time steps were employed to obtain an efficient temperature relaxation and the multicomponent system stabilization. At room temperature (298 K) the diblock copolymer chains are soluble in the water phase, the PNIPAM–PEO chains show a configuration of extended chains, see Fig. 4(a). At this temperature, the interaction parameters between block copolymer fragments and water are small. At $T \approx$ 303 K there is a turning point in the behavior of χ(PNIPAM–water), see Fig. 3 (line 3), and in χ(PEO–water) (line 5). This behavior generates the hydrophobic association of thermosensitive segments (formation of hydrophobic cores of PNIPAM segments with a shell of PEO segments) of diblock copolymer and consequently the formation of polymeric micelles into the water phase (micellization process),[27] Fig. 4(b). It can be seen that the PEO chains appear stretched. The average radius of the polymeric micelle in the water phase after 2.5 $\times$ 10^5 time steps was 4.6017 (DPD units). The polymeric micelles are kept in the water phase up to a temperature of 332 K. Fig. 4(c) shows that the PEO blocks are also collapsed and are ready to shuttle the whole micelle to the ionic liquid phase.

The affinity of the polymeric segments to the ionic liquid increases as the temperature increases (or the affinity increases as the χ_{ij} decreases). The micellar shuttle takes place due to an important decrease of the interaction parameter between hydrophobic cores (formed by PNIPAM fragments) and the ionic liquid (see line 4 of Fig. 3) and between the PEO shell segments and the ionic liquids (see line 2 of Fig. 3). This occurs at a temperature T = 333 K, Fig. 4(d).

The average radius of the polymeric micelle in the ionic liquid phase (after 4 $\times$ 10^5 time steps) was 4.9190 (DPD units). This corresponds to an increase of 6.89% in radius (this is a swelling of the polymeric micelle by the hydrophobic effect) with respect to the polymeric micelle in the water phase. This is consistent with solvent penetration. For comparison, Z. Bai *et al.*[9] reported for their system a hydrodynamic radius $R_h \approx$ 15 nm at T = 40 °C (313 K, micelle in water), and for T = 75 °C (348 K,
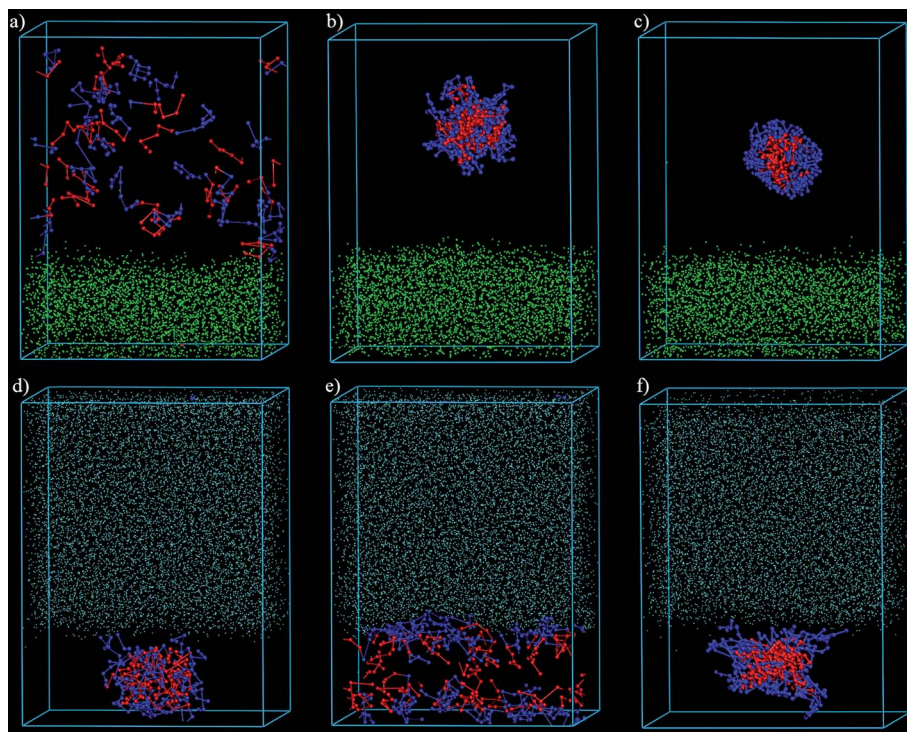

Fig. 4 Snapshots of the micellization–demicellization process and the micellar shuttle in a water/[BMIM][PF$_6$] system at different temperatures. (a) At 298 K, polymeric chains are miscible in aqueous phase (1 $\times$ 10^5 time steps); (b) formation of polymeric micelles into the water phase at a temperature of 303 K (2.5 $\times$ 10^5 time steps), in this frame it can be seen that the PEO chains appear stretched; (c) increasing the temperature a little shows that the PEO blocks are also collapsed and ready to shuttle the whole micelle to the ionic liquid phase, (d) the micellar shuttle to the hydrophobic phase was observed over a temperature of 333 K (4 $\times$ 10^5 time steps), (e) the demicellization process in an ionic liquid environment was observed at temperatures as high as 346 K (5.5 $\times$ 10^5 time steps), and (f) reversing the temperature, now to 333 K, shows the formation of the micelle (7.0 $\times$ 10^5 time steps). A further increase in temperature makes the micelle go through the water phase.

micelle in ionic liquid), $R_h \approx 20$ nm, so there is an increment of around 3.3%.

The demicellization process in the ionic liquid phase was observed at temperatures of around 346 K. Fig. 4(e) shows the mesoscopic simulation (5.5×10^5 time steps) where this demicellization occurs. The micellar dissociation is a consequence of solubility and interaction parameters between polymeric segments with ionic liquid. At high temperatures the interaction parameters between the block copolymer segments and the ionic liquid phase are very small. According to our calculations, at a temperature of 346 K they are $\chi_{\text{PEO–[BMIM][PF6]}} = 0.49289$ and $\chi_{\text{PNIPAM–[BMIM][PF6]}} = 0.28833$. This implies that all the chemical species are highly compatible under these thermal conditions. One important fact of the simulation is that the demicellization process occurs in a continuous way: on increasing slowly the temperature from 339 K it is observed that the micelles begin to lose fragments until $T \approx 346$ K where the chains are completely dissolved in the ionic liquid.

It must be emphasized that the above simulations are based on knowledge of the Flory–Huggins χ parameter, eqn (6), which links the polymer properties to solubilities and mixing energies. The molecular origin of the temperature dependence of χ is that the different configurations of pairs have different energies and their contribution to ΔG is temperature dependent. As commented before, these temperature effects are taken into account by weighting the distribution with the Boltzmann factor, $\exp(-E_{ij}/RT)$. The average binding energy $\langle E \rangle$ at temperature T is the average of the weighted distribution function. With the availability of $\chi(T)$ the entropy and heat of mixing can be calculated.

There is thus an interplay between the conformational equilibrium, increased (or decreased) water–polymer and polymer–ionic liquid interactions. For example, the (ethylene-oxide)–water interaction becomes more favorable at higher temperatures. It is generally agreed that the hydrophobic molecule induces a structuring of the water in its vicinity. This structuring is associated with an energetic gain and an entropic cost. The interaction between water and an EO segment may be of a hydrogen bonded nature and is energetically favored and entropically disfavored. The (ethylene-oxide)–ionic liquid interaction becomes more favorable as the temperature is increased. The water–PNIPAM interaction becomes less favorable as the temperature is increased. This means that when the temperature is increased the effective water–polymer interaction becomes more repulsive; this would lead to a separation.

Finally the thermo-reversibility of the micellization–demicellization process and micellar shuttle was confirmed with DPD simulation. Fig. 4(f) shows that the process is reversible: reversing the temperature now to 333 K shows the formation of the micelle (7.0×10^5 time steps). A further decrease in temperature makes the micelle go back to the water phase. We must mention that this reversible effect has also been observed by Schubert *et al.*[12] in studying a different system, poly(2-nonyl-2-oxazoline-*block*-2-ethyl-2-oxazoline) block copolymer micelles.

4. Conclusions

The DPD approach has been successfully applied to the investigation of the micellization–demicellization process and micellar shuttle of PNIPAM–PEO copolymer in a biphasic system. The molecular structures involved in the micellar-shuttle process were replaced with coarse-grained models. The physical nature and dynamical behaviour of each mesoscale model in the DPD simulation was described by mesoscopic parameters. The micellization–demicellization process and micellar shuttle are controlled by the solubility and interaction parameters of all chemical species involved in the multicomponent system. The diblock copolymer changes from hydrophilic to hydrophobic (and micellization of polymeric chains) in the water phase by the temperature effect as a consequence of the thermosensitivity of PNIPAM segments. The simulation results confirm that the polymeric micelles (once formed) move from one phase to another as an entity during the thermal process. The demicellization process in the ionic liquid phase was observed at high temperatures, the decrease of interaction parameters by the temperature effect promotes the micellar dissociation and solubility of diblock copolymer chains in the hydrophobic environment. Finally, the results obtained from DPD simulations are consistent with the micellar-shuttle mechanism proposed by Bai *et al.*[9] The values reported by us for the micellization temperature ($T_m \approx 303$ K or 30 °C), the transfer temperature ($T_t \approx 333$ K or 60 °C) and the demicellization temperature ($T_d \approx 346$ K or 73 °C) are a little different of those reported by Z. Bai *et al.*[9] because they must depend on the molecular weight of the PNIPAM–PEO block copolymer. For example Topp *et al.*[35] reported that for $M_{\text{PNIPAM}}/M_{\text{PEO}} = 700/5000$ the LCST (in water) was 30.9 °C and for 3800/12 000 it was 29.7 °C; these values are very close to ours.

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