

Transport Properties of Water and Sodium Dodecyl Sulfate

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*In this work, results from atomistic molecular dynamics studies investigating the effect of surfactant concentration on the transport properties of bulk surfactant aqueous solutions, focusing on the anionic surfactant sodium dodecyl sulfate (SDS), are reported. The surfactant self-diffusion and the thermal conductivity of bulk aqueous SDS solutions were computed at a range of concentrations at room and boiling temperatures. Additionally, MP2f (Akin-Ojo et al., 2008, "Developing Ab Initio Quality Force Fields From Condensed Phase Quantum-Mechanics/Molecular-Mechanics Calculations Through the Adaptive Force Matching Method," J. Phys. Chem., **129**, p. 064108), one of a new generation water potentials is assessed for its suitability in reproducing the transport and thermal properties of bulk water. The thermal conductivity of MP2f water model was found to be: 0.64 W/(m·K) at 298 K and 0.66 W/(m·K) at 373 K, in much better agreement with the experimental values compared to both the rigid and the flexible TIP3P water model. [DOI: 10.1115/1.4025652]*

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1 Introduction

Nucleate pool boiling is a very efficient and widely used cooling method with a wide variety of heat dissipation applications in industry and technology, e.g., in aircraft thermal management, electronics, and nanofluidics. A better understanding of the mechanisms and details of the multiscale phenomena involved in the process of boiling is needed to provide an insight into ways to control and enhance the boiling heat transfer.

Additives have long been recognized and studied for the purposes of enhancing the boiling heat transfer [1–4] and heat transfer with surfactant additives in pool boiling is the topic of active research in thermal management [5–10], spray-cooling [11], micro and nanofluidics [12–16]. Additives can enhance or diminish the effectiveness of boiling heat transfer depending on their chemistry or concentration [1,3,4,9,13–15,17–21]. On a macroscopic level, solution additives contribute to dynamic surface tension [2,6,17,22] and modify the surface wettability [23]. Since nucleate boiling is such ubiquitous thermal management method, there is a sustained interest in its enhancing, better understanding, and control [5,11,12,16,24–27]. There have been a number of microscopic models attempting to describe nucleate boiling with additives [28–30] but there is still a need for better understanding on a molecular level. Recently, the effect of concentration, chemistry, temperature, and pH on thermal conductivity and viscosity of bulk aqueous surfactant solutions were studied experimentally by Zhou et al. [27]. It was observed that while the addition of any surfactant decreases the thermal conductivity of the solution, non-ionic surfactants reduce the thermal conductivity more than the ionic ones.

Our research interest is in the advancement of molecular-level understanding of the processes involved in the phenomenon of boiling with additives. The present effort attempts to address two specific aspects of the problem of interest: exploring the effect of

adding the surfactant SDS on the thermal conductivity of the solutions at room and boiling temperature as well as the concentration dependence of the diffusion of SDS in water.

We carry out classical molecular dynamics (MD) simulations [31], where the individual atoms are approximated by spheres with van der Waals radii and partial charges, the intramolecular interactions are approximated via (harmonic) potentials for chemical bonds, angles, and dihedrals, while the intermolecular interactions are modeled by the long-range Lennard-Jones and Coulomb interactions. At each simulation step, the Newtonian equations of motion are solved i.e., numerically integrated for each atom in the potential created by the rest of the atoms in the system. The force field parameters are usually optimized to correctly reproduce some experimental properties and/or are developed from ab initio or density functional theory (DFT) calculations of gas or condensed phase.

There exist a large number of theoretical MD model potentials for water [32–38] and each of them reproduces well only some of the water properties and only within certain thermodynamic conditions. The variety of water models can be broadly divided into: rigid, flexible, and polarizable. Rigid models keep the bond lengths and angles at their equilibrium positions which significantly reduces the computational cost, especially for large systems. Additional computational savings come from the opportunity to use larger simulation steps. Since the timestep of the integration is chosen to be smaller than the period of the fastest motion in the system, usually, a timestep of 10^{-15} s is chosen to account for the fast motion of the hydrogen atoms in water molecules. If rigid bond models are used via algorithms like SHAKE [39] the timestep can be increased to 2×10^{-15} s. Flexible water models allow the water molecule to deform, i.e., bond distances and the bond angle change in the course of the simulation, at the expense of increased computational cost. Polarizable force fields additionally allow for variable partial charges on the atoms of the water molecule in accordance to the changing environment and this is why they are exceptionally computationally costly. All force fields, therefore, account for the many-body effects to a varying degree since including the polarization effects is computationally demanding. Moreover, any classic force field description of quantum molecular bonds is inherently approximate [40,41]. On the other hand, there exist a variety of force fields that are

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parameterized for more or less specific system or class of systems in mind. For example, AMBER [42], CHARMM [43], and OPLS [44] force fields, to mention a few, are optimized for biomolecular simulations, while CLAYFF [45] was developed with the goal to be general enough and suitable for modeling aqueous solutions and interfaces of inorganic mineral materials. The complexity of the problem of choosing a water model and force field parameters to describe a molecular system is additionally increased by the specific suitability and compatibility of the water model with the model parameters to describe the rest of the simulated system. Therefore, the choice of a force field depends on its range of applicability and on the molecular system to be studied [34,46].

Bulk liquid properties using rigid water models are extensively studied and available in the literature [32,34,38,41,47–49]. Recently, the transport and thermal properties of well established and widely used rigid and flexible water models were studied and compared. Mao and Zhang [46] evaluated the thermal conductivity, shear viscosity, and specific heat of seven rigid water models. The work of Sirk et al. [50] studied the thermal conductivity of common classic flexible water models, compared the computational approaches for evaluating thermal conductivity, and observed that although both rigid and flexible water models overestimate the thermal conductivity of neat water, the rigid water models provide values closer to experiment. It was hypothesized that the increased number of degrees of freedom of the flexible water models is responsible for the overestimation of the heat transfer. Although the rigid water models are better suited for simulating heat transfer in bulk fluids, it was also suggested that the appropriateness of rigid versus flexible water models at interfaces needs further investigation.

We report a computational study on the effect of surfactant concentration on the diffusion and thermal properties of aqueous SDS solutions at room and at boiling temperatures. We also assess the performance of a relatively new water model [38] derived from condensed phase ab initio calculations, in simulating transport behavior of bulk water near boiling conditions along with room temperature. The structure of the paper is as follows. In the first part of the paper, a model for SDS by Schweighofer et al. [51] was adopted which combines all-atom approach for the hydrophilic sulfate headgroup and united-atom course-grained approach for the hydrophobic tail of SDS. The diffusion coefficient of SDS and the thermal conductivity of the aqueous surfactant solution are computed for different concentrations of SDS at room and boiling temperatures. The solvent model used is a standard TIP3P [49] water model. The results for the diffusion of SDS in water and the thermal conductivity of surfactant aqueous solutions are compared to experimental results. In the second part, we introduce the ab initio flexible water model developed by Akin-Ojo et al. [38] in 2008 using the relatively new adaptive force-matching method [52,53] and compute the diffusion and thermal conductivity of bulk water predicted by this model.

2 Transport Properties of Aqueous Surfactant Solutions at Room and Boiling Temperatures

2.1 Surfactant Model and Simulation Details. In this work, we adopted the hybrid model of SDS [51,54–57] which combines all-atom description of the hydrophilic sulfate headgroup of SDS with a united-atom approach to describe the hydrophobic aliphatic tail of SDS, bottom structure in Fig. 1. The top structure of Fig. 1 shows the atomic structure of the anionic surfactant SDS. An all-atom approach describes each atom with its own set of parameters and was used to describe the water molecules in this work. The united-atom approach is in a sense a coarse-graining approach in which a group of atoms is described as one “united-atom” with its own set of parameters. Only the hydrophobic tail is described by united-atom approach where the hydrogen atoms belonging to each carbon atom are grouped into a new united-atom. For example, the terminal CH₃ group of SDS is represented by the C3

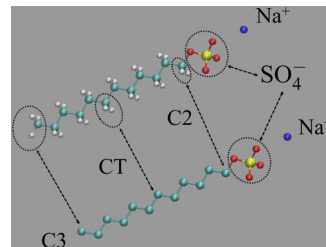


Fig. 1 Top: All-atom model of SDS. Bottom: Hybrid all-atom united-atom model of SDS.

atom in united-atom approach. The CH₂ groups are represented by a new atom type CT, and the last CH₂ group bonded to the hydrophilic head is designated as C2.

2.1.1 Self-Diffusion of SDS in Water. The diffusion coefficient of a solute in water can be computed from the mean square displacement (MSD) of the center of mass of each solute molecule as follows:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \quad (1)$$

where $\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$ is the mean square displacement averaged over all solute molecules and time origins.

In the simulations for obtaining the diffusion coefficient of SDS in water, the water potential used was TIP3P [49]. Two sets of simulations were performed: with rigid and flexible TIP3P, at room temperature, 298.15 K, and at boiling temperature, 373 K. The initial size of the simulation box was 100 Å × 100 Å × 100 Å containing approx. 33,000 water molecules. The initial simulation boxes were built using Packmol [58] and were further minimized and equilibrated at the respective temperature. Periodic boundary conditions were imposed in all three directions to simulate bulk properties and particle-particle particle-mesh method as implemented in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [59,60], also related to Ewald summation [31,61], was applied to correctly account for the long-range electrostatic interactions. All simulations were carried out using the LAMMPS [60]. The input files for LAMMPS were prepared using VMD [62]. After a standard procedure of minimization and equilibration, we performed 2-ns equilibrium MD runs at constant volume and temperature of the system at 298.15 K and 373 K, respectively, in order to obtain the self-diffusion of SDS in water.

2.1.2 Thermal Conductivity. Thermal conductivity can be computed from equilibrium MD simulations using the Green-Kubo formula [63] or by nonequilibrium MD (NEMD) simulations by imposing a known heat flux in the system. We computed the thermal conductivity by carrying out NEMD simulations where heat flux is introduced in the system which leads to establishing a temperature gradient across the system as proposed by Müller-Plathe [64]. We used the Müller-Plathe method of imposing heat flux [65] which involves swapping the kinetic energy of the hottest particle in a predefined “cold” region of the system with the kinetic energy of the coldest particle in the predefined “hot” region of the system thus conserving the total energy of the system while inducing heat flux from the hot region (heat source) to the cold region (heat sink). In response to the heat flux through the system, a temperature gradient is established. After equilibrating the simulation systems at the respective temperature and constant volume, NEMD runs at constant volume and energy were performed, during which a steady temperature gradient in z-direction was established. From the last 700 ps of the simulations, the temperature profiles were recovered and the temperature gradient, dT/dz , was computed from linear fits of the temperature profiles. The temperature gradient is induced by the heat flux, J , imposed

Table 1 Diffusion coefficient D_s in 10^{-6} cm²/s of aqueous SDS solutions at room temperature, 298.15 K, computed for a range of concentrations. The experimental results (η) are taken from Ref. [66].

| C (mol/L) | Exp η | TIP3P(f) | TIP3P(r) |
|-----------|------------|----------|----------|
| 0.0016 | — | 0.51 | 8.18 |
| 0.0050 | — | 7.16 | 4.64 |
| 0.0082 | — | 5.89 | 4.81 |
| 0.0100 | 1.76 | 2.87 | 6.12 |
| 0.0164 | 3.00 | 8.47 | 12.34 |
| 0.0500 | 4.03 | 6.32 | 13.18 |
| 0.1250 | 4.53 | 3.09 | 4.23 |

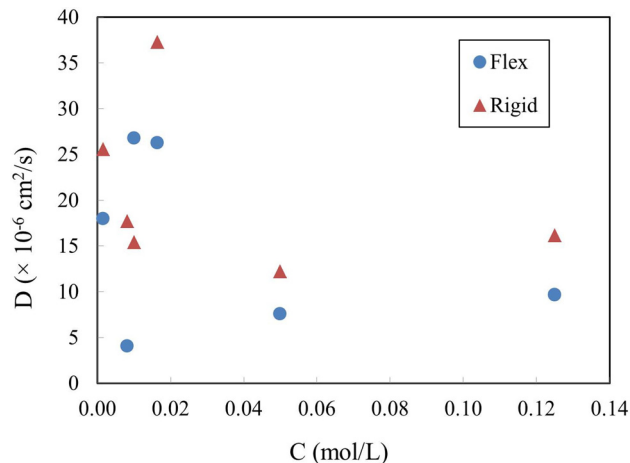


Fig. 2 Diffusion coefficient of SDS at different surfactant concentration and 373 K computed with flexible TIP3P (Flex) and rigid TIP3P (Rigid) water potential

on the system and the coefficient of proportionality is the thermal conductivity, λ , of the material: $J = -\lambda dT/dz$.

2.2 Diffusion of SDS in Water: Results and Discussion.

When SDS ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) dissolves in water, the ionic bond between Na^+ and DS^- ($\text{C}_{12}\text{H}_{25}\text{SO}_4^-$) breaks and sodium counterions dissociate. The degree of dissociation and the fraction of sodium ions that is associated in the first and second solvation shells can be determined from the sodium-sulfur radial distribution function [55]. For the purposes of computing the diffusion of SDS in water and comparing to the experimental values [66], and since the light sodium ion is far more mobile than the DS^- anion, hereafter we consider the diffusion of the anion DS^- and refer to it as SDS. The diffusion coefficient of SDS was computed from the MSD of the center of mass of each molecule, according to Eq. (1). The computed values at 298.15 K are shown in Table 1 and compared with the experimental values from Ref. [66]. It should be noted that the computation of the MSD at low surfactant concentrations is inherently less accurate than at larger concentrations. Surfactant concentration of 0.0016 mol/L corresponds to a single SDS molecule in our simulation box whereas a surfactant concentration of 0.125 mol/L corresponds to 75 SDS molecules in the simulation box which provide better statistics for MSD. From Table 1, it is clear that the computed values of the diffusion coefficient of SDS in water are of the correct order of magnitude. At higher concentrations, where we expect better accuracy, the rigid TIP3P water potentials systematically predicts larger values than the flexible one. Similar trend is also observed at boiling temperature, as it can be seen from Fig. 2, where diffusion coefficient of SDS computed at 373 K is plotted as a function of the surfactant

Table 2 Thermal conductivity λ (W/m·K) of aqueous SDS solutions at 298 K and 373 K and different surfactant concentration

| C (mol/L) | 298.15 K | | 373 K | |
|-----------|----------|----------|----------|----------|
| | TIP3P(f) | TIP3P(r) | TIP3P(f) | TIP3P(r) |
| 0.0 | 0.96 | 0.82 | 1.00 | 0.68 |
| 0.0016 | 0.91 | 0.80 | 0.96 | 0.83 |
| 0.0082 | 0.92 | 0.72 | 0.95 | 0.76 |
| 0.0164 | 0.91 | 0.80 | 0.96 | 0.84 |
| 0.0500 | 0.90 | 0.80 | 0.94 | 0.83 |
| 0.1250 | 0.88 | 0.79 | 0.92 | 0.82 |

concentration. Again, the diffusion coefficients of SDS in rigid TIP3P water are always larger than the values predicted by using flexible water potential.

The calculations from simulations with rigid water model seem to systematically overestimate the diffusion coefficient of SDS at higher surfactant concentrations. At lower surfactant concentrations, the accuracy of the simulated results is lower, probably, due to insufficient statistics and simulations of longer duration and/or larger scale can improve the accuracy of the estimates.

2.3 Thermal Conductivity of Aqueous SDS Solutions: Results and Discussion. The thermal conductivities of aqueous SDS solutions at a range of surfactant concentrations were computed by Müller-Plathe's method [64,65] from NEMD simulations. The values of the thermal conductivity of aqueous SDS solutions, computed with flexible and rigid TIP3P water model at room and boiling temperature and different surfactant concentrations are listed in Table 2.

Recently, an experimental investigation of the effects of the surfactant concentration, temperature, and pH on the thermal conductivity of aqueous solutions of nonionic, cationic, and anionic surfactants, was reported [27]. Compared to the reported values in Ref. [27], both water models lead to higher than experimental thermal conductivity of the aqueous SDS solutions. As in the case of pure water, the flexible water potential leads to an overestimate of the thermal conductivity of the solution. Both models correctly predict the increase of the thermal conductivity with increase of temperature. Zhou et al. [27] experimentally observed an increase of the room temperature thermal conductivity ratio ($\lambda/\lambda_{\text{water}}$) of the ionic surfactants SDS and SDBS at lower concentrations, approx. 0.1 wt. % for SDS, and gradual decrease of the thermal conductivity ratio of the solution with increasing the concentration. At lower concentrations, it was observed that the thermal conductivity of the ionic surfactant solution was larger than the thermal conductivity of neat water. Our simulations did not reproduce the enhancement of the thermal conductivity of the surfactant solutions at low concentrations but did reproduce the experimentally observed slow decrease trend at concentrations higher than the critical micelle concentration (CMC). Clearly, further simulations on a much larger scale are needed to better understand the thermal properties of low concentration surfactant solutions, as well as to explore the effects of the chosen surfactant and solvent models, simulation length and system size on the computational results. Studies with increasingly large simulation systems can be the subject of future works.

3 MP2f Water Model and Simulation Details

With respect to reproducing the transport properties of water, and more specifically, the self-diffusion of water, the modified TIP3P [49] water potential used in this work is the most commonly used and reliable force field as it was optimized to better reproduce not only the experimental water density, heat of vaporization, and dielectric constant but also the experimental bulk diffusion coefficient of water.

The flexible force field MP2f [38] was developed by the relatively new adaptive force matching method from condensed phase quantum-mechanics/molecular-mechanics (QM/MM) calculations. The force matching (FM) method was first proposed in 1994 [52]. The FM method optimizes the force field parameters not to best reproduce any experimental bulk water properties, as is the case in the empirical force fields, nor to best fit single point energies from ab initio gas phase calculations, as is the case in the usual ab initio force fields, but, instead, to reproduce ab initio forces derived from DFT calculations in the condensed phase [67]. The adaptive force matching (AFM) method is an improvement upon the original FM schemes in that it uses QM/MM calculations and avoids the need for expensive condensed phase electronic structure calculations [38]. Therefore, one major appeal of the AFM method lies in the fact that the force field parameters are derived from condensed phase calculations as opposed to the usual gas phase calculations, since those force field parameters are intended to be used to simulate bulk liquid water.

In order to investigate the transport properties of the MP2f water model, we computed the diffusion constant of the model and the thermal conductivity of water at room temperature 298.15 K and boiling temperature 373 K.

3.1 Self-Diffusion of Bulk Water. We performed 2-ns equilibrium MD runs to compute the diffusivity of water at two temperatures, 298.15 K and 373 K, using MP2f water potential. The simulation step was 0.001 ps. The simulation runs were performed at constant volume and temperature using Nose-Hoover thermostat as implemented in LAMMPS [60]. Snapshots of the atomic positions and velocities were output every 100 simulation steps or every 0.1 ps. The self-diffusion coefficient of water is computed from the MSD of the center of mass of each water molecule or, to a very good approximation, the position of the oxygen atom in each water molecule, according to Eq. (1).

As it is well known that the computed values of the diffusion coefficient depend on the size of the simulation box [68–70] when periodic boundary conditions are applied, we set up a series of six simulation systems, containing 128, 256, 512, 1024, 2048, and 4096 water molecules, at normal water density of 33.0 nm^{-3} . If L is the length of the periodic water box, and D_L is the computed diffusion coefficient in the same periodic water box, then the dependence of D_L on the length L is given by

$$D_L = D_0 - \frac{2.837k_B T}{6\pi\eta L} \quad (2)$$

In Eq. (2), η is the shear viscosity of water. Therefore, we can extrapolate the size-independent diffusion coefficient D_0 and the viscosity of water from the series of simulations of increasing simulation box size.

3.2 Self-Diffusion and Thermal Conductivity of MP2f Water Model: Results and Discussion. The values of the self-diffusion coefficient of water obtained from simulations in different size periodic simulation boxes were fitted with a linear function of $1/L$ as shown in Fig. 3. From these fits, the size-independent values of the diffusion coefficients in infinitely large bulk system were extrapolated. The fitting procedure provides an estimate of the viscosity of the water model as well. The extrapolated size-independent values of the diffusion coefficient of MP2f water model are shown in Table 3. In the table, we provide also literature values obtained by the same extrapolation technique. The three literature water models are rigid. Our estimate of the viscosity of the MP2f water models is: $3.24 \times 10^{-4} \text{ kg(m}\cdot\text{s)}$ at 298.15 K and $3.84 \times 10^{-4} \text{ kg(m}\cdot\text{s)}$ at 373 K. From Table 3, it can be observed that MP2f water potential is somewhat better than rigid TIP3P with respect to the predicted value of the size-independent diffusion coefficient but SPC/E [71] and TIP4P/2005 [72] predict size-independent values of diffusion coefficient and

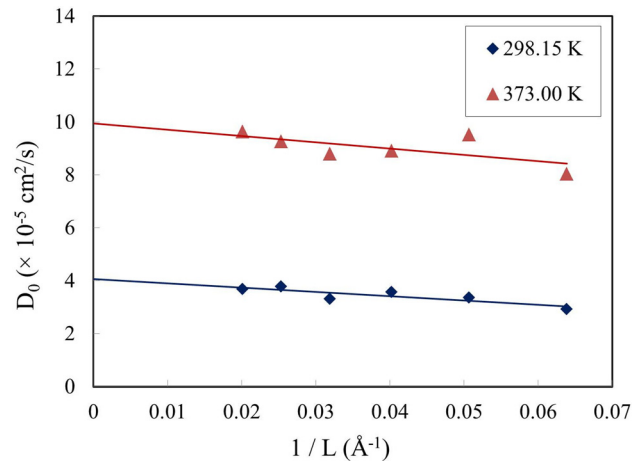


Fig. 3 Diffusion coefficient as a function of the inverse length of the periodic simulation box. From a linear fit of the data, the size-independent diffusion coefficients for MP2f water model were extrapolated to be $4.06 \times 10^{-5} \text{ cm}^2/\text{s}$ at 298.15 K and $9.95 \times 10^{-5} \text{ cm}^2/\text{s}$ at 373 K.

Table 3 Size-independent diffusion coefficient (D_0) and viscosity (η) of MP2f water model at 298.15 K and 373 K. For comparison, estimates of the size-independent diffusivity of other water models and experimental values are also provided. (†) Ref. [73], (‡) Ref. [74], (§) Ref. [69], (¶) Ref. [70], (‡) Ref. [46], (‡) Ref. [46], this value was calculated at 363 K.

| Model | $D_0 [\times 10^{-5} \text{ cm}^2/\text{s}]$ | | $\eta [\times 10^{-4} \text{ kg (m}\cdot\text{s)}]$ | |
|------------|--|-------|---|-------------------|
| | 298.15 K | 373 K | 298.15 K | 373 K |
| MP2f | 4.06 | 9.95 | 3.24 | 3.84 |
| IP3P | 6.05 [§] | — | 3.18 [¶] | 2.17 [‡] |
| SPC/E | 2.97 [‡] | — | 6.4 [‡] | — |
| TIP4P/2005 | 2.49 [‡] | — | 8.3 [‡] | — |
| Exp. | 2.3 [†] | — | 8.96 [‡] | — |

Table 4 Computed thermal conductivity λ in $\text{W}/(\text{m}\cdot\text{K})$ of neat water at room and boiling temperature. The experimental values are: (§) from Ref. [75] and (†) from Ref. [76].

| | 298.15 K | 373 K |
|----------|--------------------|---------------------|
| TIP3P(f) | 0.96 | 1.00 |
| MP2f | 0.64 | 0.66 |
| TIP3P(r) | 0.82 | 0.68 |
| Exp. | 0.607 [§] | 0.6723 [†] |

viscosity of water in better agreement with experiment. Table 3 also lists recently reported values for the shear viscosities of a number of rigid water models computed using the Green-Kubo method [46].

The values of the computed thermal conductivity of water are shown in Table 4. It was reported [50] that the computed value of the water thermal conductivity was found to be independent on the size of the simulation box (provided it is larger than 40 \AA), therefore, we performed all simulations in a periodic box containing 4096 water molecules. The results in Table 4 confirm the observation from Ref. [50] that the flexible water models tend to overestimate the thermal conductivity of water, TIP3P(f) versus TIP3P(r). Our results further show that the flexible MP2f water model performs exceptionally well in reproducing thermal conductivity of water at room and boiling temperature, compared to both the rigid and flexible TIP3P.

In conclusion, the flexible MP2f water potential, derived by AFM method from condensed phase QM/MM calculations is shown to perform reasonably well in reproducing the diffusion

coefficient of water and very well in reproducing the thermal conductivity of water at both room and boiling temperature.

4 Conclusions

We performed an extensive series of MD simulations computing the transport properties of bulk aqueous surfactant solutions at room and boiling temperatures for a range of surfactant concentrations. The effect of the water model on reproducing the surfactant diffusivity and the thermal conductivity of aqueous SDS solutions was investigated by using flexible and rigid TIP3P water. It was observed that at higher surfactant concentrations, the rigid water model overestimates the values for surfactant diffusion. At lower concentrations, the results were less reliable due to insufficient statistics and further simulations with larger systems are required to improve the accuracy of the estimates. It was recently observed in the case of pure water [50], that the flexible water models are not only more computationally costly but also they tend to overestimate the thermal conductivity of neat water. Our results for the thermal conductivity of aqueous SDS solutions confirm this but also show that when the thermal conductivity enhancement of the solution with respect to pure water is concerned, the flexible water model reproduces the experimental trend more reliably, at least at concentrations higher than CMC. Future larger-scale MD studies are needed to further explore and better understand the transport properties of surfactant solutions at low concentrations.

We also studied the ability of MP2f, an ab initio water potential derived from condensed phase calculations, to reproduce the diffusion coefficient and thermal conductivity of water at room and boiling temperatures. The size-independent diffusion coefficient of water was derived from a series of MD simulations with increasing size of the simulation system. The bulk water self-diffusion coefficient was estimated to be $4.05 \times 10^{-5} \text{ cm}^2/\text{s}$ at 298 K and $9.95 \times 10^{-5} \text{ cm}^2/\text{s}$ at 373 K. The computed values of the thermal conductivity were: 0.64 W/(m·K) at 298 K and 0.66 W/(m·K) at 373 K, in much better agreement with the experimental values compared to both the rigid and the flexible TIP3P.

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