Journal of Molecular Liquids 193 (2014) 139–151

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Molecular processes of ion effects on aqueous nanofilm rupture

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ARTICLE INFO

Article history:
Received 21 July 2013
Received in revised form 10 December 2013
Accepted 17 December 2013
Available online 30 December 2013

Keywords:
Molecular dynamics
Thin film
Film rupture
Ion effect

ABSTRACT

Much progress has been made in the understanding and application of specific ion effects; however, a detailed interpretation of film stability regarding the ion effect has not yet been achieved. This research aims at developing an understanding of the physico-chemical colloidal aspects in an endeavor to acquire an ability to predetermine specific ion effects on nanofilm rupture. Despite the series of reports published regarding the surfactant-free films, the experimental technique proved nearly to be unable to provide further convincing interpretation towards this issue. Molecular dynamics (MD) technique was applied to investigate the effect of salt ions on film stability in various concentrations with pair-additive and many-body polarizable water–ion potentials to validate with certainty the rupture process of aqueous nanofilms in the absence and presence of salts. Properties of the liquid film including dipole moment, molecular distribution profiles, together with a detailed quantitative analysis of film rupture, potential energy, evidences e.g. ion–water binding energy, Dipole Autocorrelation Functions (DAFs) and disjoining pressure isotherm data were examined. The DAFs of water within the film were observed to be stronger in salt films than in a pure water film. The results show that salt ions destabilize the nanofilms at low concentrations, while the ability of salt to break the films depends on the strength of the ion–water interaction and the molecular partition at the film surfaces.

1. Introduction

The ion specific effect plays an important role in colloidal and biological systems. During the last few decades, significant progress has been made in the understanding of specific ion effects in many areas, e.g. specific ion effects at air/water interface [1], which resulted in specific properties and a unified picture of the ion distributions at the aqueous surface. Yang et al. [2] performed MD simulations on water-surfactant film rupture to investigate foam stability, and their results showed that the stabilization of a water film decreases in the order of SDS (sodium dodecyl sulfate) > LAS (linear alkylbenzene sulfonate) > $C_{12}E_7$ (heptaethylene glycol monododecyl ether). Yang et al. [3] investigated the influence of calcium ions on foam stability with surfactants, and results showed that, as the Ca^{2+} concentration increased, SDS significantly decreased foam stability, but LAS and $C_{12}E_7$ did not significantly change foam performance. The marginal effect of calcium ion on foam stability in the presence of surfactants is related to enhanced interaction configurations at short distances. Yang et al. also reported the calcium ion effect on foam stability performance in the presence of a mixed LAS and SDS surfactant system, and found that the performance of the surfactant mixture became worse than that of LAS and better than that of SDS in terms of the influence of calcium ions on foam stability [4]. There are also some other reports within complex systems [5–12] regarding such an effect in aqueous films with and without electrolytes, some studied relevant factors, e.g. hydrophobic forces or pH values.

The abovementioned studies investigated the effects of salt on water films stabilized by surfactants, but did not examine the effect of ions on pure water film stability. This may be due to the fact that there are many experimental results on these systems (films stabilized by a surfactant) to compare with and classical theory is able to explain the ion effect satisfactorily (usually adding of salt affects the Electrostatic Double Layer or non-DLVO surface forces). However, the situation is very different for a pure water film, e.g. there is no definite conclusion regarding the stability of pure free water films, and thus the effect of ions on water film stability is more difficult to investigate. There is inconsistency among the experimental results [13–19] with different setups and methods regarding water film stability, possibly due to the sensitivity of the experimental procedures and the interplay of various factors. For example, pure water may have trace contamination, which can lead to inconclusive results. Additional factors such as concentration, approaching speed and evaporation may also alter the results. On the other hand, a system of films stabilized with a surfactant containing multiple components is complicated and also difficult to fully rationalize and comprehend (since we are not sure of the effect of ions on water film stability and the true interpretation, even for an ion–water system in a thin film). Thus, the ion effect on the stability of pure water films should be studied.

Many inorganic salts (such as NaCl) tend to inhibit bubble coalescence, which is one of the reasons why foam is formed when waves break in the ocean but not in freshwater lakes. To cover specific ion

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http://dx.doi.org/10.1016/j.molliq.2013.12.031

effects at all possible aqueous interfaces would be impossible. To understand the ion effect on water film stability, we start with halide sodium salts including NaF, NaCl, NaBr and NaI. Both structural and dynamic properties of the aqueous films will be explored and examined as to how the specific interactions between ions and water molecules influence these properties. In order to make sure that the results are not model dependent, two different non-polarizable water models, SPC/E and TIP4P-Ew, were used extensively. As there are many water models, three-point (e.g. SPC, SPC/E), four-point (TIP4P, TIP4P-Ew), five-point, and polarizable Dang-Chang model [20], models which can better reproduce interfacial (surface potential, surface tension, IR spectra) properties and may be more realistic in describing the interaction in film geometry. For the three-point model, SPC/E had overall better performance in terms of IR and Raman [21] spectra and could reproduce the thermodynamic properties at a relatively low computational cost. The TIP4P-Ew-ion potential [22] was developed to reproduce the bulk, interfacial, static structural and dynamic properties of aqueous ionic solutions.

The novel aspects of this work are that this is the first study on the effect of ions on water film stability by MD using the popular models; the effect of ions was investigated at different geometry sizes and concentrations; detailed analyses of water–ion–water interactions within the film were performed. The study is the extension on the study of analysis for water film [22] and the developed TIP4P-Ew-ion parameters [23], which may help with the development of a theoretical framework to guide experimental phenomenon. The organization of this research is as follows. The molecular models, simulation details, and procedures are described in Section 2. Section 3 includes the properties and a quantitative description of aqueous film rupture. The conclusions and outlook are presented in Section 4.

2. Methods and computational details

2.1. Methodology

The whole view of the modeling method and the MD part is shown in Fig. 1.

When two bubbles approach, a film will be formed. MD simulations were applied to model this thin film. Salts were added to the water film to study the influence of ions.

2.2. SPC/E-ions in GROMACS

SPC/E and the corresponding ion-parameters from the OPLS-AA force field [24] were used to describe ion–water interactions. Total potential energy included bonded interactions (bond, angle, and torsion interactions) and non-bonded interactions (Lennard-Jones and Coulomb interactions). Particle mesh Ewald (PME) [25] was used to describe the Coulomb long-range interactions and a potential truncation of 14 Å for the Lennard-Jones and Coulomb interactions. The temperature was maintained at 300 K using the V-rescale method with a T coupling of 0.1 ps. V-rescale [26] is a new method similar to Berendsen coupling, but can give a proper canonical ensemble.

Simulations were performed with a time step of 1 fs by using periodic boundary conditions at three directions. First, a box of aqueous solutions with randomly packed ions was created. The box was equilibrated first under NPT (isothermal–isobaric ensemble) condition, followed by a further equilibration in an NVT (Canonical ensemble) ensemble. The equilibrated box was then put into the center of a vacuum box ($L_x = L_y = L_z/3$) to simulate the liquid–vapor interface. Slab geometry as follows was employed: the size of the box was set to $L_x = L_y, L_z = 3\ L_x$ with the film lateral dimension ($L_x = L_y$) being the same as the box. MD simulations were performed using the open-access software package GROMACS 4.5.3 [27–29]. The main process was to test whether the added salts had a breaking effect or not on the stability of the water film.

2.3. TIP4P-Ew-ions in AMBER

To make sure that the results were not model-dependent, the TIP4P-Ew [30] model was applied to study the effect of ions on water film stability. This model is a re-parameterization of the TIP4P model under an Ewald regime as its simulated bulk density with proper incorporation of long-ranged electrostatics is significantly better compared to other models. The potential parameters for the ion–water interactions were developed to reproduce the available experimental results and reported earlier [22].

All simulations were carried out with a time step of 2 fs, a potential cutoff of 11 Å and temperature fixed at 298 K. The *SHAKE* algorithm was used to constrain the bond lengths of water molecules. All electrostatic interactions (ion–ion, ion–solvent, and solvent–solvent) were evaluated by the Ewald method. Because the TIP4P-Ew-ion potentials were developed using the AMBER suite of programs, thus the simulation with TIP4P-Ew was also carried out using AMBER in this study. Following the same methodology, the properties and final states of the films were studied. The time step of 2 fs in TIP4P-Ew-ion did not significantly affect the final results (properties e.g. radial distribution function, also film rupture results), since the water was constrained.

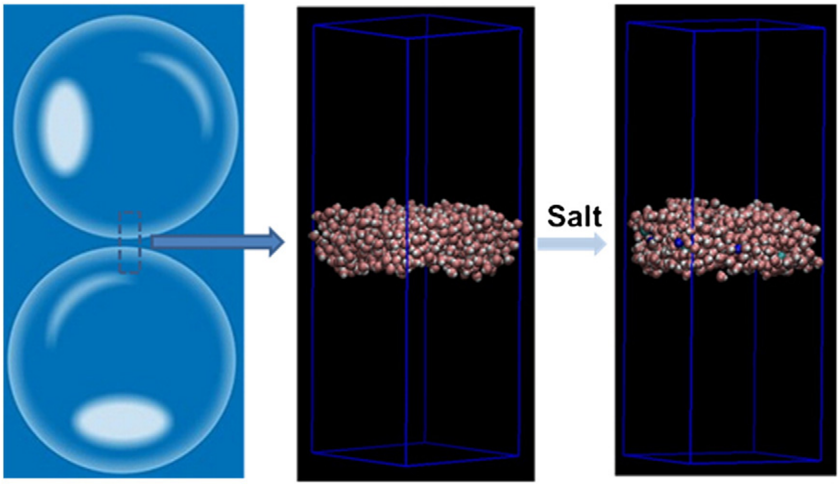

Fig. 1. Illustration of an aqueous film between two bubbles (the image on the left shows two bubbles in a water solution) and the MD parts (the center image is a pure water film and the image on the right is a salt film).