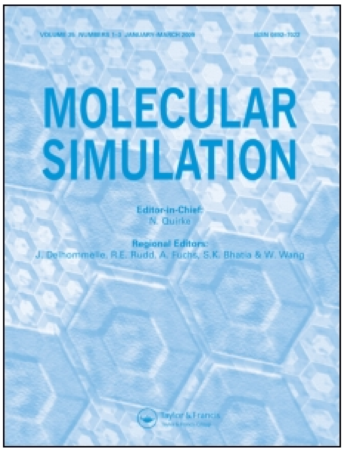

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MONTE CARLO SIMULATION OF NONIONIC SURFACTANTS AT THE OIL-WATER INTERFACE

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A Monte Carlo simulation method has been developed for modelling amphiphiles at an oil-water interface. Properties are calculated for the mixture water, benzene and tetraoxyethylene glycol dodecyl ether.

KEY WORDS: Monte Carlo surfactant oil-water interface

1. INTRODUCTION

The structure and properties within the region of the oil-water interface are of great importance in detergency, oil recovery and some processes in biological systems.

In particular, the presence of amphiphilic molecules composed of a hydrophilic group and a hydrocarbon chain play a critical role in understanding interfacial phenomena. Information at the molecular level on these interface should give a deeper insight into the properties from the viewpoint of chemistry, applied chemistry and biophysics.

To this end, a Monte Carlo simulation method for modelling amphiphiles at an oil-water interface has been developed. In this report, the molecular distribution along the direction perpendicular to the interface is calculated for the system comprising of water, benzene and a nonionic surfactant, tetraoxyethylene glycol dodecyl ether ($CH_3(CH_2)_{11}$-$(OCH_2CH_2)_4OH$).

2. MOLECULAR MODEL AND POTENTIAL FUNCTIONS

The surfactant model is based on Jorgensen's OPLS [1] potential which has fixed bond lengths and bond angles. The CH_3 and CH_2units of an alkyl chain are treated as united atoms. Parameters describing the $-(O-CH_2-CH_2)-$ moiety are assumed to be comparable to an ether whilst those of the $-OH$ end-group are assumed to be the same as those of an alcohol. The TIP4P 4-sites model [2] is used to simulate water molecules. Benzene is expressed by six aromatic carbons with the OPLS potential.

The general form of the potential functions includes Lennard-Jones and Coulombic terms,

$$E_{ij} = \frac{q_i q_j e^2}{r_{ij}} + \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}}$$

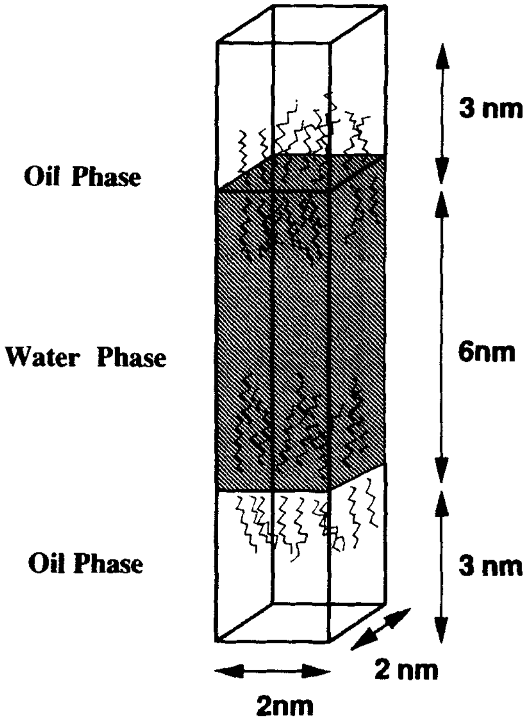

Figure 1 The schematic description of unit cell.

where E_{ij} is the interaction energy between two atoms i and j and Standard combining rules using the geometric mean are used such that $A_{ij} = (A_{ii}A_{jj})^{1/2}$ and $C_{ij} = (C_{ii}C_{jj})^{1/2}$.

The only internal motion is the dihedral angle torsion as all bond angles and bond lengths are fixed throughout the simulation. The Amber force parameter [3] is used for the torsion energy calculation.

3. SIMULATION PROCEDURES

The system is enclosed in a unit simulation box of dimension $L_xL_yL_z(L_x = L_y = 2\,\text{nm}, L_z = 12\,\text{nm})$. The water phase is located in the middle and forms two interfaces with the upper and lower oil phases, as shown in figure 1. Molecules are distributed randomly in each phase at the beginning of the simulation. The system contains 595 water molecules and 125 benzene molecules. Nine surfactant molecules are inserted at each interface so that their hydrophilic chains are in the water phase (figure 1). All dihedral angles of the initial chain conformation are in the "trans" state.

Constant volume sampling is carried out at 300K. One Monte Carlo step corresponds to the movement of one molecule which is randomly chosen from the whole system. One trial movement of the surfactant is composed of molecular re-orientation, translation or torsion of one dihedral angle. The maximum displacements of translation and rotation are around 0.2 nm and 36.0° respectively.

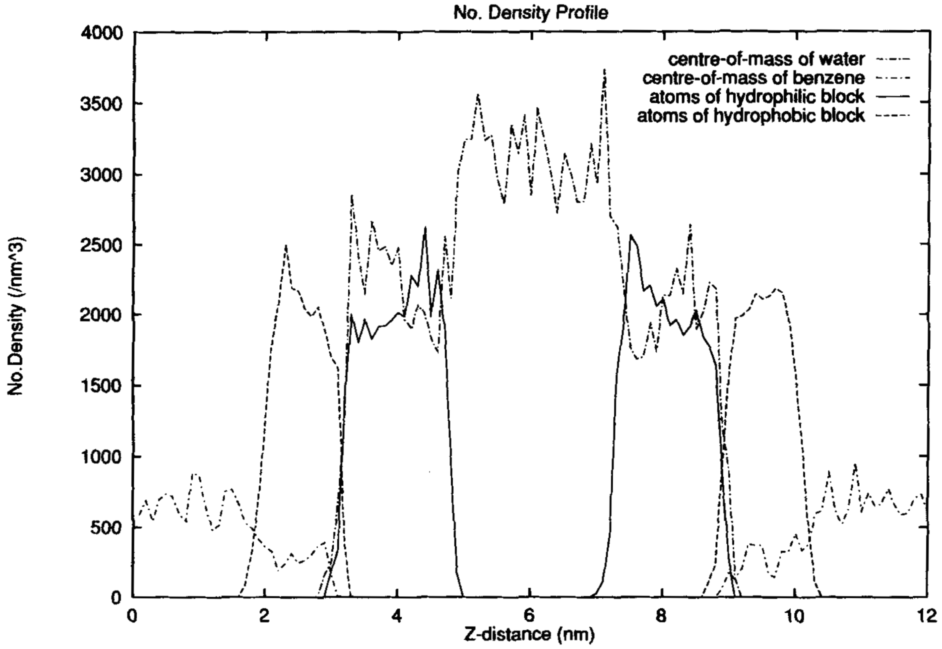

Figure 2 Number density profile along the z-direction of the unit cell. The surfactant molecules is divided into the hydrophobic block, $C_{12}H_{25}-$, and the hydrophilic block, $-(OCH_2CH_2)_4OH$. The acceptance ratio in the sampling of solvent molecules is about 50% and that of the surfactant is about 30%.

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The pair interaction potential calculation is truncated at 1.2 nm, where the long-range coulombic potential function is shifted so that it smoothly decays to zero at the cut-off distance. The computation is performed on a Intel i860 processor of Meiko Computing Surface at the University of Bristol, School of Chemistry.

4. RESULTS AND DISCUSSION

Figure 2 gives the averaged number density profile over 4 runs with different random number seeds. The first two million steps of each run are discarded and next three million steps are used for the sampling. In figure 2, the general feature of the surfactant distribution is just what is expected: the hydrophilic block is preferentially distributed in the water phase and the hydrophobic block in the oil phase.

The investigation of amphiphilic chain molecules at the interface has, so far, mainly relied on mean-field calculations and lattice-type simulations. In this report, the atomistic modelling tool has been developed, which will become the groundwork for a systematic study of the interfacial behaviour of amphiphiles of different chain lengths and the prediction of the interfacial tension.

Acknowledgements

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