Metropolis Monte-Carlo Computer Simulation of the Phase Behavior of Quaternary Water/Reactant/Oil/Surfactant Systems

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Abstract

A Metropolis Monte-Carlo computer simulation of quaternary water / reactant / oil / surfactant system is developed and the phase behavior of the system is studied. The simulation program is implemented based on the method by Larson et al. However, in our system a two dimensional ‘hexagonal-lattice’ system is used in place of square lattice and a quaternary system is implemented in stead of a ternary system. The goal of this work is to investigate the influence of reactant on the phase behavior of the microemulsion regions using computer simulation. Addition of reactants into the system and the possible reactant-surfactant interaction can lead to significant changes in the phase behavior and particle size. Experiments in laboratory are time consuming and cost intensive. Thus, experiments using computer simulation can be a good alternative for this purpose. To evaluate the performance of the implemented simulation model, the results obtained from the simulation program are compared with the existing laboratory data. The comparison reveals that computer simulation can be helpful for investigating microemulsion region of quaternary system.

KEY WORDS: microemulsion, quaternary system, Monte Carlo simulation, hexagonal lattice.

Introduction

Research on nanomaterials is getting increasing scientific interest for their wide variety of technological applications like catalysis (Cao and Bergens, 2004), pharmaceuticals (Otsuka et al., 2003), semiconductor (Chhabra et al., 1997) etc. Different methods are proposed and investigated for the large scale production of nanoparticles. Among them the use of microemulsion is found to be a potential alternative in the literature (Rauscher et al., 2005a; Lisiecki et al., 1997; Boutonnet et al., 1982). Microemulsions are thermodynamically stable and optically clear mixture of water, a non-polar solvent and an appropriate surfactant. Addition of reactants into microemulsions makes them act as small reactors where the fusion-fission phenomena between the droplets lead to a controlled uniform micro mixing (Voigt et al., 2005). Hence, controlled particle size and particle size distribution can be achieved. However, the successful application of this process in production requires extensive amount of experiments. This would be very costly and time consuming. Suitable computer simulation of the process could be helpful in this case and would allow a wide range of experiments. In this work, a computerized Monte Carlo (MC) simulation is developed to investigate the influence of reactants on the phase behavior of the micro-emulsion regions and particle size.

State of the Art

Monte Carlo computer simulation is a widely used method for studying the behavior of microemulsions. Larson et al. (1985) developed a model of MC simulation to study the behavior of amphiphile-oil-water systems in (Larson, 1985). In their work they used a 2D square lattice model to represent the system where oil and water occupy single lattice cell and amphiphiles occupy chains of cells. Zapta et al. (2004) presented a 2D simulation model to study the self-assembly process of nonionic surfactant considering second-neighbor interaction between surfactant molecules. Voigt et al.
(2005) studied the BaSO₄ nanoparticle precipitation in microemulsion using MC simulation. They studied the influence of feed rate and initial volume ratio on the particle size and distribution. In our work we basically followed the approach presented by Larson et al. (1985). However, there are two basic differences: i) in the system presented in this paper, the phase behavior of a quaternary system (water-reactant-oil-surfactant) and the influence of reactant is studied, in place of a ternary (amphiphile-oil-water) system ii) a hexagonal lattice model is used in place of a square lattice model, that provide us certain computational advantages without decreasing the neighborhood information significantly. Rauscher et al. (2005b) also used hexagonal lattice model, but their model was for a ternary system. In our opinion, primary contribution of this paper is that it sensibly combines the existing approaches with new ones to present a computerized simulation model for studying quaternary system.

Materials and Methods

Microemulsion

Microemulsions exhibit strong phase behavior that is basically caused by the molecular structure of the surfactant. Surfactants have hydrophilic group or water-loving head and hydrophobic chain or oil-loving tail. Thus, surfactants are capable of reducing the interfacial tension and can help the formation of microemulsion regions by placing themselves in water-oil interface. Two types of microemulsions are available: oil-in-water and water-in-oil microemulsion (shown in Figure 1). However, water-in-oil microemulsions are considered as ideal templates for the synthesis of inorganic nanoparticles. Though both types of microemulsions can be experimented with our system, here the results of the water-in-oil microemulsions will be presented.

Quaternary System

We are intended to build a simulation model for quaternary system. There are basically two approaches commonly used. One is Molecular dynamics calculations (Alder and Wainwright, 1959), where the system is built following the behavior of classical fluids. Intermolecular forces for a set of molecules and their motion is calculated by solving Newton’s equations of motion. Another is Monte Carlo calculations (Metropolis et al., 1953) where ensemble averages of the mechanical properties of interest are calculated over a finite, yet large sample of configurations and are chosen in a semi random fashion. In our work, we used the second approach.

In our MC computer simulation, microstructures are represented by hexagonal lattice cells (Figure 2). Each molecule of the quaternary system occupies a specific number of lattice cells. Their occupation in the lattice cells are chosen randomly. Since we are interested in water-in-oil system, at first occupancies of water, ionwater and surfactant molecules in the lattice is chosen randomly and the rest of the sites are assumed to be occupied by oil molecules. From this randomly generated initial state, hypothetical system energy is calculated using the neighborhood information of each molecule using interaction parameters. Then the MC algorithm tries to minimize this energy by randomly moving the molecules. The potential rearrangement is either accepted or discarded. This process is performed as a function of temperature, starting at a high temperature the system is slowly cooled (simulated annealing). At high temperature the movements of the molecules are more random and
frequent (simulating the behavior of boiling liquid). The MC algorithm will stop when the system reach at equilibrium i.e. no more energy minimization is possible or the temperature reaches to zero.

The Lattice Model

The system uses N x N lattice cells with periodic boundary condition, completely occupied by four molecular species – oil, water, reactant and surfactant. Oil, water and reactant molecules occupy single sites on the hexagonal lattice and surfactant molecules occupy sequence of adjacent sites. The number of water, oil and surfactant in the system is calculated using the oil weight fraction, $\alpha$ and surfactant weight fraction, $\gamma$ (Adityawarman et al., 2005).

\[
\alpha = \frac{m_{oil}}{m_{oil} + m_{water} + m_{surfactant}} \tag{1}
\]

\[
\gamma = \frac{m_{surfactant}}{m_{surfactant} + m_{oil} + m_{water}} \tag{2}
\]

Addition of the reactant i.e. salt like Na$_2$CO$_3$ or CaCl$_2$ into the system gives rise to a certain amount of ionized water in the system. Number of water molecules ionized by the salt depend on the molar salt concentration, msc and can be calculated using equation 3 (Rosenberg and Epstein, 1996).

\[
\text{Ion_{water}} = \frac{\text{No.ofWater Molecule \times msc \times N}}{((1 \text{Litres} \times (1 \text{Kg/Litre})/W_{\text{weight}}) \times N) \tag{3}
\]

where

$N = \text{Avogadro’s number} = 6.023 \times 10^{23} \text{ mol}^{-1}$, $W_{\text{weight}} = \text{Weight of the water molecule} = 18 \text{ kg/kmol}$

$msc = \text{Molar Salt Concentration}$

Hexagonal Lattice

Hexagonal lattice is the least anisotropic compared to all other regular 2D lattices. This characteristic of hexagonal lattice makes simulation more natural. In addition, it reduces the computational cost of simulation as in this lattice only 6 neighbors have to be considered instead of 8 neighbors in square lattice (Figure 3).

Monte Carlo Algorithm

In Monte Carlo method a system changes stochastically. In the proposed quaternary system, a potential rearrangement of the molecules is randomly chosen from the set of allowed rearrangements. The potential rearrangement then either realized or not realized with a probability which is a function of the energy change, $\Delta E$ associated with the potential rearrangement. In the scheme used here, the probability of realizing the rearrangement is 1 if,

\[
\text{Energy}_{\text{new}} < \text{Energy}_{\text{old}}
\]

i.e. $\Delta E < 0 \tag{4}$

where $\Delta E = \text{Energy}_{\text{new}} - \text{Energy}_{\text{old}}$

or

\[
\text{P} > \text{random number}
\]

where $P = \frac{\text{Energy}_{\text{old}} - \text{Energy}_{\text{new}}}{\text{Temperature}} \tag{5}$

Figure 3: Square lattice (left): arrows indicate 8 neighbors of the cell in the middle. Hexagonal lattice (right) of size 5×5; arrows indicate six neighbors of the cell in the middle.
To find the global minimum of the system we utilized the simulated annealing (Kirkpatrick et al., 1983) for optimization. In the annealing process starting at sufficiently high temperature to randomize the molecular configuration, the system is slowly “cooled”. As cooling proceeds, the system becomes more ordered and microstructures spontaneously self-assembled at low temperatures.

**Different Modes of Rearrangement**

Three different modes of rearrangement are used in this system as in (Larson et al., 1985).

**Interchange of position**

The molecules that occupy a single site (water, oil and ionwater) in the lattice can change their position by exchanging position among them. In spite of the distance among them they can exchange position in a single step. The allowed movements for this type of molecules are depicted in the Figure 4.

**Chain Twisting**

The chain of surfactant molecule occupies multiple sites in the lattice. One of the movements of the surfactant chain can be the chain twisting where a unit of the chain can exchange its place with any neighboring sites providing that the chain is not broken in this process (Figure 5).

**Chain Reptation**

The reptation movement is happened when one end unit of a chain exchanges place with any neighboring site and rest of the units occupies the place that formerly occupied by its earlier unit in the chain (Figure 6). This movement will remain valid as long as it fulfils the condition of no chain is broken.

**Interaction Parameters**

Interaction parameters play an important role in the system to have microemulsion regions. The system realization is done in terms of energy and the MC algorithm searches for the global energy minimum. Therefore, higher the interaction parameter between two species of molecules, less likely that the system will try to place them side by side as it will increase the total energy contribution of the system. If proper interaction parameters are not chosen, formation of microemulsion region can not be obtained. In the water-in-oil quaternary system, it is deserved that the water should be surrounded by the surfactant head and the ionwater should be surrounded by water molecule. Thus, in the experiment with the implemented simulation the water-tail or water-oil interaction parameter is kept higher than the water-head or water-water or water-ionwater interaction. For the ionwater, all other interaction parameters are kept higher than ionwater-water or ionwater-ionwater interaction parameter.

**Results and Discussion**

We have already mentioned that the evaluation of the results obtained from the computer simulation will be done by comparing the results obtained with laboratory experiments. For this purpose the results presented in Rauscher et al. (2005b) will be used as gold standard. Therefore, it will be worthwhile to have a brief presentation of their findings.
Laboratory Results

Rauscher et al. (2005b) used water/cyclohexane/Marlipal O13/40 as reaction medium for the precipitation of calcium carbonate (CaCO₃) from sodium carbonate (Na₂CO₃) and calcium chloride (CaCl₂). The primary findings of their experiments are that the dissolved salts cause shrinkage of one-phase region if compared with the system without salts and varying salt concentration has no significant influence on the droplet diameter (for details please see Rauscher et al., 2005b).

Simulation Results

We run the simulation program several times with different combination of parameter values. Phase behavior is observed in the final graphical output. Development of one phase microemulsion can be declared if all the water and ionwater cells are surrounded by the surfactant and there is no free water or ionwater cells in the system. Development of two-phase can be declared if there remains some free water or ionwater in the system. If most of the water and ionwater remains free, it can be declared that no microemulsion region is formed at all. The droplet (water and ion water cells that are completely surrounded by the surfactant) diameters (calculated using boundary fill algorithm) and the droplet diameter density are calculated by the system. We have experimented with all combinations of $\alpha$, $\gamma$ and msc as mentioned in Rauscher et al. (2005) and we found that the simulation program is capable of producing similar phase behavior as reported by Rauscher et al. obtained in laboratory experiments. In Figure 7, snapshot of the initial system generated by the simulation is shown for $\alpha = 0.98$ [kg/kg], $\gamma = 0.15$ [kg/kg], and msc = 0.2mol/l. According to Rauscher et al. (2005b) one phase microemulsion region is expected with these parameters. After the system has been optimized final snapshot of the system is shown in Figure 8, where formation of one phase microemulsion region is evident.

In Figure 9, droplet diameter (obtained from the simulation) as a function of oil weight fraction, $\alpha$ is shown. Droplet diameters are qualitatively consistent with the laboratory result. The size of the droplets has the increasing tendency with the increase in water content. We also observed the effect of the molar salt concentration on the droplet diameter (Figure 10) using simulation and here we also did not find any significant change in droplet size as in (Rauscher et al., 2005b). Observation on the number density of the droplet diameter obtained from simulation also shows the similar behavior as in the laboratory results. In Figure 11 it is evident that the sizes of the droplets found from the simulation are normally distributed which is also the case in laboratory obtained droplet size distribution as reported in (Rauscher et al., 2005b).
Conclusions

A Monte Carlo computer simulation of a quaternary water/reactant/oil/surfactant system is implemented. The influence of the dissolved reactant on the phase behavior and the droplet diameter is studied using this computer simulation. The comparison of the simulation results and the laboratory results assures the proper working of the simulation. Thus, the simulation model developed by us can be utilized for further investigation of the quaternary system as well as the ternary system (by setting the value of msc =0). Though, the 2D MC simulation program implemented by us is capable of providing reasonable results. There are scopes to improve the system further. 3D representation will allow more realistic results and is very straightforward to implement. In the implemented system interaction parameters are obtained by trail and error basis. This process can be automated. To make the simulation program capable of providing more realistic results, second neighbor interaction can be introduced in the system as well.

References


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