

# Study of Winsor I to Winsor II Transitions in a Lattice Model

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Experiments show that with increasing temperature, microemulsion systems undergo Winsor transitions. The transitions occur from Winsor I (oil droplets in water media) to Winsor II (water droplets in oil media) via Winsor III (bicontinuous phase) with an increase in the temperature. In this paper, it has been shown, for the first time, how one can study the qualitative effects of temperature, head, tail, and oil chain lengths, on these transitions. Simple cubic lattice with excluded volume and periodic boundary conditions is used to mimic the box of the simulation as a bulk of solution. The simulations have been done using the standard traditional Metropolis algorithm in the canonical ensemble ( $N, V, T$ ). Configurational bias Monte Carlo and reptation moves are used with an equal probability to relax the systems. A very simple interaction model, i.e., the repulsions of water (or heads of surfactants) with oil (or tails of surfactants), is used due to the main characteristic of oil–water mixtures or amphiphilic molecule that is the hydrophobicity. The interfacial tension between oil and water ( $\gamma_{ow}$ ) is related to the averaged total energy of the lattice. The model shows that the Winsor III has a minimum interfacial tension ( $\gamma_{ow}$ ) similar to experimental results. Changing the phase structure from Winsor III to Winsor I (or Winsor II), increases the interfacial tension which is in agreement with experiments. To relate interfacial tension with the interaction parameter, the simple theory of Bragg–Williams has been used. All of the results such as the effects of oil chain length, head and tail beads number are all similar to the experimental results. Using the Davies method for calculating hydrophilic–lipophilic Balance (HLB), similar to the experimental results, Winsor III phase is formed at HLB value nearly to 10.

## 1. Introduction

The microemulsion systems are used in many industrial and biological processes. They are used as a reactor for chemical reaction to produce nanomaterials, as a catalyst in producing colloidal materials or even in oil-enhanced recovery.<sup>1–3</sup> The phase transition of a microemulsion depends on the different factors including interfacial molecular structure, surfactant structure, surfactant and co-surfactant concentrations, oil and water concentrations, and temperature.<sup>4–6</sup> This subject provokes theoretical, experimental and simulation researchers about studying these systems.<sup>7–13</sup>

Microemulsions are thermodynamically stable dispersions of two immiscible liquids, usually water and oil that stabilized by a surfactant and, in many cases, also a cosurfactant.<sup>7,11</sup> A well-known classification of microemulsions is that of Winsor, who identified four general types of phase equilibria.<sup>14</sup> In Winsor I, the surfactant is preferentially soluble in water, and oil-in-water (o/w) microemulsions are formed. The surfactant-rich water phase coexists with the excess oil phase where surfactant is only present as monomers at small concentration. In Winsor II, the surfactant is mainly in the oil phase, and water-in-oil (w/o) microemulsions are formed. The surfactant-rich oil phase coexists with the surfactant-poor aqueous phase. There are also nondroplet type microemulsions, referred to as middle-phase microemulsions (Winsor III). In Winsor III, a three-phase system is formed where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases. One possible structure of this middle-phase microemulsion, characterized by randomly distributed oil and water microdomains and bicontinuity in both oil and water domains, is known as the bicon-

tinuous microemulsion. Finally, it is possible that a single-phase (isotropic) of droplet type microemulsion is formed upon addition of a sufficient quantity of surfactant plus alcohol. Many experimental investigations have shown that one can get a transition from a two-phase system composed of an oil-in-water droplet-type microemulsion phase to a two-phase system composed of a water-in-oil droplet-type microemulsion phase by passing through a three-phase system containing a bicontinuous microemulsion.

Such phase transitions can occur, by raising the temperature when the surfactant employed is nonionic or by increasing salinity for ionic surfactant systems containing an electrolyte, and by increasing the concentration of alcohol when the surfactant is ionic, nonionic, or zwitterionic. Theoretical studies of microemulsions have focused on various features of the complex systems mentioned.<sup>7,11,12</sup>

Amphiphilic systems have been investigated in many fields of research by various techniques. These systems have been examined experimentally using different approaches such as conductometry,<sup>15</sup> calorimetry,<sup>16</sup> differential scanning calorimetry,<sup>17</sup> small-angle neutron scattering (SANS),<sup>18</sup> spectroscopy,<sup>19</sup> and viscosity measurements.<sup>20</sup> In addition, theoretical studies have been carried out aimed at explaining and predicting the behavior of these complex systems.<sup>21,22</sup> Lattice models have been developed in which each surfactant molecule is treated as connected beads of the lattice. A bead may be water-site-like (H), or oil-site-like (T). Water-like sites have the property of hydrophilicity, and oil-like sites are hydrophobic. The phase behavior of this model can be studied theoretically as has been done in the Flory–Huggins model. In the Flory–Huggins solution model, a wide variety of type of microemulsion phase diagrams is modeled by regressing interaction parameters, which

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depend upon surfactant concentration. A key tool in the theoretical modeling of amphiphilic systems has been molecular simulation. Various simulation strategies have been developed to cope with the enormous range of time scales of the motions within these systems. Four simulation techniques that have proved popular are Monte Carlo, molecular dynamics, Brownian dynamics and time dependent Ginzburg–Landau equations.<sup>23</sup> Monte Carlo and molecular dynamics techniques have been implemented as lattice<sup>24</sup> and off-lattice<sup>25–27</sup> models. Lattice models are simpler and more efficient than off-lattice models because they do not include atomistic details of molecules. Instead of such details, the “molecules” on the lattice are modeled as strings of beads that interact via pre-defined interaction parameters. Therefore, the results of lattice model for these complex systems are only qualitatively.

In this work, using a lattice model, for the first time, it is tried to investigate the role of the interaction parameter on the phase transitions for a microemulsion system from Winsor I to Winsor II. Meanwhile, interfacial tension and average energy of these transitions are also studied using the simple theory of Bragg–Willimas. It is shown how a model containing only repulsive interactions can predict effects of temperature variations on these transitions.

We have considered surfactant molecules as connected beads with two different characteristics. Beads that are like with water have hydrophilic properties and are named as heads (H), and beads that behave like oil are hydrophobic and named as tails (T). In this study we have considered a chain containing  $i$ H and  $j$ T beads ( $H_iT_j$  with  $i, j \geq 1$ ) as a surfactant molecule. Molecules with only tail beads represent the oil molecule. The length of beads in oil molecules in this work ranges from one ( $T_1$ ) to ten ( $T_{10}$ ). Each H-bead, T-bead, and water molecule occupies only one site of the lattice.

## 2. Model

A number of models have been used to simulate amphiphiles in lattice models. One family of models that has been widely used consists of a simple square or cubic lattice with only nearest neighbor interactions. The coordination numbers of these lattices for two and three dimensions are 4 and 6, respectively. In comparison with off-lattice Monte Carlo simulations, lattice techniques have much more approximates such as using pre-defined simple potential model with only nearest neighbor interactions, deleting the details of surfactant molecules and representing these molecules by only two kinds of beads. It has been shown in the literature that it is possible to simulate correctly the behavior of these complex systems qualitatively using these simple models.<sup>28–37</sup>

There are different potential models in the literature for the lattice Monte Carlo works. In some models it is assumed that the repulsive forces are dominate; whereas in other models the attractive forces are dominate. Care and his co-workers<sup>32,33,35</sup> considered repulsive interactions between tail-solvent and head-head but attractive interactions for head-solvent beads. On the other hand, some authors have utilized Larson’s model in which a lattice site is either oil-like (L) or water-like (H).<sup>10,38–41</sup> In Larson’s model the repulsive interactions between unlike beads and attractive interactions between like beads have been considered. It must be noted that introducing additional interaction parameters in the potential model may lead the results to be artificial. We believe that a model is the best one when it can predict different behaviors of surfactant systems, correctly.

In the present work the model is a modified version of Larson’s model with reducing cutoff range of interactions from

$z = 26$  to 6, where  $z$  is coordination number. This kind of potential model have been used by us in different topics of micellization, and we have proved that using this simple version of the lattice model it is possible to simulate the interaction of polymer with micelles, shape transition and cluster-size distribution, correctly.<sup>42–46</sup> In this paper we will test that this simple model can show correctly the Winsor transitions or not. In the model the repulsions between unlike sites are only considered, i.e., tail beads with head beads (T–H) and tail beads with water beads (T–W). In other words, we did not use attractive interactions such as T–T and H–H that have been used in Care or Larson’s model.

Our simulations are based on the standard Metropolis algorithm.<sup>45</sup> we have used reptation in conjunction with configurational bias Monte Carlo moves to translate molecules. Reptation is a snake-slithering like move. Probability of  $P = \min(1, \exp(-\beta\Delta E))$  has been chosen as in the literature for a reptation move. Configurational bias Monte Carlo allows a molecule to be completely translated to improve the acceptance probability. In a configurational bias Monte Carlo move, at first, an amphiphile is chosen at random, and its Rosenbluth weight is calculated. The Rosenbluth weight is computed by counting the number of vacant sites,  $Z_u(i)$ , around the next bead to be removed, that is, the total sites that the old bead could have chosen. The weight of the chain,  $W_{old}$ , is defined as the product of these weights divided by the lattice coordination number  $z$ ; that is,  $W_{old}$  is the probability that the chain can have, if it starts with site  $i$

$$W_{old} = \prod_{i=n-1}^1 \frac{Z_u(i)}{z} \quad (1)$$

where  $n$  is the chain length. To insert the chain back into the cell, a random site is chosen and the chain is grown starting from that site. Because the lattice is completely filled, the sites where the chain is taken from have to be filled by the sites removed during the chain regrowth. The regrowth is done using the configurational bias scheme, and the Rosenbluth weight of the new chain configuration is calculated as in above equation except that now the number of vacant sites is calculated around the bead where the next chain site is to be added. Detail balance is manipulated by using the ratio of the two Rosenbluth weights in the acceptance criterion

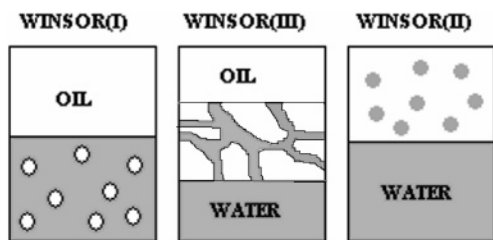
$$P_{acc} = \min\left(1, \frac{W_{new}}{W_{old}} e^{-\beta\Delta E}\right) \quad (2)$$

where  $W_{new}$  is the new Rosenbluth weight,  $\Delta E$  is the energy change in performing the move, and  $P_{acc}$  is the probability of accepting the move.

In the present work, we focus only on the main characteristic of amphiphile molecules, that is, the repulsion between unlike sites (tail–water, oil–water, oil–head or tail–head). So, we used following model:

$$\frac{E}{k_B T} = \frac{\epsilon}{k_B T} (n_{T,w} + n_{T,H}) \quad (3)$$

where  $E$  is the total energy of the configuration,  $k_B$  is the Boltzmann constant,  $n_{T,w}$  is the number of tail–water or oil–water contacts, and  $n_{T,H}$  is tail–head or oil–head contacts which are in the nearest neighbors of each other. In this paper we change the value of  $\epsilon/k_B T$  (interaction parameter) and study the effects of interaction parameter on the microemulsion process.



**Figure 1.** Schematic of Winsor transition from Winsor I to Winsor III to Winsor II with increasing the temperature.

Because increasing or decreasing interaction parameter affects the value of temperature, it is possible to investigate the role of temperature on the phase transition of a microemulsion.

Only nearest neighbors ( $z = 6$ ) is considered and a lattice with dimensions of  $50 \times 50 \times 50$  is used in all of the simulations. Since the reptation move is nonergodic,<sup>46</sup> reptation in conjunction with configurational bias Monte Carlo move is used with equal probabilities.

### 3. Results and Discussion

**3.1. Interfacial Tension.** With an increase in surfactant hydrophobicity, a transition occurs from a two phase system consisting of an o/w microemulsion (Winsor I) via a system comprising a microemulsion coexisting with both oil and water (Winsor III) to a two phase system consisting of w/o microemulsion (Winsor II).<sup>47</sup> This kind of transition has been shown in Figure 1. It has been found that oil–water interfacial tension has a deep minimum in the three phase region (Winsor III); i.e.,  $\gamma_{ow}$  decreases as a system goes from Winsor I to Winsor III and increases as it moves from Winsor III to the Winsor II region. The Winsor transitions can be achieved by raising the temperature for a system based on nonionic surfactant and by increasing salinity for a system based on ionic surfactant.<sup>48</sup> The condition at which the hydrophilic and lipophilic properties of a surfactant are balanced is called the phase inversion temperature.<sup>4,49,50</sup> Temperature is usually the most important variable for the nonionic surfactants.<sup>4–6</sup> For ionic surfactants this state is often referred to as optimal conditions, e.g., optimal salinity.<sup>4,7</sup> At this point there is an equal volumetric solubilization of oil and water in the middle phase microemulsion and the interfacial tensions are at minimum.<sup>51–53</sup>

Using Bragg–Williams theory (as a very simple theory), it is possible to derive an equation that relates interaction parameter to the interfacial tension. In our lattice, there are only two different kinds of sites. Water and head beads of surfactants are the same and can be shown by A in Bragg–Williams theory. Oil and tail beads of surfactants are like to B sites in Bragg–Williams theory. In Bragg–Williams theory the total energy of pure A is  $zN_Aw_{AA}/2$ , where  $z$  is coordination number of lattice,  $N_A$  is number of sites occupied by type A, and  $w_{AA}$  is the interaction parameter between two nearest neighbor sites of A (AA). For pure B the total energy is  $zN_Bw_{BB}/2$ , which is similar to pure A system. The energy for the mixture of A and B can be written as  $E_{AB} = N_{AA}w_{AA} + N_{BB}w_{BB} + N_{AB}w_{AB}$ , where  $E_{AB}$  is the total energy for the mixture of A and B,  $N_{AA}$  is the number of interactions between two nearest neighbor sites both of type A,  $w_{AA}$  is the interaction parameter for these interactions (AA),  $N_{BB}$  is the number of interactions between two nearest neighbor sites both of type B,  $w_{BB}$  is the interaction parameter for these interactions (BB),  $N_{AB}$  is the number of interactions between two nearest neighbor sites one of type A and the other of type B, and  $w_{AB}$  is the interaction parameter for these interactions (AB). According to Bragg–Williams theory, the above number

of interactions can be written as follows:<sup>4</sup>

$$N_{AA} = \frac{z}{2} \frac{N_A^2}{N_A + N_B} \quad (4)$$

$$N_{BB} = \frac{z}{2} \frac{N_B^2}{N_A + N_B} \quad (5)$$

$$N_{AB} = \frac{z}{2} \frac{N_A N_B}{N_A + N_B} \quad (6)$$

The change in internal energy upon mixing becomes

$$\Delta E = E_{AB} - E_{AA} - E_{BB} \quad (7)$$

using above equations and the equations for total energy of pure and mixed systems, we have

$$\Delta E = E_{AB} - E_{AA} - E_{BB} = \frac{zwN_A N_B}{(N_A + N_B)} \quad (8)$$

where  $w = w_{AB} - (w_{AA} + w_{BB})/2$ .<sup>4</sup> In our model we have set  $w_{AA} = w_{BB} = 0$ , so that  $E_{AA} = E_{BB} = 0$ , and

$$\Delta E = E_{AB} = \frac{zwN_A N_B}{(N_A + N_B)} \quad (9)$$

It can be shown that the interfacial tension can be related to the interaction parameter through following equation:<sup>4</sup>

$$\gamma_{AB} = \frac{1}{a} (E^{\text{interface}} - E_A^{\text{bulk}} - E_B^{\text{bulk}}) = \frac{zw}{a} = \frac{m}{a} kT\chi \quad (10)$$

where  $\chi$  is Flory–Huggins parameter and can be related to our interaction parameter through  $\chi = z\epsilon/kT$ .  $m$  is the fraction of nearest neighbors in a plane above of interface plane and  $a$  is the area of interface. On the other hand,  $\chi$  can be related to the total energy of the simulation box, as follows:

$$\chi = \frac{zE}{kT} \left( \frac{N_A + N_B}{N_A N_B} \right) \quad (11)$$

therefore, with replacing  $\chi$  from eq 11 to eq 10, we can write

$$\gamma_{AB} = \frac{mzE}{a} \left( \frac{N_A + N_B}{N_A N_B} \right) \quad (12)$$

So, the interfacial tension is directly proportional to the interaction parameter between molecules or to the antipathy between the two liquids.<sup>4,6</sup> Thus, for a liquid pair with a large antipathy the interfacial tension is large, as for example in the water–alkane system. If the liquid pairs are made more compatible, the interfacial tension will decrease and eventually becomes zero. This occurs at the critical miscibility point. Note that the treatment given here is only approximate since it assumes no mutual solubility of the two liquids and does not take into account any entropic contribution.

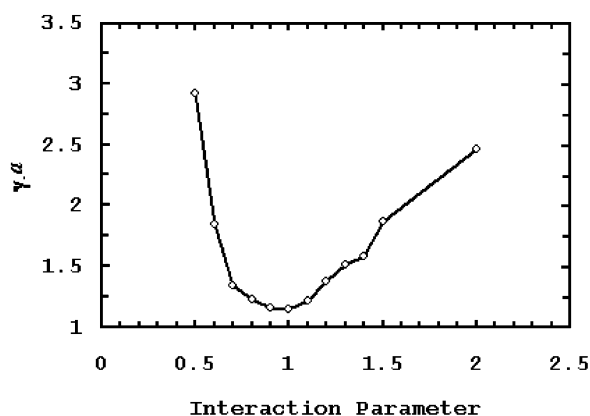
It has been shown in the literature that the relation between the diffusion coefficients of the two solvents in a microemulsion is very different at different temperatures.<sup>54</sup> At low temperatures, water diffusion is close to that of neat water while oil diffusion is strongly reduced and gives evidence for oil confinement into closed domains. At high temperatures, the relative diffusion coefficient is inversed. i.e., the oil diffusion is similar to the



**TABLE 1: Average Total Energy for a System Containing  $T_1$  and  $H_4T_4$  as an Oil and a Surfactant Molecule, with Volume Fractions of 0.2 and 0.02, Respectively<sup>a</sup>**

interaction parameter	averaged total energy
2	34054
1.5	25850
1.2	18979
1	15943
0.9	16016
0.8	16997
0.7	18593
0.6	25719
0.5	40348

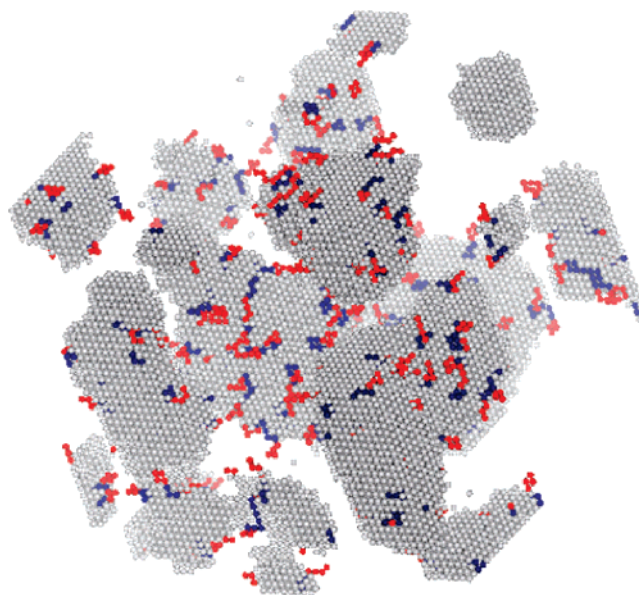
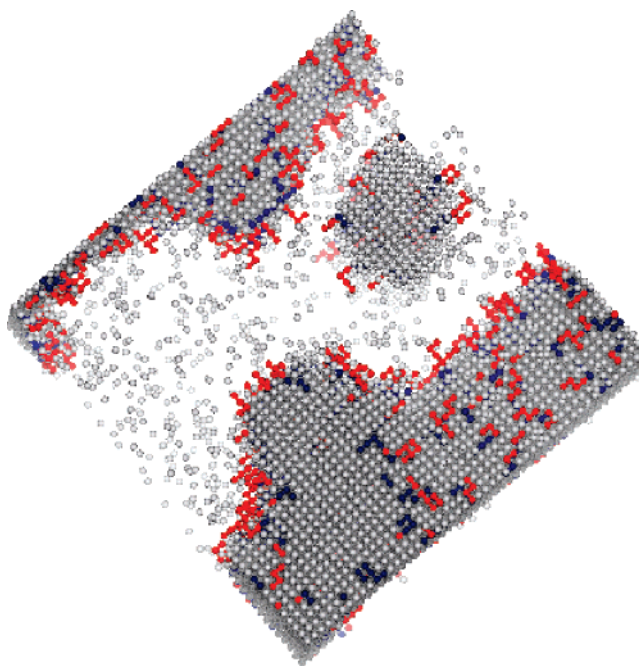
<sup>a</sup> The total energies are related to the interfacial tension according to the eq 12.

**Figure 2.** Product of interfacial tension to area ( $\gamma \times a$ ) vs the interaction parameter ( $\epsilon/k_B T$ ). In this figure we have set  $m = 0.25$ .

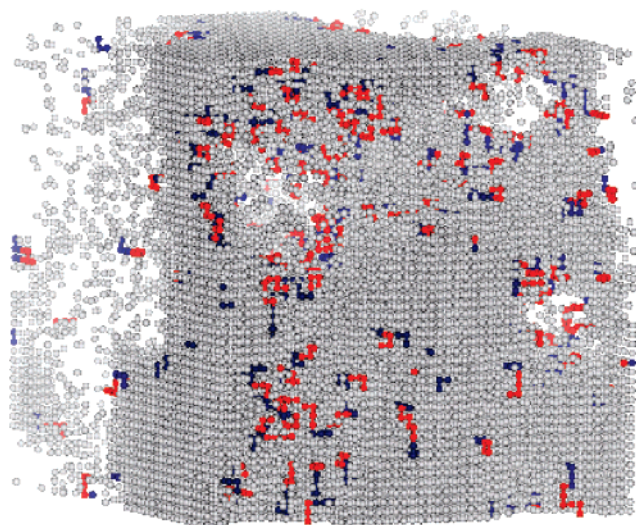
pure oil phase, while water diffusion is much less than that of pure water phase which gives evidence for water confinement into closed domains.

At intermediate temperatures, the relative diffusion coefficients of both solvents are high which gives evidence for a bicontinuous microstructure, i.e., with both oil and water domains being connected over macroscopic distances. The change of diffusion coefficient can be calculated by molecular dynamics simulation. We hope that this subject provoke persons who are professional in MD simulation.

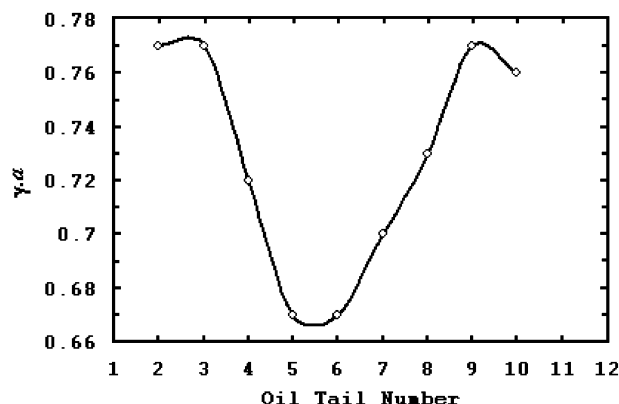
The type of microemulsion system moreover the temperature, depends on the other parameters containing oil to water ratio, surfactant concentration, and the type of surfactant. So, to study the temperature effects, other factors must be constant. To do this, we have used  $H_4T_4$  as a surfactant molecule with volume fraction of 0.02 and  $T_1$  as an oil molecule with volume fraction of 0.2. During the study of the temperature effect, the concentrations of oil and surfactant molecules are constant. Table 1 represents the changes of averaged total energy with the interaction parameter (temperature). Figure 2 shows that the product of interfacial tension to area ( $\gamma_{AB} \times a$ ) versus interaction parameter. Equation 12 shows the relation between the above product and averaged total energy. In eq 12 we have set  $m = 0.25$  according to ref 55.<sup>55</sup> This kind of behavior for interfacial tension has been reported previously, by experimental and theoretical scientist.<sup>4,7,50,51</sup> From this figure, it is found that the interfacial tension changes with changing the interaction parameters (or inverse it, temperature). It can be understood that by a decrease in the interaction parameter (or increase in the temperature), the interfacial tension reduces until it is minimized. So, in the intermediate temperature we have a minimum at the interfacial tension. However, at higher tem-

**Figure 3.** Snapshot of a system with interaction parameter equal to 1.4 (as a low temperature). The shape of aggregates represent Winsor I. The volume fraction of oil ( $T_1$ ) and surfactant ( $H_4T_4$ ) are equal to 0.2 and 0.02, respectively. Gray points are oils; blue points and red points are tails and heads of surfactants, respectively.**Figure 4.** Snapshot of a system with interaction parameter equal to 1 (as an intermediate temperature). The shape of aggregates represent Winsor III. The volume fraction of oil ( $T_1$ ) and surfactant ( $H_4T_4$ ) are equal to 0.2 and 0.02, respectively. Gray points are oils; blue points and red points are tails and heads of surfactants, respectively.

perature, interfacial tension increases with a decrease in the interaction parameter. Figures 3–5 show the results of our simulations for the mixture of surfactant ( $H_4T_4$ ) and oil ( $T_1$ ). Figure 3 shows the behavior for the system at interaction parameter equals to 1.4 as a low temperature. In this temperature oil in water microemulsion (Winsor I) is formed. With increasing the temperature, Winsor III is formed as has been shown in Figure 4. Increasing the temperature, changes the behavior of surfactant molecules to form Winsor II as has been shown in Figure 5. From the above figures it is clear that the curvature of surfactant film (interface) toward the oil (positive curvature)



**Figure 5.** Snapshot of a system with interaction parameter equal to 0.6 (as a high temperature). It can be considered as Winsor II. The volume fraction of oil ( $T_1$ ) and surfactant ( $H_4T_4$ ) are equal to 0.2 and 0.02, respectively. Gray points are oils, and blue and red points are tails and heads of surfactants, respectively.



**Figure 6.** Changing the  $\gamma_{AB} \times a$  parameter with change of oil chain length. The interaction parameter is equal to 0.7, and the volume fraction of oil and surfactant ( $H_4T_4$ ) are equal to 0.4 and 0.02, respectively. These parameters are kept constant for these data.

for Winsor I tends to be nearly zero for bicontinuous or Winsor III and finely changes toward the water for Winsor II at low interaction parameter.

Experimentally, it has been shown that for the nonionic surfactants the interfacial tension has a minimum for specific length of oil molecules.<sup>4</sup> To investigate this subject, some simulations have been done for different oil chains with taking the interaction parameter to be equal to 0.7 and volume fractions of oil and surfactants to be equal to 0.4 and 0.02, respectively. From Figure 6, it is found that the interfacial tensions have different values for different oil chain lengths. From this figure it is clear that for the systems containing oil molecule with 5 and 6 beads ( $T_5$  and  $T_6$ ), the interfacial tension is minimized in comparison with the other oil chain lengths. Although the model is very simple, it can predict the main character of transitions, correctly.

**3.2. Hydrophilic–Lipophilic Balance (HLB).** Various investigators have focused on the interactions occurred in the adsorbed interfacial film to explain the direction and extent of interfacial curvature. The first concept was that of Bancroft.<sup>56</sup> By this rule it is concluded that a phase will be external in which the emulsifier is most soluble. For example, oil-soluble emulsifiers will form w/o microemulsions and water-soluble emulsi-

**TABLE 2: HLB Numbers for Different Surfactants with 8 Beads**

$H_iT_j$	HLB
$H_6T_2$	13.5
$H_5T_3$	11.7
$H_4T_4$	10
$H_3T_5$	8.2
$H_2T_6$	6.4

fiers o/w microemulsions. However this rule is totally qualitative. To quantify this property, Griffin has used the concept of hydrophilic–lipophilic balance (HLB).<sup>57</sup> Using this parameter it is possible to relate between molecular structure, interfacial packing and film curvature. HLB is generally expressed as an empirical equation based on the relative proportions of hydrophobic and hydrophilic groups within the molecule. The concept was first introduced by Griffin who characterized a number of surfactants, and derived an empirical equation for nonionic alkyl polyglycol ethers ( $C_iE_j$ ) based on the surfactant chemical composition:<sup>58</sup>

$$HLB = \frac{1}{5}(E_j \text{wt}\% + OH \text{wt}\%) \quad (13)$$

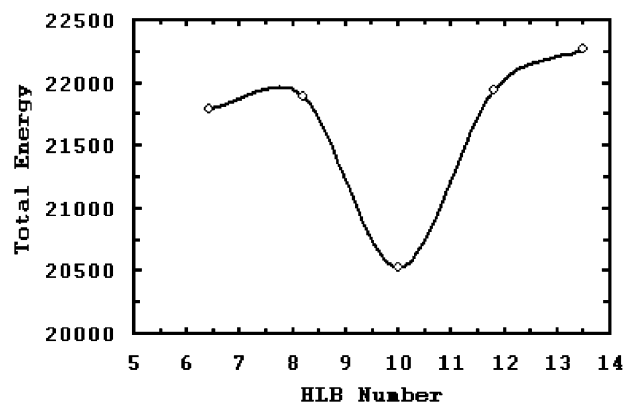
where  $E_j$  wt% and OH wt% are the weight percent of ethylene oxide and hydroxide groups, respectively. Davies et al., proposed a method that using it, it is possible to assign a HLB value to each of chemical segment composing the amphiphile molecule. The equation of Davis is as follows:<sup>59</sup>

$$HLB = [(n_H \times H) - (n_L \times L)] + 7 \quad (14)$$

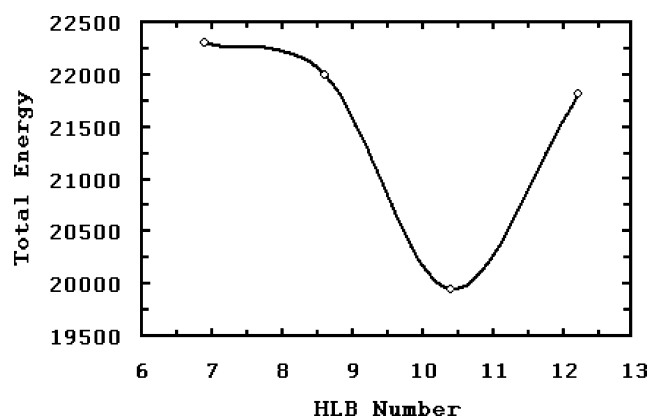
here,  $H$  and  $L$  are constants assigned to hydrophilic and hydrophobic groups, respectively, and  $n_H$  and  $n_L$  are the number of these groups per surfactant molecule. At room temperature, Davies' concept of HLB is useful for the prediction of emulsifier; however problems arise if the temperature changes. Non-ionic surfactants are very sensitive to the temperature changes. Many of them give o/w emulsion at normal temperature, but the emulsion changes to w/o at higher temperature. Such behavior has been seen in our simulation, too. For bicontinuous structures (Winsor III), i.e., zero curvature, it has been shown that  $HLB \approx 10$ .<sup>60</sup> Then w/o microemulsion (Winsor II) is formed when HLB is less than 10, and o/w microemulsion (Winsor I) is stable when HLB is greater than 10. HLB and packing parameter describe the same basic concept, though the latter is more suitable for microemulsions.

The model used here for the presentation of surfactant molecules can be adapted to the real amphiphile molecules of polyoxyethylene referred to as  $C_mEO_n$ . However, at the end of a polyoxyethylene, there is a hydroxide group. In our previous paper, we have described that a polyoxyethylene with formula of  $C_mEO_n$  can be related to the lattice one with the formula of  $H_iT_j$  with considering  $j + 2 = m$  and  $n + 1 = i$ .<sup>61</sup> So,  $H_4T_4$  is equal to  $C_6EO_3$ . According to Davies' HLB numbers for the groups of hydroxide, methylene, and ether, the HLB for  $H_4T_4$  is equal to 9.95 which is nearly to 10. Therefore, for  $H_4T_4$  in comparison to the other lattice amphiphiles with the same total beads of 8 (total beads equals to  $i + j$ ), Winsor III is preferred. It must be noted that this behavior is very sensitive to the temperature. For example,  $H_4T_4$  has minimum energy when the interaction parameter is equal to 0.69. This means that for other interaction parameters it is possible that another lattice amphiphile has minimum energy. The HLB number for different surfactant listed in Table 2, and the total energy for these surfactants also shown in Figure 7. From this figure it is clear





**Figure 7.** Total energy vs HLB numbers. System containing ( $H_4T_4$ ) surfactant with HLB equal to 10 has a minimum energy compare to other surfactants. The interaction parameter is equal to 0.69, and volume fraction of oil ( $T_1$ ) and surfactant are 0.2 and 0.02, respectively, and kept constant during the simulations.



**Figure 8.** Total energy vs HLB numbers. System containing ( $H_4T_3$ ) surfactant with HLB equal to 10 has a minimum energy compare to other surfactants. The interaction parameter is equal to 0.69, and volume fraction of oil ( $T_1$ ) and surfactant are 0.2 and 0.02, respectively, and kept constant during the simulations.

**TABLE 3: HLB Numbers for Different Surfactants with 7 Beads**

$H_iT_j$	HLB
$H_5T_2$	12.2
$H_4T_3$	10.4
$H_3T_4$	8.6
$H_2T_5$	6.9

that the interfacial tension has a minimum (at interaction parameter of 0.69) for  $H_4T_4$  with  $HLB = 9.95$ . Calculating HLB in our model, we can identify which lattice amphiphile is the best choice for Winsor III. For the surfactant with 7 beads, the calculated values of HLB have been listed in Table 3. From Figure 8, it is clear that a system containing  $H_4T_3$  has a HLB equal to 10.4 (Table 3) which represents a minimum energy (or minimum interfacial tension) comparing to the other surfactants with the same total beads.

#### 4. Conclusion

Using simple version of Larson's model of lattice oils and amphiphiles the transition between different microemulsion phases known as Winsor I, Winsor II, and Winsor III are studied. This kind of potential has been used widely in the literature for the study of micellization. Using Bragg–Williams theory an equation has been derived to be used for relating interfacial tension to the interaction parameter. Results show that this

simple model can simulate the behaviors for the Winsor transitions, correctly. Some of the parameters have been studied containing temperature, oil, head, and tail chain lengths effects. Furthermore, HLB is also calculated in a detailed manner.

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