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Simulation of Surfactant-Oil-Solvent Ternary System: Mean Field Theory

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The properties of ternary mixtures of surfactant-oil-water based on the use of the single chain mean-field (SCMF) theory is presented. A new methodology is applied where the chains of surfactant and oil are thrown randomly onto a three-dimensional lattice of size L × L × L. We determine the critical micelle concentrations, density distribution and the cluster size distributions for the H_4T_4 amphiphile and oil molecules, T_x, of length x in a water solvent. A good agreement of the critical micelle concentration values with those of Monte Carlo simulations is obtained.

Key Words: Mean field theory, Amphiphile, Oil, Ternary systems.

INTRODUCTION

There has been an increasing interest, experimentally, theoretically and simulations, in studying the properties of ternary mixture of water, oil and surfactants and developing theories based on statistical thermodynamics to explain the special features of such systems[1,2]. This interest has several sources. First, surfactant systems have potentially significant material properties because they display extraordinarily varied phase diagrams in which lamellar phases, hexagonal arrays of cylinders and complex bicontinous phases compete for stability. The second reason is that these systems serve as models for biological membranes insight into simple amphiphilic mixtures which may help to explain the structural basis of living cells[3,4].

Experimentally, ternary mixtures of oil, water and amphiphile have been intensively studied for the past several years[5]. By using the homologous series of *n*-alkyl polyglycolethers C_iE_j, it has been possible to observe how several properties of these ternary systems evolve as a function of i and j. Kahlweit[6] have summarized an experimental literature survey.

Theoretically, most attempts to elucidate the properties of such systems have been employed phenomenological theories[7-10]. A good historical review of these phenomenological models is presented by Safran *et al.*[11]. A second effort of theories uses a Landau-Ginzburg model, in which the free energy is taken to be a functional of one or more order parameters. The disadvantage of this approach is that the coefficients in the expansion of the free energy are arbitrary and their relationship to real interaction potentials is not evident.

Other attempts used microscopic models are continuous and lattice. In continuous space, Smit *et al.*[12] in his molecular dynamics simulations treat the amphiphlic molecules as short copolymers with hydrophilic and hydrophobic chains connected at the middle. Karaborni *et al.*[13] also studied the oil solubilization in surfactant solutions considering the water molecules as particles that interact *via* a Lennard-Jones potential with a cutoff chosen to be large enough to include excluded volume effects and attractive forces and oil-oil interactions are treated similarly to water-water interactions, while oil-water interactions are modeled using only the repulsive part (excluded volume) of the Lennard-Jones potential. Such simulations provide detailed information about particular state points, but it is difficult to explore a large range of parameter space or qualitative trends because of the length of each calculation.

On the lattice side, once lattice geometry is chosen and the interactions between the three species are specified, the resulting statistical mechanical problem is well defined. These lattice models are summarized by Ben-Shaul *et al.*[14]. The phase behaviour and some properties of micellar aggregates of oil-water-amphiphile systems are also investigated by Monte Carlo simulations[15-19]. Recently, using the histogram-reweighting grand-canonical Monte Carlo method, it has been shown that the CMC decreases linearly as the volume fraction of oil increases and also as the length of the oil chains increases[20].

In mean-field lattice theories, Kim *et al.*[20] used the Single Chain Mean Field (SCMF) theory in a lattice model to calculate the density distribution of oil, water and surfactant as a function of the distance from the center of the micelle. In their SCMF calculations, they forced the first segment of surfactant and oil to be located at the several positions in space. We find that the results are sensitive to the choice of these positions. To eliminate this problem, we adapt our methodology as shown in the previous work[21,22] to throw the first segment of surfactant and oil molecules randomly onto the lattice. Furthermore, we study the effect of oil length and number of oil molecules on the CMC and the cluster size distributions which are not studied by Kim *et al.*[20].

MODELS AND THEORY

Mass action model: For a ternary system of surfactant, water and oil, the size distribution of the aggregates is calculated using the mass action model by considering the micelle and oil floated in water:

$$X_{N_m+m} = \left(X_1^{S/W}\right)^{N_a}\left(X_1^{O/W}\right)^{m} \exp\left[-\frac{1}{k_B T}\left(N_a\left[\mu^{\theta}_{N_a+m,S} - \mu_1^{\theta,S/W}\right] + m\left[\mu^{\theta}_{N_a+m,O} - \mu_1^{O/W}\right]\right)\right] \quad (1)$$

where,

$X_1^{O/W}$	denotes the concentration of free oil in the water phase;
$X_1^{S/W}$	denotes the concentration of free surfactant in the water phase;
X_{N_a+m}	denotes the concentration of an aggregate made up of N_a-surfactant and m-oil molecules;
$\mu_1^{S/W}$	denotes the chemical potential of free surfactant in the water phase;
$\mu_1^{O/W}$	denotes the chemical potential of free oil in the water phase;
$\mu_{N_a+m,S}$	denotes the chemical potential of surfactant in an aggregate made up of N_a-surfactant and m-oil molecules;
$\mu_{N_a+m,O}$	denotes the chemical potential of oil in an aggregate made up of N_a-surfactant and m-oil molecules.

Lattice model: The lattice model proposed by Larson *et al.*[23] is used. A lattice is specified where space is divided into a cubic lattice of sites in three dimensions with a coordination number (number of nearest neighbor sites), equal to 26. In the original Larson model, oil and water molecules occupy single sites, whereas amphiphile molecules occupy chains of connected sites. In this work we consider that oil molecules consist of chains of sites rather than single sites. We refer to these amphiphile molecules as H_xT_y where x and y represent the number of segments in the head-group H and tail T, respectively. In our notation T_x is an oil molecule with x sites and H a single-site water molecule.

Interactions of strength ε_{HH} (ε_{TT}) occur between two head (tail) groups, a head (tail) group and water (oil) monomers and two water (oil) monomers. Interactions of strength ε_{HT} occur between head or water groups and tail or oil groups. With these interactions the whole system can be described by one energy parameter

$$\varepsilon = \varepsilon_{HT} - \frac{1}{2}\varepsilon_{HH} - \frac{1}{2}\varepsilon_{TT} \quad (2)$$

temperature, T, is conveniently normalized by this dimensionless temperature, $T^* = k_BT / \varepsilon$, where k_B is Boltzmann's constant.

Mean field theory: The Hamiltonian of SCMF theory has two parts: one is the intramolecular interactions and the other is the intermolecular interactions (repulsive and attractive). The intramolecular interactions are exactly accounted for in the chain (oil and amphiphile) configurations. The intramolecular interaction per amphiphile chain is given by

$$< E_a^{intra} >= \varepsilon_{TT} < n_{TT}^{intra} >= \varepsilon_{TT}\sum_{\alpha} P_a(\alpha) n_{TT}^{intra}(\alpha) \quad (3)$$

and for the oil chain is given by

$$< E_{O}^{intra} >= \varepsilon_{TT} < n_{OO}^{intra} >= \varepsilon_{TT} \sum_{\gamma} P_{O}(\gamma) n_{TT}^{intra}(\gamma) \qquad (4)$$

where the summations are taken over the set of all possible amphiphile chain conformations α and oil chain conformations γ. $< n_{TT}^{intra} >$ and $< n_{OO}^{intra} >$ are the average number of intramolecular contacts between T-beads and T-beads per amphiphile chain and oil-beads and oil-beads per oil chain, respectively. The brackets < > denotes an average over the probability distribution function, pdf, of chain conformations of amphiphiles $P_a(\alpha)$ and of the oil $P_O(\gamma)$. ε_{TT} is the tail-tail interaction.

The intermolecular repulsive interactions among all the components are taken into > account through the volume-filling constraints. Namely, each segment of an oil, water and amphiphile can occupy only one lattice site (single-occupancy). The volume-filling constraints are given by

$$\phi_s(r) + <\phi_a(r)> + <\phi_O(r)> = 1 \qquad (5)$$

where r is the radial distance from the center of the micelle. $\phi_s(r)$, $<\phi_a(r)>$ and $<\phi_O(r)>$ are the water, amphiphile and oil volume fraction in layer r.

The configurational free energy of the aggregate with the packing constraints eqn. 5 is given by:

$$\beta F = \beta N_a \left[< E_a^{intra} > + < E_a^{inter} >\right] + \beta m \left[< E_O^{intra} > + < E_O^{inter} >\right] - \frac{S}{k_B} - \beta \sum_r n_w(r)\mu_w + \sum_r \pi(r) V(r) \left[\varphi_w(r) + < \varphi_a(r) > + < \varphi_O(r) > - 1\right] \qquad (6)$$

where the fourth term is necessary because the aggregate is considered to be in contact with a bath of pure water with chemical potential μ_w. The fifth term represents the packing constraints and $\pi(r)$ is the Lagrange multiplier.

The minimization of the free energy (eqn. 6) with respect to $P_a(\alpha)$ gives the pdf of the amphiphile chains:

$$P_a(\alpha) = \frac{1}{q_a} \exp\Big\{ -\sum_r \pi(r)\left[n_H(r,\alpha) + n_T(r,\alpha)\right] - \chi_{TT} n_{TT}^{intra}(\alpha) - \frac{\chi_{TT}}{2} \sum_r \frac{N_a}{V(r)} \left[n_{n,T}(r,\alpha) < n_T(r) > + < n_{n,T}(r) > n_T(r,\alpha)\right] - \frac{\chi_{TT}}{2} \sum_r \frac{m}{V(r)} \left[n_{n,T}(r,\alpha) < n_O(r) > + < n_{n,O}(r) > n_T(r,\alpha)\right] \Big\} \qquad (7)$$

where $\chi_{TT} = \beta\varepsilon_{TT}$ is the dimensionless interaction parameter and

$$q_a = \sum_{\alpha} \exp\Big\{ -\sum_r \pi(r)\left[n_H(r,\alpha) + n_T(r,\alpha)\right] - \chi_{TT} n_{TT}^{intra}(\alpha) - \frac{\chi_{TT}}{2} \sum_r \frac{N_a}{V(r)} \left[n_{n,T}(r,\alpha) < n_T(r) > + < n_{n,T}(r) > n_T(r,\alpha)\right] - \frac{\chi_{TT}}{2} \sum_r \frac{m}{V(r)} \left[n_{n,T}(r,\alpha) < n_O(r) > + < n_{n,O}(r) > n_T(r,\alpha)\right] \Big\}$$

From the minimization of the free energy, eqn. 6, with respect to $n_w(r)$, we obtain the water density profile

$$f_w(r) = \exp[-\pi(r) + \beta\mu_s] \qquad (8)$$

RESULTS AND DISCUSSION

The necessary input data that is needed to solve the set of non-linear self-consistent equations are the surfactant and the oil chain conformations, the number of surfactants and the oil chains, shell volume, box volume and the temperature. The outputs are the set of the lateral pressures, $\pi(r)$. With these quantities and the pdfs of the surfactant and oil, any desired average conformational and thermodynamic property of the micellar aggregate can be obtained. Intramolecular interactions of the surfactant and oil were calculated exactly for all the configurations. Once a set of configurations is obtained, the surfactant and oil chain distributions can be counted as a function of the radial distance.

The mixture of surfactant, oil and water molecules is simulated in the $L \times L \times L$ three dimensional lattice base with periodic boundary conditions in the x, y and z directions. L has be taken equal to 19 for all the calculations and 5×10^6 chain configurations were randomly generated on a lattice divided into spherical shells. The same results were obtained when 5×10^7 configurations were used. The lattice contains a symmetric H_4T_4 amphiphile which has four hydrophilic head H beads and four hydrophobic tail T beads, oil molecules Tx with different lengths (x = 1,2) are also present and the remainder of the lattice is filled with water.

Fig. 1 shows the density distribution of the micellar aggregate and oil as a function of the radius containing 66 H_4T_4 amphiphile and 6 oil T_4 chains at $T^* = 8$. Fig. 1(a) represents the results of SCMF theory on comparing with Grand-Canonical Monte Carlo, GCMC, simulations[20]. We find a good agreement between SCMFT and GCMC. As expected most of the adding oil migrates to the core of the micelle, this is clear from the oil distribution which has a maximum value at the center of the micelle and then decreases as we go away from the center towards the interface. We find that the volume fraction of tail amphiphile in the first shell is approximately equal to one for the case where no oil in the system (pure surfactant tail in the core) while the presence of oil in the system makes the volume fraction of tail amphiphile in that shell less than one because the oil component occupies part of that shell as shown in Fig. 1(b).

To calculate the size distribution the standard chemical potential of the aggregate, which consists of surfactant and oil chains, must be known. They are calculated by summing over the set of chain configurations and the different positions.

The size distribution, in three dimensions, of the micellar aggregate of H_4T_4 and oil (T_1) at total mole fraction of surfactant and oil equal to 0.03 and 0.0167, respectively is presented in Fig. 2. The size distribution of an aggregate where used in the previous chapters is modified to account for the presence of oil molecules. Therefore we define the size distribution of

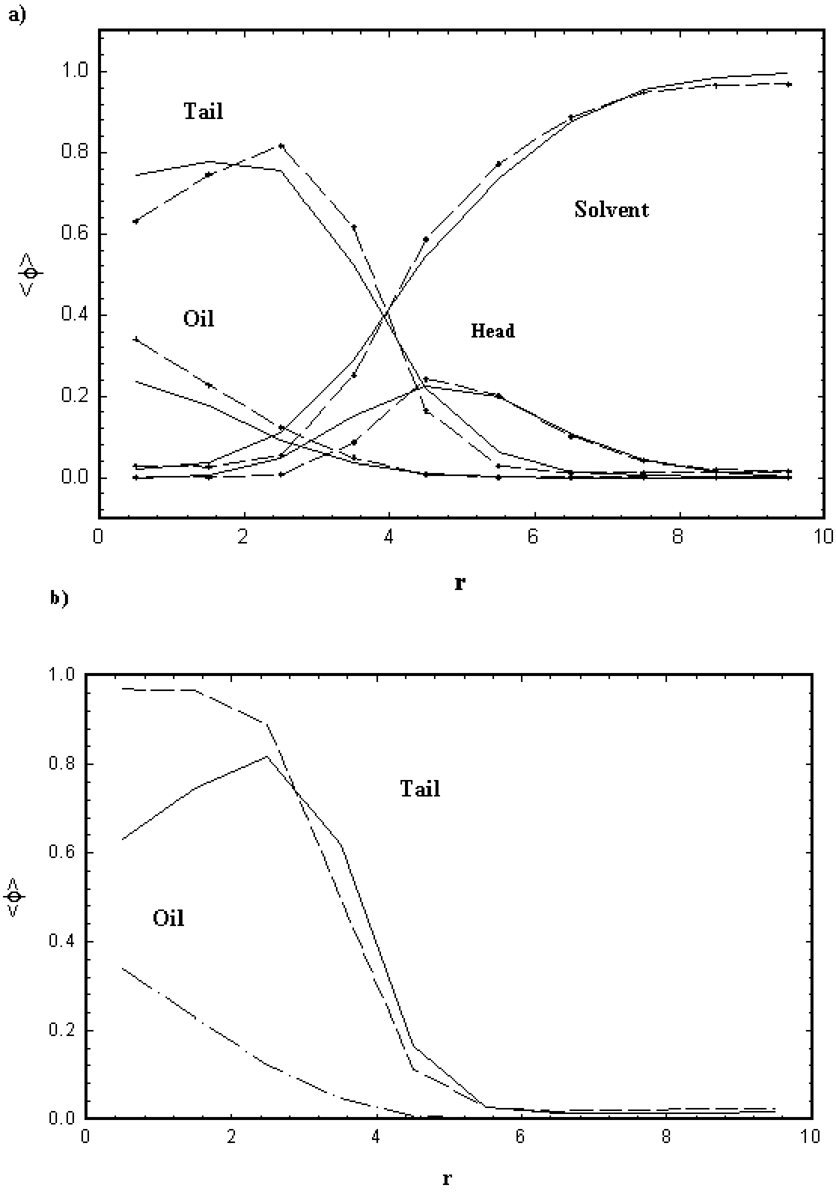

Fig. 1. Average volume fraction, ϕ, of H_4T_4 tail and head sites, oil (T_4) and water as a function of radius, r, through a micellar aggregate consisting of 66 amphiphile chains and 6 oil chains at T* = 8. (a) GCMC results are given by solid lines and SCMF theory is given by long-dashed lines with symbols. (b) Represents the results of SCMF theory. Solid and long-dashed lines refer to amphiphile tails with and without oil in the system respectively. Dashed-dotted line refers to oil molecules

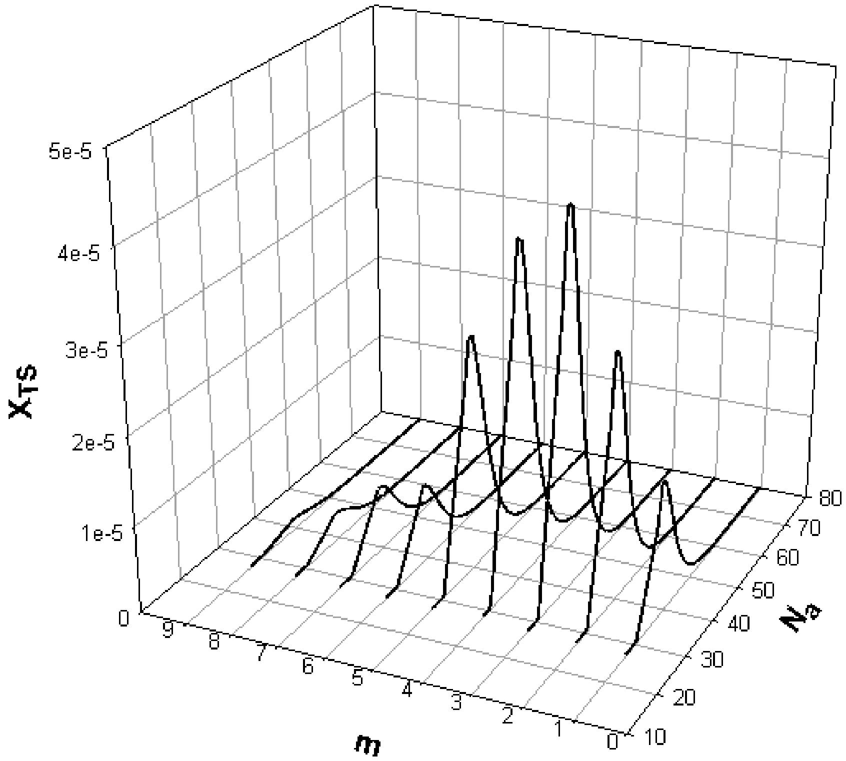

Fig. 2. Cluster size distribution of surfactant, X_{TS}, for spherical H_4T_4 amphiphile and T_1 oil molecules at $T^* = 8$ as a function of the number of surfactant, N_a and number of oil, m. The total mole concentration of surfactant and the oil are equal to 0.03 and 0.01 mol, respectively

an aggregate as a collection of surfactant tails and oil molecules that are touching each other. It is no longer necessary for all the amphiphile tails of an aggregate to touch each other directly, since they may be connected by region of oil molecules. The peak in the distribution shifts to lower surfactant aggregation number as the oil number, m, increases. It can also be noted that the height of the peak increases as m increases up to m equals 3 and then decreases reaching approximately zero height at m equals 9. This behaviour was expected because the free energy of the oil has a minimum around m = 2 to 3 (at fixed amount of the amphiphile, $N_a = 50$, where its free energy has maximum).

We define the critical micellar concentration, CMC or critical micro-emulsion concentration (CμC) as the monomer concentration at which the line of unit slope passing through the origin intersects of free chain volume fraction, ϕ_1, *vs.* total surfactant volume fraction, ϕ_{TS}. The physical meaning of this definition is that it corresponds to the volume fraction at which micelles start appearing in the system. To calculate the CMC at fixed total oil concentration, we calculated the overall volume fraction of surfactant as a function of the free surfactant chain at fixed the total oil concentration. The total oil concentration is maintained fixed by manipulating the free oil chain concentration.

Figs. 3 and 4 show the critical micelle concentration (CMC) or critical microemulsion concentration (CμC) as a function of total oil concentration in the box for oil molecules T1 and T2, respectively. The result in these figures indicates that cmc decreases monotonically with increasing oil concentration. It probably due to the fact that the oil molecules are short beads with no hydrophilic head group attached. This allows the oil beads to move freely through the interior and the surface of the oily core of the micelles. This serves to increase the packing efficiency of the oily core and help smooth and roughness in the surface. A good agreement is obtained comparing with GCMC simulation. We point out that GCMC simulation[20] suggests that the CMC decreases linearly with the total oil concentration while our result decreases non-linearly which is in good qualitatively with experimental results[24].

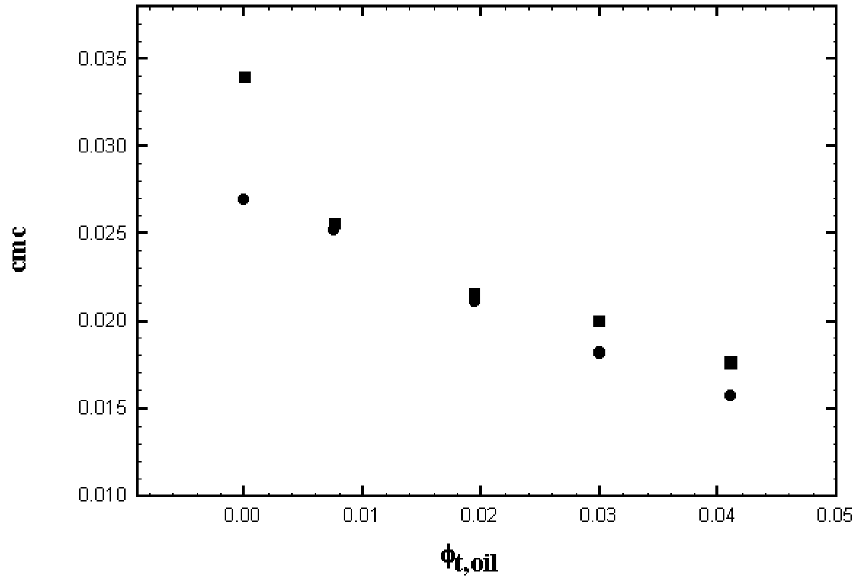

Fig. 3. Critical micelle concentration (CMC) in volume fraction for H_4T_4 amphiphile and T_1 oil molecules as a function of the total oil volume fraction. Filled circles for GCMC and filled squares for SCMF. T* = 8

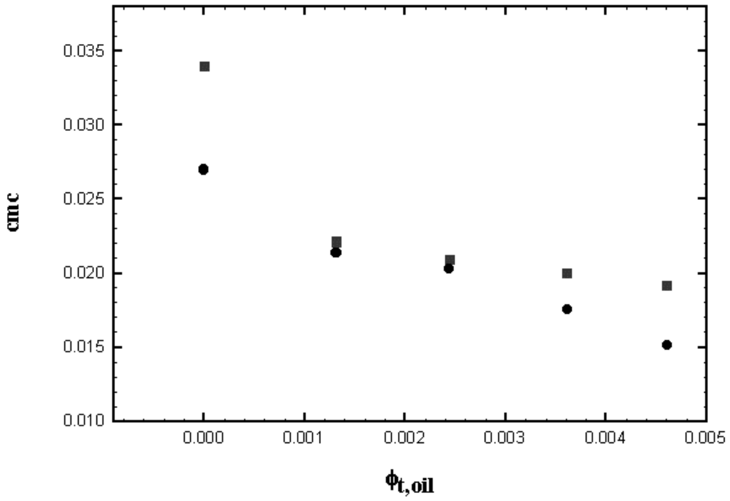

Fig. 4. Critical micelle concentration (CMC) in volume fraction, for H_4T_4 amphiphile and T_2 oil molecules as a function of the total oil volume fraction. Filled circles for GCMC and filled squares for SCMF. T* = 8

We consider the effect of the temperature on the CMC as shown in Fig. 5. It is noted that the CMC increases as the temperature increases. This result is in qualitatively agreement with observations for binary mixtures of surfactant and solvent.

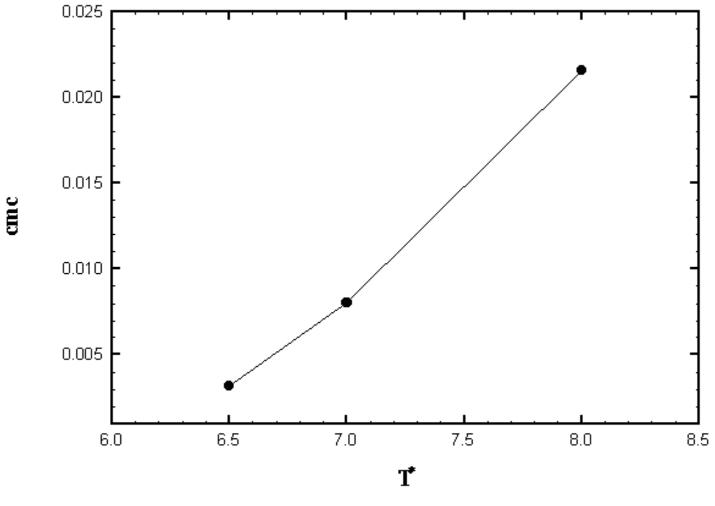

Fig. 5. Critical micelle concentration (CMC) in volume fraction for H_4T_4 amphiphile and T_1 oil molecules as a function of the temperature at the total oil volume fraction equals to 0.01942

Conclusion

In present studies, a SCMF theory have been presented which described the properties of the ternary system of oil-water -surfactant. In the SCMF theory, the aggregate are assumed to be spherical. The mass action model is derived for the ternary system to calculate the cluster size distribution and the critical micelle concentration. The critical micelle concentrations, density distribution and the cluster size distributions have been determined for the H_4T_4 and oil molecules of different length T in a water solvent at a dimensionless temperature scale, T*, equals to 8. The results show that the CMC decrease as the total volume fraction of oil increases. The density distribution indicate that the core of the micelle consist of oil and tail segments of amphiphile. The results indicate that there are no significant difference between SCMF theory calculations and those of the GCMC simulations for the cmc and the density distributions.

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