

Model for water-in-oil microemulsions: Surfactant effects

J.-M. Jin, K. Parbhakar,^{*} and L. H. Dao

*Laboratoire de Recherche sur les Matériaux Avancés, Institut National de la Recherche Scientifique, Énergie et Matériaux,
1650 boulevard Lionel-Boulet, Case Postale 1020, Varennes, Québec, Canada J3X 1S2*

(Received 3 June 1996; revised manuscript received 4 September 1996)

We have simulated, using a Monte Carlo technique, a mixture of oil, water, and surfactant on a two-dimensional square lattice. The computations are performed for water-in-oil microemulsion (i.e., inverse emulsion) where we have explicitly included, besides the interaction energy ϵ between the water (oil) and the head (tail) of surfactant molecules, the molecular length m as a parameter. We find that as ϵ increases, the size of the water droplets decreases due to a reduction in the interfacial energy between water and oil in the presence of surfactant molecules. We further show that the effect of m on the surfactant efficiency in determining the water solubility in oil depends strongly on ϵ . When $|\epsilon|$ is small, the influence of m is strong; however, when $|\epsilon|$ is large, m virtually has no effect in determining the efficiency of the surfactant molecules, which is explained using a simple thermodynamic argument. Finally, the structure of the system is profoundly affected by the surfactant concentration and, most important, when this concentration is high enough the system evolves into a highly ordered lamellarlike structure. [S1063-651X(97)08301-3]

PACS number(s): 82.70.Kj, 64.75.+g, 82.20.Wt, 83.70.Hq

I. INTRODUCTION

When two immiscible fluids are mixed in the presence of a surfactant, one obtains what is commonly known as an emulsion. This metastable system has a wide range of applications in various industrial processes such as paint, oil recovery, road surfacing, cosmetics, pharmaceuticals, food, and medicine [1]. Direct emulsions are formed when oil droplets are dispersed in an aqueous continuous phase, whereas inverse emulsions are made of water droplets in oil. Because of many interesting properties involved in the microemulsion systems, considerable efforts (both experimentally and theoretically) have been devoted to their studies [2–4]. It is well known from experimental observations that oil and water do not mix in the absence of surfactants and the addition of only a very small amount of surfactants can cause water and oil to form an isotropic phase (i.e., microemulsion) where water and oil regions are separated by layers of surfactant molecules. Upon increasing the surfactant concentration, the structure of the system changes from isotropic to ordered phases where many different kinds of arrangement are possible, ranging from lamellar, hexagonal to cubic or other liquid-crystalline phases [4]. A surfactant molecule consists of a hydrophobic tail that prefers to be surrounded by oil environment and a hydrophilic head interacting preferentially with water molecules [5]. Therefore, the surfactant molecules position themselves at the interface between water and oil with their heads pointing to water and their tails to oil, drastically reducing the water-oil interfacial energy, usually by several orders of magnitude [6]. Theoretically, both phenomenological and microscopic (mostly lattice model) approaches have been employed in the studies of microemulsions. The former approach [7–9] calculates the free energy of the system and its dependence on various parameters such

as bending energy and entropy of mixing, while the latter bases its analysis on the Hamiltonian of the system [10–16]. However, because of the complexity of the analysis most of the lattice models usually oversimplify the surfactant molecule by describing it either as a simple molecule (with or without asymmetry) occupying a single lattice site or as a dumbbell, which takes two sites representing, respectively, its head and tail. The only exception in the lattice model is the Monte Carlo (MC) simulation by Larson, Scriven, and Davis [17], which includes the structure of the surfactant molecules in a more sophisticated way in the sense that the length of the surfactant molecule is considered explicitly. However, in regard to interaction energy, their model distinguishes neither between the head of the surfactant and the water molecules nor between the tail of the surfactant and the oil molecules, their analysis giving rise to the aggregates of heads and tails thus considerably reducing the surfactant efficiency in solubilizing water in oil. As it is well known, the head of a surfactant molecule in the real world should have a strong preference for water as compared with their self-interaction, and likewise the tail of a surfactant molecule has a strong preference for oil. Furthermore, the efficiency of surfactant molecules, besides depending on the molecular length, is strongly influenced by the strength of the interaction energy between water and the head of the surfactant molecule as well. In fact, experiments [18,19] have already shown that the efficiency of the nonionic surfactants can be manipulated by adding lyotropic or hydrotropic salts (and presumably by changing the interaction energy between water and surfactant). However, theoretical investigation in these aspects, to the best of our knowledge, has not yet been systematically carried out; therefore, it would be very important if one can tell how these parameters come into play in determining the efficiency of the surfactant molecules.

In this work, we carry out two-dimensional (2D) MC simulations and study the efficiency of the surfactant molecules in terms of their molecular length m and the interaction energy ϵ between their head and water molecule (head-

^{*}Author to whom correspondence should be addressed.
Fax: (514) 929-8102.

water pair). We note here that the interaction energy between the tail of a surfactant and the oil molecule (tail-oil pair) is assumed to be the same as that of head-water pair. As a result, our discussions for the head-water pair also apply to the tail-oil pair. Our model is similar to that of Larson, Scriven, and Davis, where each surfactant molecule occupies multiple lattice sites instead of only one or two sites as in other lattice models, but differs from their model in three aspects. (i) The head of the surfactant molecules has a strong preference for the water environment, i.e., the interaction between the surfactant head and water molecule is considered attractive, while the head-head pair has no interaction at all. (ii) Instead of assuming the same size for water and oil molecules, which is apparently not appropriate, our model does not specify the length of the oil molecule, but considers the oil as a uniform background. (iii) For simplicity, only one site is assigned to the head of each surfactant molecule, whereas m sites are assigned to the tail.

We point out that there are limitations in our 2D MC model when comparing with the real 3D experiments. For example, the phase diagrams will not be the same, as well as the detailed structure of the system being different. However, since our model uses the same thermodynamical analysis (e.g., the free-energy formula and Metropolis algorithm [20]) as in 3D systems, the general conclusions based on our 2D system should, to the first-order approximation, equally apply to the 3D cases.

II. MODEL

The mixture of water, oil, and surfactant molecule is simulated on an $L \times L$ two-dimensional square of unit lattice constant with periodic boundary conditions in the x and y directions; $L=60$ is chosen for most of our calculations, but a few tests are also carried out for $L=100$, giving only minor modifications. Each water molecule occupies one site and each surfactant molecule is assigned $m+1$ sites with its head and tail taking one and m sites, respectively. For a given system containing N_W water and N_S surfactant molecules, the oil molecules (which act as a uniform background) occupy a total of $N_O = N - N_W - N_S(m+1)$ sites, where $N=L^2$ is the total number of sites in the lattice. Only nearest-neighbor interactions are considered and the interaction energy for water-water pair ϵ_{WW} is assumed negative and that for water-oil pair ϵ_{WO} is positive to favor the separation between water and oil, whereas the interaction energy between the surfactant head and water molecule is assumed negative in order to give the head of the surfactant molecules preference for water. The interaction energies of the other pairs, namely, oil-oil, water-tail, oil-head, head-head, head-tail, and tail-tail, are all assumed zero, which is not always true in the real world (we will return to this point later). Each simulation starts with some initial configuration where a certain number of water and surfactant molecules is randomly distributed on the square lattice; then the water and surfactant molecules are randomly selected to make a move subject to steric restriction (i.e., double occupancy of any site is forbidden). Since oil acts as a uniform background water and surfactant molecules can exchange positions with oil in each move. Each water molecule moves at random to one of its four nearest neighbors, whereas each surfactant molecule

moves by reptation [21], in which one of its ends (head or tail) moves randomly to one of its nearest neighbors and the other segments slither one site forward towards that end along its own contour. The probability of such a move, according to the standard Metropolis algorithm [20] depends on the change in energy $\Delta E (=E_f - E_i)$ of the system and is proportional to $\exp(-\Delta E/kT)$, where k is the Boltzmann constant, T is the temperature of the system, and E_i and E_f are the total energy (a summation of the interaction energies of the water-water, water-oil, water-head, and oil-tail pairs) of the system before and after the move. Any attempted move is accepted when the condition $\min[\exp(-\Delta E/kT), 1] \geq \zeta$ is satisfied, where \min stands for taking the minimum of the two quantities and ζ is a random number uniformly distributed between zero and unity. After a large number of moves (about the order of 3×10^8) the system eventually evolves into its equilibrium state where the physical quantities are calculated.

III. RESULTS AND DISCUSSION

The main objective of this work is to study the efficiency of the surfactant molecules in solubilizing water in oil in terms of the interaction energy between the surfactant head and water, as well as the molecular length of the surfactant. Throughout our calculations we fix the interaction energies of water-water and water-oil pairs, i.e., $\gamma_{WW} = \epsilon_{WW}/kT = -3.0$ and $\gamma_{WO} = \epsilon_{WO}/kT = 1.0$, respectively. Since our concern here is in the microemulsion of water in oil (i.e., inverse microemulsion), the concentration ratio between water and oil is chosen to be $c = N_W/N_O = 0.25$ for most of the calculations and for comparison $c = 1.0$ is used in one computation. Our model is general in its formulation and we believe that our results for the inverse microemulsion can be readily applied to direct microemulsions. For a given concentration ratio c between water and oil and a given concentration ratio $k (=N_W/N_S)$ between water and surfactant, the efficiency of the surfactant molecule is reflected in the size of the water droplets, i.e., the smaller the water droplets, the more efficient the surfactant molecule. In order to make a quantitative analysis of the size of water droplets it is useful to focus on the correlation function $G(r)$ [15] of the water molecules, which measures the concentration fluctuations and oscillates with distance r between water molecules with its first minimum r_{\min} roughly measuring the average size of the water droplets. In this study, instead of averaging over all directions, we calculate $G(r)$ by averaging over eight special directions, namely, (10), (01), (-1 0), (0 -1), (1 1), (1 -1), (-1 1), and (-1 -1). The inset in Fig. 1 is a typical example of the dependence of $G(r)$ on r where the first minimum r_{\min} (indicated by an arrow) measures the average size of the water droplets.

A. Effect of interaction energy $\gamma = \epsilon/kT$

The nondimensionalized interaction energy $\gamma (= \epsilon/kT)$ between the water and the surfactant head is an important parameter in influencing the surfactant efficiency; our first calculation is on the dependence of the size of water droplets on γ . Figure 1 shows the variation of the first minimum r_{\min} of the correlation function $G(r)$ with $-\gamma$ (since the interaction between water and the surfactant head is attractive, γ itself is

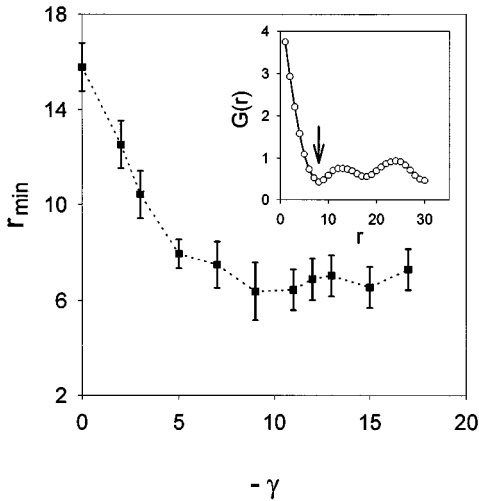


FIG. 1. Variation of the first minimum r_{\min} of the $G(r)$ curve with $-\gamma$, where the error bar is shown as a vertical line at the data point. The parameters used are $c=0.25$, $k=6.5$, and $m=9$. The inset shows an example of the dependence of the correlation function $G(r)$ of water molecules on distance r , where $\gamma=-3.0$ is used and the first minimum r_{\min} is indicated by an arrow. Since the lattice constant in the simulations is unity r and m are normalized.

negative), where each data point (with a vertical line as an error bar) represents an average over several different computer runs with the same physical parameters but different random numbers. It is evident from Fig. 1 that an increase in $-\gamma$ reduces the value of r_{\min} , i.e., the size of the water droplets decreases with the strength of the interaction energy between water and the surfactant head. As pointed out earlier, water and oil do not mix, i.e., water intends to separate from oil so as to reduce the interfacial energy of the system in the absence of surfactant molecules since the interaction energy between water and oil is positive. With the addition of surfactant molecules, because the interaction energy between water and the surfactant head is negative, the surfactant molecules preferentially position themselves at the water-oil interface with their head pointing to water and the tail to oil. The corresponding change in the interfacial free energy can be written as $\Delta F = \Delta E_I - T\Delta S$, where ΔE_I (negative, since the surfactant molecules reduce the interfacial energy) is the change in interfacial energy, ΔS (positive) is the change in interfacial entropy, and T is the temperature of the system. Therefore, ΔF is negative, in other words, the incorporation of the surfactants reduces the interfacial free energy F , with a larger value of $-\gamma$ giving rise to a larger decrease in F . As a result, the water-oil interface can be readily generated by thermal fluctuations, with a larger value of $-\gamma$ giving rise to a larger water-oil interface and therefore a smaller size of water droplets (note that the total volume of water is fixed here). It is also observed that when $-\gamma$ increases further, r_{\min} does not decrease much, but reaches a constant value due to the fact that for a given system the number of surfactant molecules is fixed, therefore the size of the water droplets can only be reduced to some critical value. As a rough estimate, since the ratio k between water and surfactant is equal to 6.5, the smallest water droplet (each surrounded by only one surfactant molecule) contains about 6 water molecules, resulting in a value of $r_{\min}=2.7$ if the

water droplet is a rectangle [since the number of molecules along the (10) direction is 2.5 (an average of 2 and 3) and 2 along the (11) direction, then the average size of the droplet is $(2.5+2\times 2^{1/2})/2=2.7$, with the factor of root 2 being the intermolecule distance along the (11) direction], which is smaller than the corresponding value of $r_{\min}=6.5$ as determined from the $G(r)$ curve, indicating that each droplet must be surrounded by more than one surfactant molecule. The dependence of the size of the water droplets on $-\gamma$ is also clearly seen from the final configuration of the system, as shown in Fig. 2, where $m=1$ for (a) and (b) and $m=9$ for (c) and (d). A comparison between (a) and (b) [or between (c) and (d)] shows that a smaller value of $-\gamma$ (note again that γ itself is negative) gives rise to bigger water droplets because the surfactant efficiency decreases with the decreasing of $-\gamma$, in accordance with the observations in Fig. 1. It is also noted from Fig. 2(b) that the water droplets are prolonged along the (10) direction with the surfactant molecules sitting at their boundaries, resembling a lamellarlike structure that will become clearer later when the concentration of the surfactant is further increased.

As pointed out earlier, we consider only a few parameters, such as water-water, water-oil, head-water, and tail-oil pairs, in the multidimensional interaction space, while the interaction energies of other pairs are assumed zero. However, our model can be readily extended to more general situations where all the interaction pairs have nonzero energy. For example, a repulsive interaction for head-oil pair should, while keeping other conditions the same, enhance the surfactant efficiency by driving the surfactant head away from oil. An attractive interaction for the head-head pair, on the other hand, would reduce the surfactant efficiency by forming head aggregates, as is the case in Larson, Scriven, and Davis's model.

B. Effect of molecular length m

The effect of the molecular length on the surfactant efficiency is shown in Fig. 3, where the first minimum r_{\min} of the correlation function $G(r)$ is drawn against the molecular length for $\gamma=-2.0$ (open symbols) and -5.0 (filled symbols), respectively, keeping the other parameters constant. In the case of $\gamma=-2.0$, r_{\min} decreases with m , i.e., the length of the surfactant molecules increases their efficiency; while for $\gamma=-5.0$, r_{\min} remains almost the same as m varies, indicating that the length of the surfactant molecules does not change their efficiency when the interaction energy between water and the surfactant head is strong. This observation suggests that there is a strong correlation between the molecular length and the interaction energy in affecting the surfactant efficiency. As discussed in Sec. III A, the surfactant molecules modify the water-oil interface and reduce the interfacial free energy F by an amount of $\Delta F = \Delta E_I - T\Delta S$. When the interaction energy between water and the surfactant head is weak, e.g., $\gamma=-2.0$, the absolute value of ΔE_I is small and the entropy term $T\Delta S$ dominates the change in the interfacial free energy ΔF . Since longer surfactant molecules give rise to a larger value of the entropy term $T\Delta S$ and therefore a lower value of the interfacial free energy F , the water-oil interface can be more easily created by thermal fluctuations. Thus the size of the water droplets decreases,

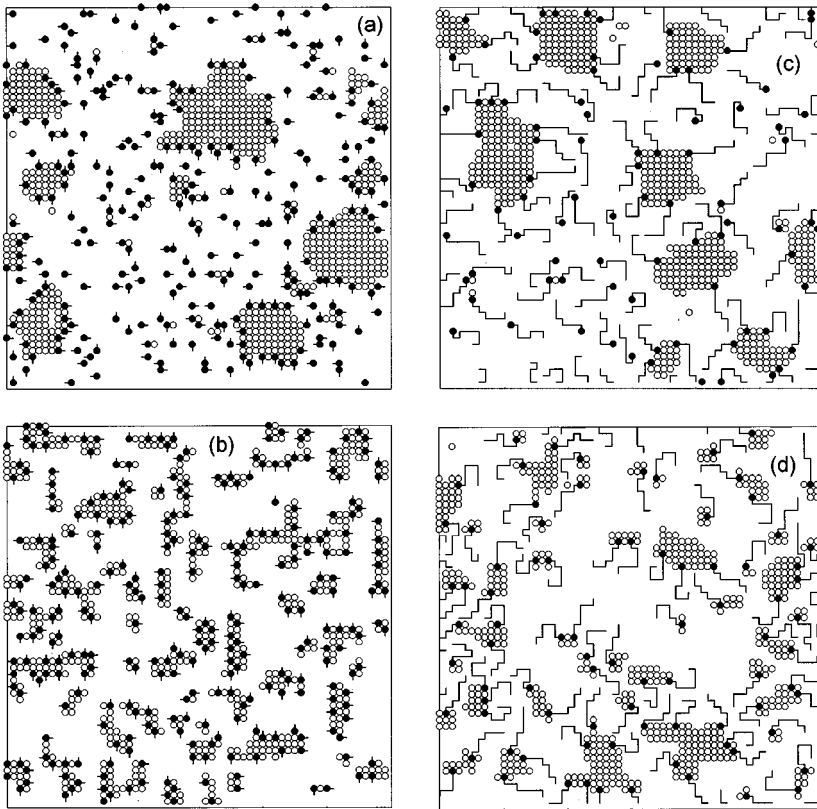


FIG. 2. Morphology of the water, oil, and surfactant system (open circle represents the water molecule, the solid circle and the short solid lines are the head and tail of the surfactant molecule, and the white background represents oil environment) with (a) and (b) $m=1$ and $k=2.0$ and (c) and (d) $m=9$ and $k=6.5$. Other parameters are (a) and (c) $c=0.25$ and $\gamma=-3.0$ and (b) and (d) $c=0.25$ and $\gamma=-7.0$.

i.e., the total area of the water-oil interface increases, with the increase of the molecular length. On the other hand, when the interaction is strong, e.g., $\gamma=-5.0$, the absolute value of ΔE_I becomes large and is dominant in determining the change in the interfacial free energy ΔF , which is therefore virtually independent of the molecular length; as a result, the size of the water droplets is independent of m . We recall that in their experiments Kahlweit, Strey, and Firman [19] observed a very rapid increase of the surfactant efficiency with the molecular length, indicating a much stronger correlation between the two than that in Fig. 3. In view of the above observation, we believe that the interaction between the water and the surfactant head in Kahlweit, Strey, and Firman's experiments must be very weak. In contrast, the lengthening of the surfactant molecule does not improve its efficiency in Larson, Scriven, and Davis's model because the head-head and head-water pairs have the same interaction energy (likewise, tail-tail and tail-oil pairs have the same energy); heads (and tails) clump together inhibiting the surfactant efficiency and the longer the molecule, the more severe the clumping.

C. Effect of surfactant concentration

Finally, since the surfactant concentration is another important parameter in determining the surfactant efficiency, we now present the corresponding results in Fig. 4, which shows the variation of r_{\min} with k for $m=4$. It is observed that the increase in r_{\min} with k is quite rapid when k is small ($k < 20$), but slows down as k increases further. Thermodynamically, as already discussed in Secs. III A and III B, the overall effect of the surfactant is to lower the interfacial free energy F in direct proportion to the concentration of the

surfactant molecules. When k is very large (i.e., the surfactant concentration is very small), water and oil are completely separated, resulting in big water droplets (therefore a large value of r_{\min}) since water and oil are immiscible; as k decreases (i.e., the surfactant concentration increases), the average size of the water droplets (and r_{\min}) decreases. The slow variation of r_{\min} with k for large k indicates that the water droplet size barely changes when the surfactant concentration is too low. The rapid change in r_{\min} takes place only when k is below some critical value (about $k=20$), which may be regarded as a transition point in the phase diagram dividing the region of two-phase coexistence of wa-

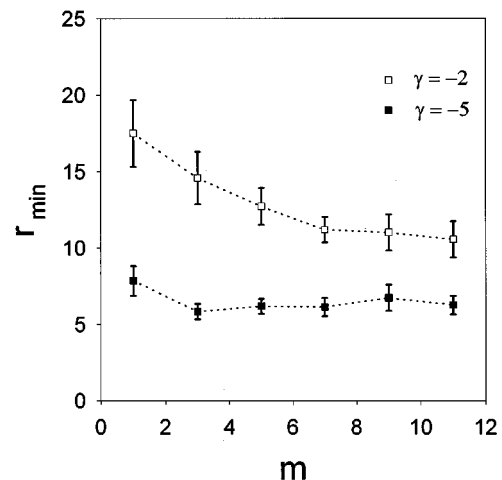


FIG. 3. Variation of r_{\min} with molecular length m , where the open and filled symbols are the data for $\gamma=-2.0$ and -5.0 , respectively, and the other parameters are $c=0.25$ and $k=4.0$.

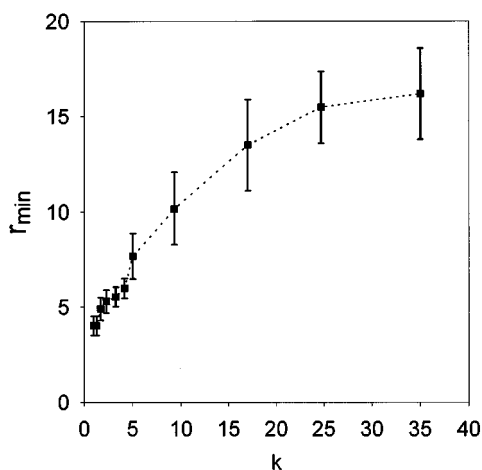


FIG. 4. Dependence of r_{\min} on the concentration ratio k between water and surfactant molecules with $c=0.25$, $m=4$, and $\gamma=-5.0$.

ter and oil from the microemulsion phase where very small water droplets are uniformly distributed in oil. In order to see how the above observation changes with the concentration ratio c between water and oil, we raise this ratio from $c=0.25$ to 1.0, i.e., the system consists of the same amount of water and oil and is said to be balanced. The main observation is the same as in Fig. 4, i.e., the size of the water droplets decreases with the decrease of the value of k (i.e., with the increase of the surfactant concentration). One also observes from Fig. 5 that the system evolves into a highly ordered lamellarlike structure when k is sufficiently reduced, which agrees with experiments and further suggests that our model, despite its simplicity, preserves the essentials of the complex water-in-oil microemulsion system.

IV. CONCLUSION

The influence of the surfactant molecules on the solubilization of water in oil has been systematically studied using Monte Carlo simulation techniques, in terms of the mutual interaction energy between the water and the surfactant head, the molecular length and the concentration of the surfactants.

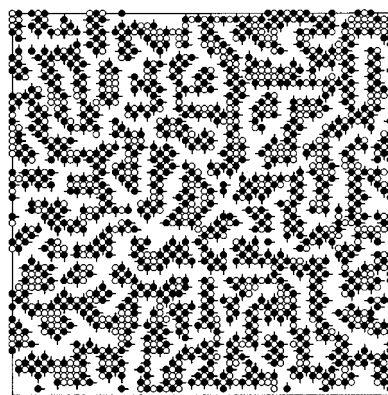


FIG. 5. Morphology of the system with $c=1.0$, $k=1.0$, $m=1$, and $\gamma=-5.0$. Other conventions are the same as in Fig. 2.

It is found that the interaction between the water and the surfactant head greatly reduces the water-oil interfacial energy, thereby increasing their mutual solubility. The influence of the molecular length is not clear-cut, but is strongly correlated with the water-head interaction. When the interaction is weak, the size of the water droplets decreases with an increase in molecular length, thereby influencing the solubility of water in oil. This behavior is due to the fact that in the expression for the interfacial free energy the entropy term $T\Delta S$, which is proportional to the molecular length, dominates. On the other hand, when the interaction is strong the interfacial free energy is independent of the molecular length, hence the solubility is not affected. As for the effect of the surfactant concentration, it is observed that the solubility of water in oil is enhanced by the increase of the surfactant concentration and the system eventually evolves into a lamellarlike structure for large values.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada. J.-M.J. would like to thank Institut National de la Recherche Scientifique for financial support.

-
- [1] P. Becher, *Emulsions: Theory and Practice* (Reinhold, New York, 1965).
- [2] K. A. Dawson, in *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution*, edited by S.-H. Chen *et al.* (Kluwer Academic, Dordrecht, 1992).
- [3] M. Kahlweit and R. Strey, *Angew. Chem. Int. Ed. Engl.* **24**, 654 (1985).
- [4] H. T. Davis, J. F. Bodet, L. E. Scriven, and W. G. Miller, in *Physics of Amphiphilic Layers*, edited by J. Meunier, D. Langevin, and N. Boccaro (Springer-Verlag, Berlin, 1987).
- [5] M. Bourrel and R. S. Schechter, *Microemulsions and Related Systems* (Dekker, New York, 1988).
- [6] A. Pouchelon, J. Meunier, D. Langevin, D. Chatenay, and A. M. Cazabat, *Chem. Phys. Lett.* **76**, 277 (1980).
- [7] D. Andelman, M. E. Cates, D. Roux, and S. A. Safran, *J. Chem. Phys.* **87**, 7229 (1987).
- [8] D. A. Huse and S. Leibler, *J. Phys. (Paris)* **49**, 605 (1988).
- [9] H. Kleinert, *J. Chem. Phys.* **84**, 964 (1986).
- [10] G. Gompper and M. Schick, *Phys. Rev. B* **41**, 9148 (1990).
- [11] M. G. Barbosa and M. Frichebruder, *Phys. Rev. E* **51**, 4690 (1995).
- [12] J. C. Wheeler and B. Widom, *J. Am. Chem. Soc.* **90**, 3064 (1968); B. Widom, *J. Chem. Phys.* **84**, 6943 (1986); K. A. Dawson, M. D. Lipkin, and B. Widom, *ibid.* **88**, 5149 (1988); J. R. Gunn and K. A. Dawson, *ibid.* **96**, 3152 (1992).
- [13] A. Ciach, J. S. Hoye, and G. Stell, *J. Chem. Phys.* **90**, 1214 (1989).
- [14] M. Laradji, H. Guo, M. Grant, and M. J. Zuckermann, *Phys. Rev. A* **44**, 8184 (1991).

- [15] F. Schmid and M. Schick, *Phys. Rev. E* **49**, 494 (1994).
- [16] Y. Hu and J. Prausnitz, *AIChE J.* **34**, 814 (1988).
- [17] R. G. Larson, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.* **83**, 2411 (1985).
- [18] M. Kahlweit, R. Strey, and D. Haase, *J. Phys. Chem.* **89**, 163 (1985).
- [19] M. Kahlweit, R. Strey, and P. Firman, *J. Phys. Chem.* **90**, 671 (1986).
- [20] N. Metropolis, A. N. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
- [21] P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971); F. T. Wall and F. Mandel, *ibid.* **63**, 4592 (1975); A. Baumgartner, *ibid.* **81**, 484 (1984); A. Baumgartner and D. W. Heermann, *Polymer* **27**, 1777 (1986).