Phase Behavior of Model Surfactants in the Presence of Hybrid Particles

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ABSTRACT

Lattice Monte Carlo simulations have been performed to study the equilibrium phase behavior of model amphiphilic solutions in the presence of hybrid organic-inorganic particles. According to the nature of the particles and the surfactant concentration, these systems are able to phase separate into a dilute phase containing a high solvent content, and a concentrated phase containing mainly the surfactant and hybrid particles. In some cases, the concentrated phase shows the presence of structured liquid crystal phases, such as hexagonally-ordered cylinders or lamellae. The solubility in the solvent, and the nature of the

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organic group belonging to the hybrid particles, are key aspects affecting the driving force for the phase separation, and hence the concentration of surfactant in the phases at equilibrium. Biphasic regions have also been generally detected by applying the quasi-chemical theory, which employs a lattice-based mean field approximation. Good quantitative agreement with the results obtained from the simulations was typically found, especially when no self-assembly into ordered aggregates was observed.

KEYWORDS Monte Carlo simulations, amphiphilic solutions, phase separation, hybrid particles, quasi-chemical theory

1. INTRODUCTION

Above the critical micelle concentration (*cmc*), surfactants are able to form micelles of different shapes and sizes¹. When the *cmc* is reached, the concentration of free monomers in the solution becomes saturated, and the concentration of the aggregates starts to increase². In this work we study what happens if we keep on increasing the surfactant concentration well beyond the *cmc* in the presence of hybrid particles, and to what extent can we increase such a concentration before some macroscopic change becomes evident.

We try to address these issues by presenting the results of lattice Monte Carlo (MC) simulations and quasi-chemical theory (QCT) performed in ternary amphiphilic systems, with particular attention to the equilibrium phase diagrams obtained by using different hybrid particles. In particular, we analyzed the phase behavior of systems formed by a diblock surfactant, different types of hybrid organic-inorganic particles, and a simple model solvent.

The peculiarity of the system chosen is that the inorganic segment of the particle has favorable interactions with the solvophilic segments of the surfactant, similar to what is expected in systems containing surfactants and inorganic oxide particles.

Lattice MC simulations have been extensively applied to study the phase separation and the formation of self-assembled structures in binary surfactant/water systems³ and ternary surfactant/water/oil systems⁴⁻⁶. In these works, amphiphilic systems containing symmetric or asymmetric linear surfactants have been studied to understand how the *cmc* or the phase separation could be affected by a change of the surfactant architecture and/or the temperature. Al-Anber et al.⁷ studied the transition from spherical to cylindrical micelles in solutions of non-ionic surfactants by applying grand-canonical MC simulations and singlechain mean field theory⁸. They showed that the second *cmc*, representing the transition between spherical and cylindrical micelles, increases with increasing the temperature and decreasing the surfactant tail length. Some studies have also considered self-assembly and phase behavior in compressible solvents, such as supercritical carbon dioxide, where the formation of spherical or elongated micelles depends on the surfactant concentration and solvent density⁹.

Off-lattice MC simulations at higher surfactant concentrations have been performed in two dimensions by Bhattacharya and Mahanti¹⁰. They observed the formation of bilayers, and also extended their analysis to ionic surfactants in the presence of host particles, being added to the solution along with the surfactants or once the micelles were formed. A qualitative understanding of the position of these particles around the micelles was obtained. Phase separation in three dimensional amphiphilic systems containing pure inorganic particles has

been analyzed by Siperstein and Gubbins¹¹ who applied a coarse-grained model⁵ to simulate the phase and aggregation behavior of a symmetric diblock surfactant in a solvent containing a pure inorganic particle, modeled according to its partial or complete solubility in the solvent. They found hexagonal and lamellar structures at surfactant volume fractions between 50% and 60%, and between 70% and 75%, respectively. Bhattacharya and Gubbins¹² used the same model to study ternary and quaternary amphiphilic solutions of triblock surfactants containing a soluble inorganic particle. The systems with four components also contained a model oil. The ternary surfactant/inorganic particle/solvent phase diagram showed cylinders in equilibrium with the dilute phase at a surfactant concentration of 60% by volume. The pure inorganic particles modeled in such works were represented by single beads interacting very favorably with the surfactant solvophilic heads, and thus creating the conditions for a phase separation. When no specific strong interaction is observed between the surfactant head and one of the segments in an hybrid particle, the system becomes similar to a solution containing a surfactant and a cosurfactant or cosolvent ¹³.

In this work, we modeled different pure inorganic and hybrid particles in order to understand how their presence affects the equilibrium phase behavior of the amphiphilic solutions considered. The particles are characterized by: the miscibility with the solvent, the presence of an organic group, and the ratio between the number of its organic and inorganic beads. In particular, this ratio is 0 for a pure inorganic particle, 0.5 for a bridging hybrid particle containing an organic group between two inorganic groups, and 1 for a terminal hybrid particle containing an organic and an inorganic group. Our aim is to explain how the driving

force for the phase separation, and, indirectly, the possibility to observe liquid crystals in the surfactant-rich phase, can be modified by changing the nature of the particles.

Inorganic and terminal or bridging hybrid particles have been largely used as precursors in the template synthesis of ordered mesoporous materials, such as MCM-41¹⁴ or SBA-15¹⁵, obtained by removing the organic template from the hybrid liquid crystal phase. It is known that the synthesis and functionalization of these materials are strongly affected by the characteristics of the precursor used¹⁶. At low surfactant concentrations, the formation of ordered liquid crystals is the result of a phase separation between a solvent-rich phase and a dense phase, mainly formed by the template and precursor. Only if the surfactant concentration in the dense phase is sufficiently high, can ordered mesoporous structures be eventually observed, and this strongly depends on the properties of the precursors. Therefore, a study of how the nature of the hybrid particles affects the phase behavior of such amphiphilic systems is of fundamental importance to know when and if ordered structures can be synthesized. The aforementioned features, namely the solubility in the solvent, the solvophilicity, and the ratio between organic and inorganic groups in the particle, determine the driving force for the phase separation and the presence of an ordered or disordered structure.

Lattice MC simulations have been used to make the system evolve from an initial arrangement in which the three components are randomly mixed to typical equilibrium configurations. Depending on the nature of the model particles and on the surfactant concentration, it was possible to observe the formation of hexagonally ordered cylinders, whose structural properties have been analyzed in a previous work¹⁷, and lamellae. The

equilibrium data obtained by performing MC simulations with different hybrid precursors have been organized in ternary phase diagrams at constant temperature. The ternary phase diagrams represent a very useful tool to get a first indicative idea about the possibility to observe liquid crystal phases in the surfactant-rich phase. A biphasic region was generally observed where a concentrated phase at high content of hybrid particle and surfactant was at equilibrium with a dilute solvent-rich phase¹⁸.

The phase diagrams obtained from MC simulations were compared to ones calculated with a lattice based mean field approximation, the QCT¹⁹. This theory was previously applied by other researchers in similar, although with fewer interaction parameters, amphiphilic systems to compare with the results of their simulations^{4,20-22}. In these works, the phase behavior in different model amphiphilic systems was investigated and a very good agreement between theory and simulations was observed except when self-assembled aggregates were formed, since QCT does not distinguish between ordered and disordered phases.

This theory presents a better treatment for the configurational energy than the one assumed by the regular solution theory, by allowing a non-random distribution of pairs of particles²³. In regular solution theory, despite the fact that the energy of mixing is not zero, the particles are considered to be completely independent from each other²³. Guggenheim separated the regular solutions from the strictly regular solutions, in which the energies of interaction between pairs of particles are no longer independent of their positions¹⁹, and the excess entropy of mixing, although not zero, is very small²³. The QCT is an approximation for the strictly regular solutions, assuming the independence of pairs of particles. It has also been

defined as first approximation, in contrast to the zeroth approximation, which postulates a complete random organization of the particles.

A complete random distribution of particles in a system where the configurational energy is not zero, can be a physically reasonable assumption at very high temperatures, or when the components in the system show a similar behavior with the solvent. In our systems, the temperature is always below the critical point, and the surfactant and the hybrid particles have quite different properties. Therefore, the effect of non-randomness becomes an important factor that needs to be taken into account.

The model used here aims to reproduce the general features of the phase behavior of hybrid amphiphilic systems, by considering only the most important variables without including those complex details which can determine fundamental differences between one real system and another. Therefore, it would be very hard to perform a quantitative comparison between the phase diagrams obtained in this work and the phase diagrams calculated experimentally. Nevertheless, we can still say that our results are in qualitative agreement with the experimental evidence of the formation of surfactant-silica liquid crystal phases obtained by the phase separation between a solvent-rich phase and a surfactant-silica-rich phase²⁴⁻²⁶.

The structure of the paper is as follows. First, we present the general features of the lattice model introduced by Larson⁵ to study similar amphiphilic systems, and the methodology applied in this work to perform MC simulations. A brief introduction to the QCT is reported in section 4. In section 5, the ternary phase diagrams for the systems with pure inorganic particles and hybrid organic-inorganic particles are presented and compared on the basis of the driving forces leading to the phase separation. The phase diagrams obtained from the MC simulations

are compared with the phase diagrams obtained with the QCT, and a quantitative analysis of the agreement observed is given in section 6. In section 7, the conclusions of this work are given.

2. MODEL

The model used in this work was proposed by Larson⁵ in 1985 to study an amphiphile-oilwater system in two dimensions, which was later extended to three dimensions by the same researcher²². The system is restricted to a cubic lattice allowing bonds and interactions between any of the 26 nearest or diagonally nearest neighbors. The surfactant and the pure inorganic or hybrid particles are modeled as chains of connected segments, whereas the solvent is modeled by single beads. The surfactant chain used in this work, H_4T_4 , is made up of four solvophilic head segments (H) and four solvophobic tail segments (T), with each segment occupying only one lattice site.

The particles can be either purely inorganic particles (IPs) or hybrid organic-inorganic particles (OIPs). The former are modeled according to their miscibility with the solvent; the latter are modeled also by considering the solvophobic/solvophilic nature of the organic group and the number of inorganic sources, being one for the terminal hybrid particles or two for the bridging hybrid particles. It should be noted that the nomenclature used here to identify the OIPs has been chosen for uniformity with the literature²⁷, and it does not aim to stress on the position of the organic group in the particle as a leading factor for the phase separation. The position of the organic group can eventually affect the organization of the particle in the

corona of the aggregate, but the key factor differentiating between the phase behavior of terminal and bridging particles is the number of inorganic sources.

We denominate the inorganic segment, I, which is completely soluble in the solvent, while I' is only partially soluble in the solvent. The solvophilic and the solvophobic organic group of the OIPs are modeled in the same way as the surfactant heads and tails respectively, and therefore are denominated with either an H or a T. The particles modeled in this work are the following: I_2 and I'_2 (purely inorganic particles); IH, I'H, IT and I'T (terminal OIPs); IHI, I'HI', ITI, and I'TT' (bridging OIPs). The solvent beads are denoted by S.

The interchange energy between different types of sites is defined as:

$$\omega_{\alpha\beta} = \varepsilon_{\alpha\beta} - \frac{1}{2} \left(\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta} \right)$$
(1)

where $\varepsilon_{\alpha\beta}$ is the individual interaction energy of a given pair of sites. For a system with four different species present, it can be shown that there are 6 independent interaction energies available¹⁷. The energies $\omega_{\alpha\beta}$ have been chosen such that the solvent will attract the surfactant heads and repel the surfactant tails. Two different cases are presented to simulate the miscibility of the inorganic particles and the solvent: in the first case, they are completely miscible ($\omega_{IS} = 0$), in the second they are as immiscible as surfactant heads and tails ($\omega_{I'S} = \omega_{HT} = 1$). The inorganic segment, *I* or *I*', has been chosen to form a stronger attraction with the head groups than with the solvent¹¹. The selection of these interaction parameters

resembles systems containing silica (or other inorganic oxides) in solution and surfactants, which are used in the formation of ordered materials¹⁶.

In Table 1, the global interchange energies, $\omega_{\alpha\beta}$, are reported for both partial and complete miscibility between the solvent and the inorganic particle.

Complete miscibility					Partial miscibility						
	I	Н	Т	S		I'	Н	Т	S		
Ι					I'						
Н	-2				Н	-2					
Т	1	1			Т	0	1				
S	0	0	1		S	1	0	1			

Table 1. Global interchange energies $\omega_{\alpha\beta}$ for the surfactant-particle-solvent interactions.

3. SIMULATION METHOD

Lattice MC simulations in the *NVT* ensemble were performed to study the phase behavior of amphiphilic systems containing pure inorganic or hybrid particles. Periodic boundary conditions were applied to a fully occupied three-dimensional lattice box. A lattice box of size $24 \times 24 \times 100$ was generally used in direct interfacial simulations to model the phase separation and to obtain the phase diagrams. The dimensionless temperature is defined as, $T^* = kT / \omega_{HT}$, where *k* is the Boltzmann constant, *T* is the absolute temperature and ω_{HT} is the head-tail

interchange energy. In particular, we selected $T^* = 8.0$ being a good compromise between the solvophobic and entropic effects for the formation of ordered structures. At least 3×10^9 MC steps were necessary to consider the system at equilibrium.

Surfactant and particle chains were moved by reptation and configurational bias moves (partial or complete regrowth)²⁸. A typical mix of the MC moves used was 80% reptation, 10% partial regrowth, and 10% complete regrowth. This choice was found to optimize the relaxation of energy as a function of CPU time. When performing a configurational bias move, not all of the 26 directions given by the selected coordination number were used to grow the chain. Instead, just 10 random directions were picked from the full 26 ones for each segment to be grown.

To generate the initial configuration for the direct interfacial simulation, the chains were randomly distributed in a concentrated region of the box of approximately 60% by volume. The simulation was considered to be equilibrated if no significant changes were observed in the total energy of the system and in the densities of each phase. Along with these verifications, a visual inspection of the phases formed was useful to determine if the system had reached typical equilibrium configurations. In systems which may be difficult to sample, especially when micelles were found to be at equilibrium with liquid crystals, we verified the validity of our results by modifying the size of the simulation box from 24×24×100 up to $35\times35\times140$, the global concentration of the mixture, the temperature, and we also followed the movement of a number of chains in the box during the simulation.

After the system reached equilibrium, the ternary phase diagrams were calculated by averaging the compositions in each phase along the direction perpendicular to the interface.

To guarantee a good estimate of the equilibrium compositions in systems presenting phase separation, the average densities are calculated in the bulk of the phases, that is, far from the interfaces. When it was not possible to clearly identify the bulk concentrations, then the length of the simulation box was increased or several composition profiles calculated from different configurations were averaged. The concentrations at equilibrium were then reported in the isothermal ternary phase diagrams and connected by tie-lines.

Considering the total number of different particles modeled, ten different phase diagrams have been calculated. We estimated the critical points in those systems presenting equilibrium data in the neighborhood of the critical point, by extrapolating the following equation²⁹:

$$\rho_{surf} - \rho_{surf}^{C} = A \left| \rho_{part} - \rho_{part}^{C} \right|^{\beta^{*}}$$
(2)

where A is a constant, ρ_{surf} and ρ_{part} are the surfactant and the particle concentrations in a given phase, respectively. The concentrations presenting the suffix C are the concentrations at the critical point. The renormalized critical exponent, β^* , is approximately 1/3 for the model used, which belongs to the Ising universality class^{29,30}. Therefore, the binodal curve associated with this equation is practically cubic in the neighborhood of the critical point, as already observed²⁹. We chose to use this value to calculate the concentrations at the critical point, as also suggested in other research works applying the same lattice model²⁰. To estimate the

coordinates of the critical points we extrapolated the coexisting densities from the two closest tie lines with our assumed value of β * = 1/3.

4. QUASI-CHEMICAL THEORY

The regular solution theory postulates the random distribution of beads even though the enthalpy of mixing is not equal to zero. Only in the limiting condition of very high temperatures, the random distribution of beads can be considered a real scenario for such solutions. This approximation, usually called the *zeroth approximation*, is improved by the quasichemical theory assuming the independence of pairs of beads. The improvement is in the fact that we are not considering anymore a random distribution of beads, but rather a random distribution of pairs of beads. An even better approximation would assume a random distribution of triplets, quadruplets or bigger clusters of particles since the probability of a particle to belong to several pairs (or clusters) would be reduced.

In the QCT the free energy of mixing is²³

$$\frac{\Delta G}{RT}\Big|_{mix} = \frac{\Delta G^*}{RT}\Big|_{mix} + \frac{1}{2}\sum_{\alpha} \left\{ \left(\sum_{i=1}^3 zq_{\alpha,i}n_i\right) \ln \frac{zX_{\alpha\alpha}}{zX_{\alpha\alpha}^*} - \sum_{i=1}^3 \left(zq_{\alpha,i}n_i\right) \ln \frac{zX_{\alpha\alpha}^{i,0}}{zX_{\alpha\alpha}^{i,0^*}} \right\}$$
(3)

where the superscript * represents the conditions in the athermal solution. In particular the free energy of mixing for athermal solution is given by²³

$$\frac{\Delta G^*}{RT}\Big|_{mix} = \sum_{i=1}^3 n_i \ln \varphi_i + \frac{1}{2} z \sum_{i=1}^3 q_i n_i \ln \frac{\xi_i}{\varphi_i}$$
(4)

z is the lattice coordination number, n_i the number of molecules of the species i, φ_i the volume fraction, $zq_{\alpha,i}$ the number of contacts formed by a site α belonging to the species *i* with its nearest neighbors not belonging to the same chain, $zX_{\alpha\beta}$ the number of nearest-neighbor

pairs,
$$zX_{\alpha\beta}^{i,0}$$
 the number of α - β contacts of the pure species *i*, and $\xi_i = q_i n_i / \sum_{j=1}^3 q_j n_j$.

At equilibrium, the chemical potentials of the species in the concentrated phase match the corresponding chemical potentials in the dilute phase, and the concentrations of the three components in the mixture can be calculated by solving a nonlinear system of three equations. The number of unknowns is given by the number of concentrations of each component in both phases, that is *6*. However, this number is reduced to *4* by the two physical constraints $\sum_{i=1}^{3} \varphi_{i}^{(dll, conc)} = 1$ Therefore, we need to fix only one concentration to solve the system, whose solutions have been found by applying the Levenberg-Marquardt algorithm for least-squares estimation of nonlinear parameters³¹.

5. RESULTS

In Figure 1, the binary phase diagrams of the systems formed by the solvent and an IP or OIP are reported. The equilibrium data have been obtained at different reduced temperatures by applying the QCT and simulating the binary systems for 10^9 MC steps in lattice boxes of size $24 \times 24 \times 100$. The phase diagram of the system containing the particle *I'T* is exactly equal to the one containing the pure inorganic particle *I'*₂, because the interactions established in the two systems are identical ($\omega_{IT} = 0$, $\omega_{IS} = \omega_{TS} = 1$). Therefore it has not been included.



Fig. 1. Binary phase diagrams of systems containing solvent and a pure inorganic or a hybrid particle. (a) I'_2/S , (b) *IHI/S*, (c) *I'HI'/S*, (d) *I'H/S*, (e) *I'TI'/S*, (f) *IH/S*. ϕ is the volume fraction of the particles and T^* the reduced temperature for the six diagrams. Solid circles: MC simulations. Dashed lines : QCT.

Those particles with an insoluble inorganic bead, $I'_{,}$ or a solvophilic organic group, $H_{,}$ show partial miscibility with the solvent. The repulsion between $I'_{,}$ and the solvent (S) or the strong

attraction between the inorganic segment (I) and the solvophilic one (H), are the driving forces for the phase separation in these binary systems. On the other hand, the binary systems containing the pure inorganic particle I_2 or the hybrid particles IT and ITI do not show phase separation even at the very low reduced temperature $T^*=2.0$, because I is completely miscible with the solvent and ω_{IT} is sufficiently repulsive to prevent a phase separation due to association of the OIPs. The agreement of the simulations with QCT is good except in the vicinity of the critical point and in the case of the system IH/S where ordered bilayers are formed. The presence of a solvophobic group 7 in an OIP is not sufficient to give rise to a phase separation, unless the inorganic bead is insoluble in the solvent too, because the interactions between I and T are quite unfavorable ($\omega_{T} = 1$) for the formation of a phase mainly composed of hybrid particles. Such a result confirms that the phase separation in the systems presented here originates from an energetic effect. In some other cases, despite the absence of any explicit interaction between the components, an entropic phase transition can be observed, as reported for colloidal, polymeric, and also amphiphilic systems³², where the presence of endcaps or junctions between the chains lead to the formation of networks and can give rise to a phase separation between a junction-poor phase and a junction-rich phase.

The phase diagrams of the systems including the surfactant are reported in sections 5.1 and 5.2, and analyzed by considering the effects of the nature of the particles on the driving force for the phase separation. The structural analysis of the systems containing IPs or terminal OIPs has been carried out in a previous work¹⁷, and a future paper will focus on the structural properties of those systems containing bridging OIPs.

5.1. IPS AND TERMINAL OIPS. PHASE DIAGRAMS.

In this section, we present the phase diagrams of six different systems: $H_4T_4/I_2/S$, H_4

Figure 2 shows the phase diagrams for the systems presenting pure IPs with complete or partial solubility with the solvent.





Fig. 2. Phase diagrams of the system $H_4T_4/I_2/S(a)$ and $H_4T_4/I_2/S(b)$ at $T^*=8.0$. Solid circles and dotted lines: MC simulations. Solid lines: QCT. The empty circles in the diagram (*a*) represent the estimated location of the critical points, based on MC data.

In both cases, a phase separation has been found both by MC as well as QCT. In particular, the agreement between simulations and QCT is very good in Figure 2.b, when the particle is only partially miscible with the solvent, especially when the volume concentration of the surfactant in the surfactant-rich phase is lower than 55%, as no long-range order is observed. At higher concentrations, the agreement is still good even though the system gives rise to ordered liquid crystal phases which are not taken into account by QCT.

For the completely miscible particle, the driving force for the phase separation is the strong attraction between its inorganic source, *I*, and the solvophilic heads of the surfactant, *H*. Such a phase separation is usually referred to as an associative phase separation, whereas a segregative phase separation is the result of a very strong repulsion between two different components, or when the two components interact with the solvent in a different way³³.

The phase separation observed in the $H_4T_4/I'_2/S$ system is a typical example of segregative phase separation, and is the result of two factors: the strong attractive interactions between the inorganic segment I' and the surfactant heads ($\omega_{HI'} = -2$), and the repulsion between the particle I'_2 and the solvent S ($\omega_{SI'} = 1$). In the system containing I_2 , the inorganic particle is strongly attracted by the surfactant heads, but it is soluble in the solvent. Therefore, the driving force for the associative phase separation observed in the $H_4T_4/I_2/S$ system results to be weaker than in the system with I'_2 .

If one of the two beads of the IPs is substituted with a solvophilic group, *H*, the size of the immiscibility gap becomes smaller regardless of the solubility of the inorganic source in the solvent, as observed in Figure 3.





Fig. 3. Phase diagrams of the system $H_4T_4/IH/S$ (*a*) and $H_4T_4/I'H/S$ (*b*) at $T^*=8.0$. Solid circles and dotted lines: MC simulations. The empty circles represent the estimated location of the critical points, based on MC data. The empty squares in the diagram (*a*) represent the equilibrium concentrations of the binary *IH/S* system, calculated with QCT.

Effectively, the driving force for the associative phase separation decreases, because the interactions formed between the surfactant heads and IH are not as strong as the interactions between the surfactant heads and I_2 , see Table 1. The same considerations are still valid if we change I'_2 with I'H. In this case, the decrease of the driving force for the phase separation is also due to the increase of solubility of the particle in the solvent, due to the presence of the solvophilic group H.

From the binary *IH/S* diagram in Figure 1, we observed that the critical temperature is close to $T^*=8.0$. The proximity of this critical point makes it difficult to observe this phase separation in the ternary phase diagram of the system $H_4T_4/IH/S$ in the region close to the *IH-S* axis, see Figure 3. In the case of the QCT, an immiscibility gap is found however it is restricted to a very small area in which the highest surfactant concentration is close to 0.5% (see Figure 4).



Fig. 4. Phase diagram of the system $H_4T_4/IH/S$ obtained with QCT at $T^*=8.0$.

The agreement between MC simulations and QCT is much better for the system $H_4T_4/I'H/S$, as observed in Figure 3.b. The main difference with the purely inorganic particle I'_{2} , is that I'H forms ordered aggregates in the dense phases at lower surfactant concentrations. Therefore deviations of the QCT from the equilibrium data of the simulations are observed at lower surfactant concentrations than with I'_{2} . Ordered liquid crystal phases are observed at surfactant concentrations higher than 50% by volume. Nevertheless the quantitative agreement between theory and simulations is still very satisfactory.

The phase diagrams of the systems with a solvophobic terminal group, *T*, are reported in Fig. 5.



Fig. 5. Phase diagrams of the system $H_4T_4/IT/S(a)$ and $H_4T_4/I'T/S(b)$ at $T^*=8.0$. Solid circles and dot lines: MC simulations. Solid lines: QCT.

The quantitative agreement between theory and simulations is remarkably good for both systems $H_4T_4/IT/S$ and $H_4T_4/I'T/S$, as no ordered liquid crystal phases are observed at any global concentration along the coexistence line. Despite the high surfactant concentration in the concentrated phase of the system containing I'T, we do not observe the formation of any ordered structure. Such a result is not associated with the interactions established between the beads I' and T, that are different to the interactions between I and T (simulations with $\omega_{TT'} = 1$

did not give ordered structures either), but more probably with the strong insolubility of the particle IT in the solvent.

Again, we detect a reduction in the immiscibility gap of both the phase diagrams in comparison to the ones observed for the IPs. In both cases, the associative driving force becomes weaker, as half of the OIP presents a net repulsive interaction with the surfactant heads (see Table 1); for the same reason, the segregative driving force increases, especially when a soluble inorganic bead is substituted with a solvophobic bead. Considering the final shape of the immiscibility gaps, the first factor seems to have more weight.

The size of the solubility gaps obtained with I'T particles are not very different from those obtained with I'H particles, although the organic terminal groups have opposite behaviors. The reason of such a tendency is the balance between two energetic effects. If we change the H group of the hybrid particle I'H for a T group, the solubility of the particle in the solvent would decrease and the immiscibility gap increase for the system containing I'T. On the other hand, the interactions between the surfactant heads and the I'T particles are less favorable than those with the I'H particles, which reduces the driving force for an associative phase separation. The balance between these two effects, the first segregative and the second associative, leads to phase diagrams presenting similar immiscibility gap sizes.

5.2. BRIDGING OIPS. PHASE DIAGRAMS.

We have modeled the bridging hybrid particles with chains formed by one solvophilic (*H*) or solvophobic (*T*) segment in between two segments of type *I* or *I*. The phase diagrams of the

four different systems ($H_4T_4/IHI/S$, $H_4T_4/I'HI'/S$, $H_4T_4/ITI/S$, and $H_4T_4/I'TI'/S$) obtained by performing lattice MC simulations, and by applying the QCT have been calculated at $T^*=8.0$.

As a general trend, we observed that a higher concentration of surfactant is achieved in the concentrated phase in comparison with the corresponding terminal precursors, and the immiscibility gaps result to be bigger. The change in the shape of the immiscibility gap can be explained by considering the nature of the driving force for the separation, that is the strong interaction between the I (or I) segments and the surfactant head segments. If we increase the number of I(I) beads in a given hybrid particle, the phase separation will be enhanced as the surfactant heads will experiment a stronger attraction towards the hybrid particle and the amount of surfactant in the concentrated phase will increase.

The phase diagram of the system containing the bridging organic particle *I'HI'* is very similar to the phase diagram of the system containing I'_{2i} because the decrease in the driving force for the segregative phase separation (higher solubility for *I'HI'* than for I'_{2}) is compensated by an increase in the driving force for the associative phase separation, due to the presence of an extra *H* group in the precursor. When we change I'_{2} with $I'TI'_{i}$ the solubility of the precursor in the solvent does not change, but its attraction towards the surfactant heads decreases due to the presence of the solvophobic group *T*, and the segregative driving force becomes weaker.

The phase diagrams obtained with solvophilic bridging particles are reported in Figure 6.

A good agreement between MC simulations and QCT predictions can be observed for the insoluble inorganic segment *I*, and in particular when the surfactant concentrations in the concentrated phases is lower than 50% by volume. At higher concentrations, the immiscibility

gap predicted by QCT becomes slightly smaller than the one calculated by MC simulations, as

ordered structures are formed.



Fig. 6. Phase diagrams of the system $H_4T_4/IHI/S$ (*a*) and $H_4T_4/I'HI'/S$ (*b*) at $T^*=8.0$. Solid circles and dotted lines: MC simulations. Solid lines: QCT. The empty circles represent the estimated location of the critical points, based on MC data.

When the surfactant concentration in the dense phase is above 50% in the system containing I'HI', the concentration of surfactant in the dilute phase starts to increase significantly, therefore the tie lines have a different tendency in the slope compared to those at lower surfactant concentrations and a second point of intersection (or pole³⁴) between the tie-lines is found. According to Campbell et al.³⁵, the isothermal tie-lines of a given ternary phase diagram, if adequately extended, should meet in one pole, usually outside the triangular diagram. This supposition has found support in some experimental ternary phase diagrams, such as the ethanol/water/n-hexane diagram³⁴, and also in the empirical rule developed by Tarassenkov³⁶, who also affirmed that the straight line connecting the critical point to the pole is the tangent of the binodal curve at the critical point. Tarassenkov tested his method with six different ternary systems, showing a reasonable agreement with the experimental results. Although these works declared that deviations from this behavior should be considered as experimental errors, other experimental phase diagrams, such as the ethanol/chloroform/water diagram^{37,38}, show a guite different trend in which at least two poles can be seen. A theoretical approach to this issue was presented for ternary liquid mixtures by Widom²⁹, who calculated the coordinates of the tie-lines intersection under some given approximations.

In our ternary amphiphilic systems, we observed either one or two poles of intersection between the tie-lines in a given phase diagram. The presence of two poles is possibly not connected to the formation of ordered structures because such a behavior is also noticed in the tie-lines calculated with the QCT, which does not predict the formation of ordered phases, but it is due merely to energetic considerations based on the origin of the phase separation in these systems. At low surfactant concentrations, the driving force for the phase separation is

mainly due to the immiscibility of the inorganic source *I'* in the solvent. When the surfactant concentration increases, then the strong interactions established between the surfactant heads and the inorganic particle acquire more weight and can become dominant at very high surfactant concentrations. As a matter of fact, the slope of the tie-lines in this region leads to a higher content of hybrid particle in the surfactant-rich phase, compared to the case in which the pole would not have changed its position. Although less evident, a similar change in the slope of the tie-lines can be also observed in the phase diagrams of those systems with a hybrid particle presenting a soluble inorganic source and ordered aggregates in the dilute phases. In these cases, two poles are also generally observed.

In Figure 7, the phase diagrams obtained for systems presenting solvophobic bridging particles are reported.





Fig. 7. Phase diagrams of the system $H_4T_4/ITI/S$ (*a*) and $H_4T_4/I'TI'/S$ (*b*) at $T^*=8.0$. Solid circles and dotted lines: MC simulations. Solid lines: QCT.

As mentioned previously, the system with *ITI* presents a bigger immiscibility gap than the one observed in the system with *IT*. However, this is not the only remarkable difference between the two systems. Spherical aggregates are formed in the concentrated phase of the system with *ITI* which are not observed in the system with *IT*. This can be also argued from the quantitative discrepancy between the immiscibility gap calculated with the simulations and the one obtained with the QCT. On the other hand, the phase diagram obtained with *I'TI* shows a very similar trend to the one obtained with *I'TT*, and its agreement with the phase diagram calculated with the QCT is very good.

The ternary systems analyzed so far, generally show an immiscibility gap in the phase diagrams, between a (dilute) solvent-rich phase and a (concentrated) surfactant-rich phase. According to the model hybrid particle, the concentrated phase can present ordered liquid crystals, and, in some of these cases, the corresponding dilute phase shows a surfactant concentration high enough for the formation of micelles or more complex aggregates. As a matter of fact, a visual inspection confirmed to us the formation of ordered aggregates in the dilute phase, as reported in Figure 8 for systems containing pure inorganic, terminal, and bridging particles.



(c)

Fig. 8. Phase separation observed at $T^*=8.0$ in lattice boxes of size $24 \times 24 \times 100$. Global concentrations: $40\% H_4T_4 - 5\% I'_2(a)$, $30\% H_4T_4 - 10\% I'H(b)$, $40\% H_4T_4 - 10\% I'HI'(c)$. Dark shading represents the surfactant tails, light shading represents the surfactant heads or the inorganic precursor. The solvent is not shown.

Such a result is not of general validity for amphiphilic systems, as reported by other researchers³, whose work focused on binary surfactant/solvent solutions. They showed that the same model for surfactants of varying head and tail lengths either forms micelles or phase

separates, but never both, and suggest that the experiments showing the opposite are a consequence of the particular solvation properties of water.

Our system is more complex as a third component, that is a pure inorganic or hybrid particle, is added and there are a total of six independent interchange energies as opposed to just one. Moreover, the dilute phase, being almost totally composed of surfactant and solvent as the particle concentration is lower than 2%, is typical of a binary H_4T_4/S system which forms micelles^{39,40}. Therefore, the simultaneous presence of micellization and phase separation is reasonable.

Nevertheless, we preferred to verify in more detail the validity of our results by

(*a*) changing the size of the lattice box from 24×24×100 up to 35×35×140 which showed that the error in the composition of each phase was less than 3%, the same structures were formed and no specific trend was observed when increasing the simulation box size;

(*b*) simulating the systems at different global concentrations belonging to the same tie-line which only changed the proportion of each phase but not its structure or composition;

(c) decreasing gradually the temperature by a $\Delta T^*=0.2$ starting from $T^*=10.0$ to $T^*=8.0$, which showed that the error in the composition of each phase was less than 2%, indicating that the initial configuration was not trapped in a local minimum; and

(*d*) following the displacement of several chains in the lattice box once equilibrium was achieved indicated that simulations were sufficiently long such that an arbitrary chain could sample the whole simulation box.

Such verifications are additional tests to confirm that these systems are properly sampled since the simultaneous presence of micelles and liquid crystals in two separate phases could be considered as a local minimum of energy in which the system is trapped.

6. QCT AND MC SIMULATIONS

In the previous sections, we observed that the phase diagrams calculated with the QCT (QCTdiagrams) are in good agreement with the ones obtained with lattice MC simulations (MCdiagrams), especially when no ordered phases are formed. In this case, the scenario predicted by the simulations does not differ so much from the one predicted by the theory which does not assume the formation of ordered structures.

Considering that MC simulations and QCT use the same model and the same parameters, and that the thermodynamic properties of the system are a result of the interaction between neighboring sites, in this section the QCT-diagrams and the MC-diagrams are compared by calculating the number of contacts formed at equilibrium between *H*, *T*, *I*, and *S* beads. As expected, the closer the number of the contacts calculated with both methods, the better the agreement between simulation and theory. It should be noted that we are counting the sum of the total number of contacts in both phases in equilibrium at the same global composition, rather than the contacts in each separate phase.

The presence of an interface can represent a problem when comparing the number of contacts if its volume is not negligible with respect to the total volume of the simulation box. Therefore, in the following comparison, we are considering those systems whose phases at

equilibrium share an interface occupying only a small percentage of the total box volume, in between 5% and 10%, and being as far as possible from the critical region, ensuring that the interface is as sharp as possible.

In Table 3, we report the number of contacts formed in MC simulations divided by the number of contacts calculated with QCT, when ordered phases are observed in the system $H_4T_4/I'_2/S$.

Table 3. Number of contacts between different kinds of beads obtained from MC simulations over the number of the same kinds of contacts calculated with QCT, for the $H_4T_4/I'_2/S$ system. Global concentrations are considered.

System	ΗH	HT	HI	HS	ΤT	ΤI	TS	Π	IS	SS
4% <i>I</i> ′2, 30% <i>H</i> 4 <i>T</i> 4	1.46	0.63	1.45	0.82	2.20	0.51	0.49	1.63	0.50	1.08
6% <i>I</i> ′2, 30% <i>H</i> 4 <i>T</i> 4	1.50	0.57	1.38	0.68	2.06	0.48	0.45	1.34	0.72	1.06
8% <i>I</i> ′ ₂ , 30% <i>H</i> ₄ <i>T</i> ₄	1.48	0.56	1.30	0.64	2.04	0.52	0.42	1.23	0.92	1.06
10% <i>I</i> '2, 30% <i>H</i> 4 <i>T</i> 4	1.48	0.54	1.29	0.57	2.08	0.55	0.39	1.18	0.90	1.06
15% <i>I</i> ′ ₂ , 30% <i>H</i> ₄ <i>T</i> ₄	1.33	0.52	1.23	0.65	1.94	0.61	0.56	1.22	0.67	1.03
20% I'2, 30% H4T4	1.22	0.49	1.17	0.91	1.83	0.65	0.96	1.21	0.59	1.02

$5\% I'_{2}, 40\% H_{4}T_{4}$ 1.53 0.64 1.47 0.78 2.27 0.49 0.43 1.49 0.53 1.17

In this case, the number of contacts between beads of the same type, that is X_{HH} , X_{TT} , X_{TT} and X_{SS} , is higher in MC simulations than when calculated from QCT. Regarding the other kinds of contacts, namely those between beads of different types, a different trend is observed: only the number of contacts between *H* and *I* sites, X_{HI} is higher in MC than in QCT; all the other contacts show an opposite tendency in order to satisfy the equation of sites balance, given below.

 $2X_{HH} + X_{HT} + X_{HI} + X_{HS} = q_{H,1}n_1$ $2X_{TT} + X_{HT} + X_{TI} + X_{TS} = q_{T,1}n_1$ $2X_{II} + X_{HI} + X_{TI} + X_{IS} = q_{I,2}n_2$ $2X_{SS} + X_{HS} + X_{TS} + X_{IS} = q_{S,3}n_3$

(5)

This result is coherent with the formation of ordered aggregates in MC simulations, where tail-rich cores are surrounded by a corona of head segments in contact with the beads of the pure inorganic particle. Since QCT does not predict the formation of microphase separated regions, the density of contacts between equal beads cannot be as high as in the simulations.

Moreover, the number of contacts between the solvent beads and the other three types of beads, that is X_{TS_i} , X_{HS} and X_{IS_i} is smaller in the simulations than when calculated with the theory. Since these types of contacts are mostly present in the surfactant-rich phase, because

of the low concentration of precursor and surfactant in the dilute phase (see Figure 2.b), there is more solvent admitted in this phase when applying QCT. This also explains the reduction of the immiscibility gap in the QCT-diagrams with respect to the MC-diagrams.

On the other hand, when no structural order is observed, the results of MC simulations and QCT are quite similar, as shown in Table 4 for the systems $H_4T_4/I'T/S$ not presenting the formation of any ordered liquid crystal phase.

Table 4. Number of contacts between different kinds of beads obtained from MC simulations over the number of the same kinds of contacts calculated with QCT, for the system $H_4T_4/I'T/S$. Global concentrations are considered.

System	HH	HT	HI	HS	TT	ΤI	TS	Ш	IS	55
10% I'T, 10% H ₄ T ₄	1.15	0.86	0.94	1.25	1.10	0.94	0.93	0.99	1.64	1.00
10% <i>I′T</i> , 15% <i>H</i> ₄ <i>T</i> ₄	1.16	0.81	0.97	1.24	1.17	0.95	0.78	1.06	1.34	1.00
15% <i>I'T</i> , 15% <i>H</i> 4 <i>T</i> 4	1.23	0.89	0.98	1.03	1.13	0.97	0.74	1.04	1.17	1.01

The immiscibility gaps of both QCT and MC simulations become practically identical, as well as X_{HH_i} , X_{II_i} , X_{SS} and X_{HI} . The number of contacts between the surfactant tails, X_{TT_i} is still slightly higher when calculated with MC simulations because, although no ordered structures are observed in the concentrated phase, small aggregates can form and peaks of tails concentration are reported. Both QCT and MC simulations have been previously applied to study oil-water-amphiphile systems with symmetric or asymmetric short surfactants^{4,5,21}, such as $H_4T_4/T/H$. In these works, only one independent interaction parameter was used, as water was modeled by a single H segment and oil by one or more T segments. The comparison between theory and simulations showed an opposite trend in the relative size of the immiscibility gaps compared to our results. In particular, the surfactant concentration in the concentrated phase was observed to be higher when calculated with QCT than with MC simulations.

The apparent discordance between the results of the two kinds of systems finds a possible explication in the equations of site balance for the ternary $H_4T_4/T/H$ system, given below

$$2X_{HH} + X_{HT} = q_{H,1}n_1 + q_{H,3}n_3$$
$$2X_{TT} + X_{HT} = q_{T,1}n_1 + q_{T,2}n_2$$

(6)

where the subscripts 1, 2, and 3, refer to the surfactant (H_4T_4), oil (T), and water (H), respectively. The number of contacts X_{TT} and X_{HH} result to be higher from MC simulations because ordered aggregates are formed, and tail segments tend to stay together as well as head segments. Since X_{TT} and X_{HH} result to be smaller when QCT is applied, then X_{HT} has to be higher to satisfy the sites balance (6). Therefore, considering that the contacts between H and T sites are mainly formed in the surfactant-rich phase, the surfactant concentration is higher when calculated with QCT than with MC simulations.

The system studied in our research work requires six different independent interaction parameters (ω_{HT} , ω_{HI} , ω_{HS} , ω_{TI} , ω_{TS} , and ω_{IS}) and hence displays a much richer behavior than the aforementioned model. The presence of the inorganic segments, *I*, being strongly attracted by the surfactant heads, introduces new and more complex features with respect to a system where only two kinds of beads (*H* and *T*) are considered.

7. CONCLUSIONS

In this paper, we have discussed the equilibrium phase behavior of ternary amphiphilic systems in the presence of different types of particles that have a strong preference for the solvophilic segment of the surfactant. The organic-inorganic particles have been modeled by considering the solvophobicity of the functional organic group, and the number of the inorganic segments *I* or *I*. Depending on these characteristics, different phase diagrams have been obtained by using MC simulations and the QCT.

The phase diagrams obtained are characterized by a phase separation between a dilute phase, mainly occupied by the solvent, and a concentrated phase presenting a high content of the amphiphilic moiety and hybrid or pure inorganic particles. In systems with nonfunctionalized particles, the phase separations can be clearly classified between associative or segregative phase separations. When hybrid particles are used, this differentiation is not that clear, as an interplay of associative and segregative effects are observed.

The agreement observed in the ternary phase diagrams between MC simulations and QCT was very good when the system does not self-assemble into organized structures, and we observe qualitative agreement if ordered structures are present. In those cases where ordered

aggregates are formed, the immiscibility gap calculated by the QCT was smaller than the one calculated by MC simulations, and in those systems containing the solvophilic particles *IH* or *IHI*, we observed that it is not possible to predict the phase separation behavior and to capture the shape of the immiscibility gap by applying QCT. This evidence is the consequence of the fact that the QCT does not predict the formation of aggregates or more complex liquid crystal phases, and leads to a higher content of solvent in that phase where the presence of solvent, according to the MC simulations, should be small.

We have already underlined that it is not straightforward to perform a quantitative comparison between the results presented in this paper and the experiments. The number of details not included in our study can be of fundamental importance to make a reasonable comparison. However, the tendencies observed by applying a very simple model have furnished a qualitative idea of the factors needed to observe the formation of liquid crystals through a phase separation. At $T^*=8.0$, we have observed phase separation in all the systems studied, but not all these systems gave rise to a concentrated phase with a surfactant content high enough to form liquid crystal phases. As a general trend, systems with bridging hybrid particles can push the phase separation further than those containing terminal hybrid particles, especially when the inorganic source is soluble in the solvent. As a matter of fact, experimentally it was observed that it is not easy to synthesize ordered materials by using amphiphilic solutions containing terminal hybrid precursors²⁷. In general, a second, pure inorganic precursor with stabilizing properties is added, or the terminal precursor is grafted after the synthesis is completed^{16,27,41}. The last method is guite expensive due to the high surfactant concentration required and to the necessity of a post-synthesis treatment.

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