

Explanation of Experimental Results of Mixed Micelles of Homologous Surfactants through a Mm2 Bidimensional Modeling

María Luján Ferreira,[§] María Belén Sierra,^{*,†,‡} Marcela A. Morini,^{†,‡} José Luis Rodríguez,^{†,‡} Rossana Minardi,^{†,‡} and Pablo C. Schulz^{†,‡}

Departamento de Química and INQUISUR, CONICET, Universidad Nacional del Sur, 8000 Bahía Blanca, Buenos Aires, Argentina, and PLAPIQUI-UNS-CONICET Planta Piloto de Ingeniería Química, Camino la Carrindanga Km 7, CC 717, 8000 Bahía Blanca, Buenos Aires, Argentina

Received: November 27, 2009; Revised Manuscript Received: September 3, 2010

A computational modeling (in gas phase) to study the disposition of the homologous surfactants in a bidimensional simple model of mixed and homogeneous micelles was performed for the case of R-trimethylammonium bromide surfactants with different linear R lengths from R = C₅ to C₁₇. First, the bidimensional homogeneous (one component) micelle was modeled, and as a second step, heterogeneous (two components) bidimensional micelles were modeled. The difference in the number of carbon atoms between hydrocarbon chains of the surfactants in the heterogeneous micelles, Δn_C , ranged from 2 to 8. Results were contrasted with experimental data obtained at our own laboratory. The exothermic values of the steric energy changes showed strong attraction between components of homologous surfactants mixture, especially when one of the surfactants has a long chain. It may be argued that the inclusion of a shorter surfactant in the mixture and the twisting of the longer surfactant makes the bidimensional arrangement formation more exothermic. All predictions were in agreement with previous experimental results.

Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications because surfactant mixtures enhance the performance of applications when compared with the use of single surfactants. When mixing surfactants, not only are the properties of components combined but also in many cases new properties are found. These properties are of both fundamental and commercial interest because surfactants used in industrial applications (e.g., detergents, tertiary oil recovery, drug carrier systems, flotation) are often mixtures. Despite their widespread use, surfactant mixtures are not well understood on a fundamental level. Surfactant mixtures for specific applications are often chosen on the basis of experience, empirical evidence, or trial and error research. To optimize the applications of surfactant mixtures, it is important to understand the interplay of forces that govern the phase behavior. The main literature work has been devoted to the electrostatic interactions, but steric and hydrophobic/hydrophilic interactions are far from being understood or properly described.^{1–8}

In a previous paper on mixed micelles,⁹ we found that the interaction between homologous surfactants in mixed micelles is not ideal, as supposed in the regular solution theory of mixed micelles. The interaction is attractive, and the interaction parameter β_M depends linearly on the difference in chain length Δn_C . The value of β_M becomes zero (i.e., the interaction becomes ideal) at $\Delta n_C < 1$. When $\Delta n_C \approx 5$, the dependence remains linear, but the slope increased 2.7 times. This relationship is independent of the nature of the polar head groups. This phenomenon can be understood as the effect of the reduction

of the hydrocarbon/water micelle interface by inclusion of a shorter homologous. This reduction can be more effective when $\Delta n_C \geq 5$.

To obtain a better knowledge of homologous surfactants in mixed micelles, the aqueous mixed system decyltrimethylammonium bromide (C₁₀TAB)-hexadecyltrimethyl ammonium bromide (C₁₆TAB) was studied by different techniques.¹⁰ We concluded that although the compositions of the monomeric and micellar phases are similar to that of the total composition, the C₁₀TAB-C₁₆TAB mixed system is strongly nonideal, producing a reduction on the critical micellar concentration (CMC) (compared with the ideal one) and an increase in the aggregation number, associated with a strong reduction on the air/solution concentration. This nonideality seems to be caused by a reduction in the hydrocarbon/water contact at the micelle surface and confirms that mixtures of homologous series of surfactants with the same polar head are not ideal, in opposition to what is supposed by the regular solution theory.¹⁰

To obtain a better knowledge of our experimental findings, a computational study of the structure of mixed micelles of homologous surfactant using a bidimensional approach was performed. These systems were modeled using both molecular mechanics (as MM2) and semiempirical methods (such as PM3).

Katritzky et al.¹¹ studied linear and nonlinear predictive models applied to 50 ammonium and quaternary pyridinium cationic surfactants. They developed for both the first and second CMCs. They also deduced an ANN (nonlinear artificial neural network) model for the first CMC of 50 cationic surfactants. Descriptors in these models were related to the size and charge of the hydrophobic tail and to the size of the head. Their multilinear model for the second CMC was related to the hydrophobic domain of the surfactant rather than that of the first CMC. Their QSPR models (linear and nonlinear) for the first CMC could provide useful predictions of the CMC of structurally similar cationic surfactants.

* To whom correspondence should be addressed. E-mail: mbsierra@uns.edu.ar.

[†] Departamento de Química, Universidad Nacional del Sur.

[‡] INQUISUR, CONICET, Universidad Nacional del Sur.

[§] PLAPIQUI-UNS-CONICET Planta Piloto de Ingeniería Química.

The intention of the Article was to validate that the conformations found through experimental results are also spontaneous because they provide a minimum in the interaction energy. In this sense, the simulations are not used to find the steric conformations but to validate some explanations to provide an approach to a theoretical frame (quantitatively, energetically consistent), where our proposal for the surfactants behavior may be explained.

Theoretical Methods

The Program. The Chem 3D software (from Cambridge Soft, version Ultra 5.0) uses a modified version of Allinger's MM2 force field and a PM3 semiempirical method. The PM3 method provides the standard enthalpy of formation ΔH_f° based on a semiempirical approach to the solution of the Hamiltonian. The MM2 force field calculation provides the steric energies of the conformation. One of the main aspects considered in this work is the ability of the program to provide steric energies that may be compared maintaining the same atoms and bonds number. Steric energy absolute values have no meaning except in relative terms, when comparing the same molecules' type, atom total number, and bonding. With the same total number of atoms, the steric energies of different conformations (without broken bond in them) can be compared. Those conformations found to be more negative are the most favored. In this sense, molecular mechanics systems allow an approximation of the van der Waals interactions, H bonding, and the hydrophobic effect, which are very difficult to simulate properly using other methods (e.g., ab initio or Hartree–Fock methods). In the case of molecular dynamics simulations, these include the impact of temperature and time. The kind of information provided by these methods is different from the information provided by molecular mechanics methodology when time or temperature are not involved.

Although it is true that a micellar system is very complex, the study of the interaction at the micelle–water interface can be separated in several parts. Local interactions are always important to understand the nature of the bonding, and these can be studied by MM2 semiempirical and ab initio theory levels with different degrees of complexity and application, depending on whether the solvent is considered. Global interactions must be considered in the analysis of the effect of thousands of water molecules. However, all interactions are conditioned by the addition of the pairwise interactions at short and long ranges. Results are commonly affected by initial structures of the modeling. Therefore, a local interaction must first be understood to give a coherent initial structure for the modeling of very large structures. These situations applied to different levels of complexity are reported in refs 12–15.

Using the same number of carbon atoms and under certain constraints (which are the most important topic of these calculations in terms of limitations), the method is sensitive enough to give values that can be compared qualitatively with experimental ones. Some possible conformations that fit with experimental work (ours and from other authors) on which we based the models were evaluated, and the results are in agreement with them. Consequently, the models used here are not the unique possible ones, but they were selected taking into account the available experimental evidence. The spherical geometry of the bidimensional model was demonstrated to be more stable than the rectangular one in a bidimensional approach. The spherical bidimensional arrangement was selected as the preferred one. This bidimensional arrangement may be part of tridimensional spherical or cylindrical wormlike struc-

tures. The amount of available experimental results is enough to design a complete modeling study.¹⁶

It is important to mention that the twisted versus nontwisted arrangements for the same composition of the micelles were studied, keeping the total number of atoms constant. When the impact of changing the composition of the mixed micelles was studied, the number of atoms varied, but the differences in the atom numbers were the same between the different compared conformations.

Theoretical Studies on Surfactants: Molecular Dynamics and Molecular Mechanics. Studies of molecular dynamics of surfactants in water are numerous but centered on one kind of surfactant, generally on its interaction with water, with other molecules of surfactant or with surfaces. They have been focused on alkaline salts of fatty acids,¹⁷ the role of water in micelles,^{15,18} and the size of the surfactant chain length.^{19,20} The literature on molecular dynamics on RTAB surfactants is scarce²² and many times related to adsorption or bilayers or its role as cosurfactant.^{20–22} The field is in continuous progress.²³ The study of the bulk aggregation behavior of mixed surfactants systems is also interesting beyond the well-known synergistic properties in mixed systems, with relevance to technical applications. As more systematic and detailed experimental data are collected (e.g., by use of scattering and direct imaging techniques), increasingly refined theoretical models are developed.²⁴ The micelles of TAB alkyl surfactants may be spherical or cylindrical, prolate ellipsoid or oblate ellipsoid in shape from a tridimensional point of view. The literature on the topic also mentions hemicylindrical structures, especially adsorbed on surfaces.²² Wormlike structures have been reported for mixtures of C₈TAB and sodium oleate.²⁵

Experimental Procedures

Previous work suggested that the interaction between homologous surfactants in mixed micelles is not ideal, as it is supposed in the regular solution theory of mixed micelles. The interaction is attractive, and the interaction parameter β_M depends linearly on the difference in chain length, Δn_C .⁹

When the activity of each surfactant in the micelle is plotted as a function of micelle composition, their behavior is similar to that of a nonideal mixture of two completely miscible liquids; that is, when the mole fraction of one component approaches unity, the activity approaches the concentration. For both components at all micelle compositions, the activity is less than the mole fraction. This confirms the miscibility of both components and their attractive interaction. Because in the mixed surfactant model the activity coefficient of each component in micelles tends to unity when the mole fraction of the component approaches unity, the standard state in mixed micelles is related to Raoult's law. In mixtures of homologous hydrocarbons, it is common to find positive deviations to Raoult's law.²⁶ This means that the activity of both components is higher than their respective concentration. Actually, the behavior of the homologous surfactant mixtures seems to be that of mixtures having negative deviations to Raoult's law. When this situation occurs, it is accepted that the partial formation of compounds involving both components may occur in the condensed phase.²⁶

Focusing on this interpretation, both components seem to be affected by the inclusion in the mixed micelles. In a pure surfactant micelle, some of the chains are extended, whereas others must be folded to fulfill the spaces between the extended surfactant molecules so as to reduce the hydrocarbon/water interface. However, some part of the chain remains in contact with water.^{26–35}

TABLE 1: Differences in Number of Carbon Atoms Studied for Different R-Trimethylammonium

difference	0	2	4	6	8
group 1	C ₅	C ₇ –C ₅	C ₉ –C ₅	C ₁₁ –C ₅	C ₁₃ –C ₅
group 2	C ₇	C ₉ –C ₇	C ₁₁ –C ₇	C ₁₃ –C ₇	C ₁₅ –C ₇
group 3	C ₉	C ₁₁ –C ₉	C ₁₃ –C ₉	C ₁₅ –C ₉	C ₁₇ –C ₉
group 4	C ₁₁	C ₁₃ –C ₁₁	C ₁₅ –C ₁₁	C ₁₇ –C ₁₁	
	C ₁₃				
	C ₁₅				
	C ₁₇				

The inclusion of a shorter molecule may be intercalated between the extreme of the folded chain of the longest component and the micelle surface, replacing part of the hydrocarbon/water interface by a polar headgroup. When Δn_C is large, the longest component can fold its distal end more easily in the space within the center of the micelle and the end of the shorter component chain. Both the longer and the shorter chains in the mixed micelle expose less hydrocarbon surface to water than in the respective pure surfactant micelles and can be less folded. This is reflected in the respective values of the activity coefficient in micelles.⁹

We have not considered the solvent (water) in the modeling of the mixed micelles formed by homologous surfactants because the influence of the solvent affects the kind of micelles formed but not the interactions in their hydrophobic core. In a previous work,¹⁰ we have experimentally determined that such micelles are spherical or nearly spherical close to the CMC. Then, we adopted this structure for the analysis of what interactions occur inside the hydrocarbon micelle core. Because in this part of the micelles there is no water, the presence of the solvent in the model does not provide any important insight into the studied phenomena, but unnecessarily complicates the modeling.

With these ideas in mind, we performed a computational modeling to study the disposition of the surfactants in a bidimensional simple model of micelles in the gas phase. We considered lengths from $R = C_5$ to C_{17} for the R-trimethylammonium bromide (RTAB) basic structures, where R is linear. First, the bidimensional homogeneous micelle was modeled. As a second step, different compositions were analyzed: 0, 0.2, 0.6, 0.8, and 0.9 mol fraction of surfactants in micelles for the shorter hydrocarbon chain (X_S) for the heterogeneous bidimensional micelles. The difference in carbon atoms number, Δn_C , ranged from 2 to 8. Table 1 presents the different calculations performed. The aforementioned methods were applied to a bidimensional model of micelles, considered to be a cut of a spherical tridimensional micelle.

As a first approach, the longer chains were considered to be all twisted or all nontwisted for comparison purposes. The composition with $X_S = 0.6$ was selected to analyze the impact of twisting in the steric energy of the heterogeneous micelles.

Results and Discussion

Homogeneous System. The homogeneous system was analyzed with the R (from RTAB) ranging from C_5 to C_{17} . Figure 1 shows a view of bidimensional cut of a spherical homogeneous micelle.

The central void in the representation of the spherical micelles is an artifact of the representation procedure and the result of the simplification here used. Figure 1a shows a picture of a bidimensional cut with 20 molecules of surfactant. If we consider the micelle as a sphere, then we must include four full “cuts” to construct a spherical micelle. This would summarize

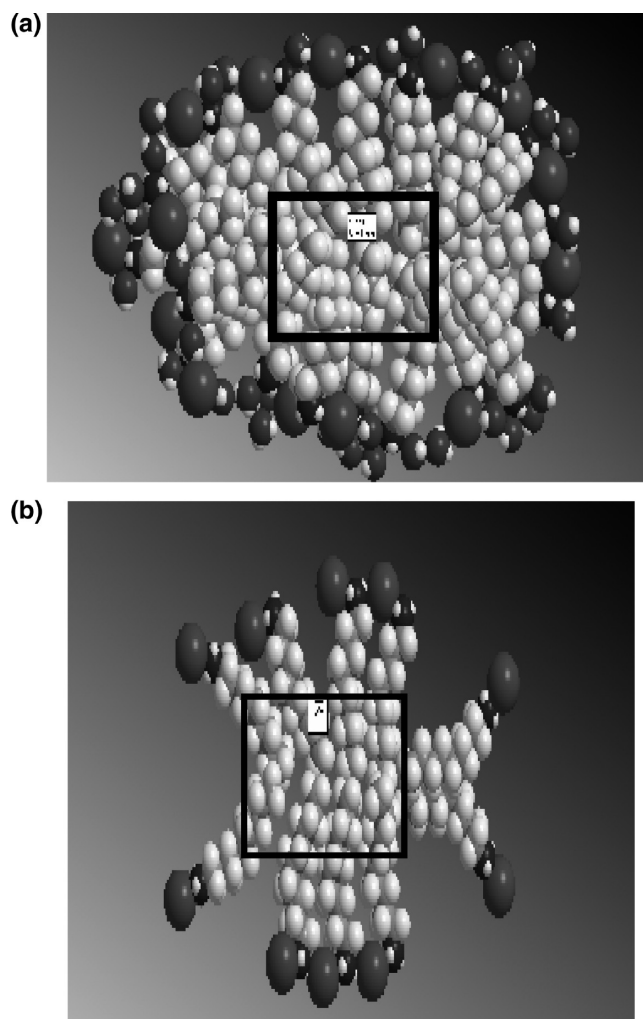


Figure 1. View of bidimensional cut of a spherical homogeneous micelle. Bidimensional cut of a micelle containing (a) 20 and (b) 10 molecules of the surfactant C_9 TAB, including two water molecules per polar head. The box shows the central core with the interaction of the hydrophobic chains.

up to 80 molecules per micelle. One aspect to consider in the modeling is that we included water molecules bonded to the polar heads: two per polar head. However, we did not include in the calculation the impact of the solvent. Because of this, the vacuum spaces that are seen in the representations are probably related to the low number of water molecules included in the calculation. In an essentially polar solvent, the hydrophobic core would be more tightly ordered. However, the main point of the manuscript is to include the simpler model that can represent the interaction of the different hydrophobic chains in different conformations. In this sense, the box in Figure 1b shows that the 10-molecule micelle takes into account the core interaction between hydrophobic chains. This kind of final structures (with voids) has also been found in more sophisticated simulations. Mailliet et al.³⁶ studied *n*-nonyl trimethylammonium chloride (C_9 TAC). Their simulated systems contained ~ 50 surfactant cations and chloride counterions surrounded by 3000 water molecules. The authors found that the penetration of water molecules inside micelles is not important in any instance examined on time scales up to a few nanoseconds. From their work, figures 4 and 10 of this reference also show “vacuum” spaces generated by the minimization of the total potential

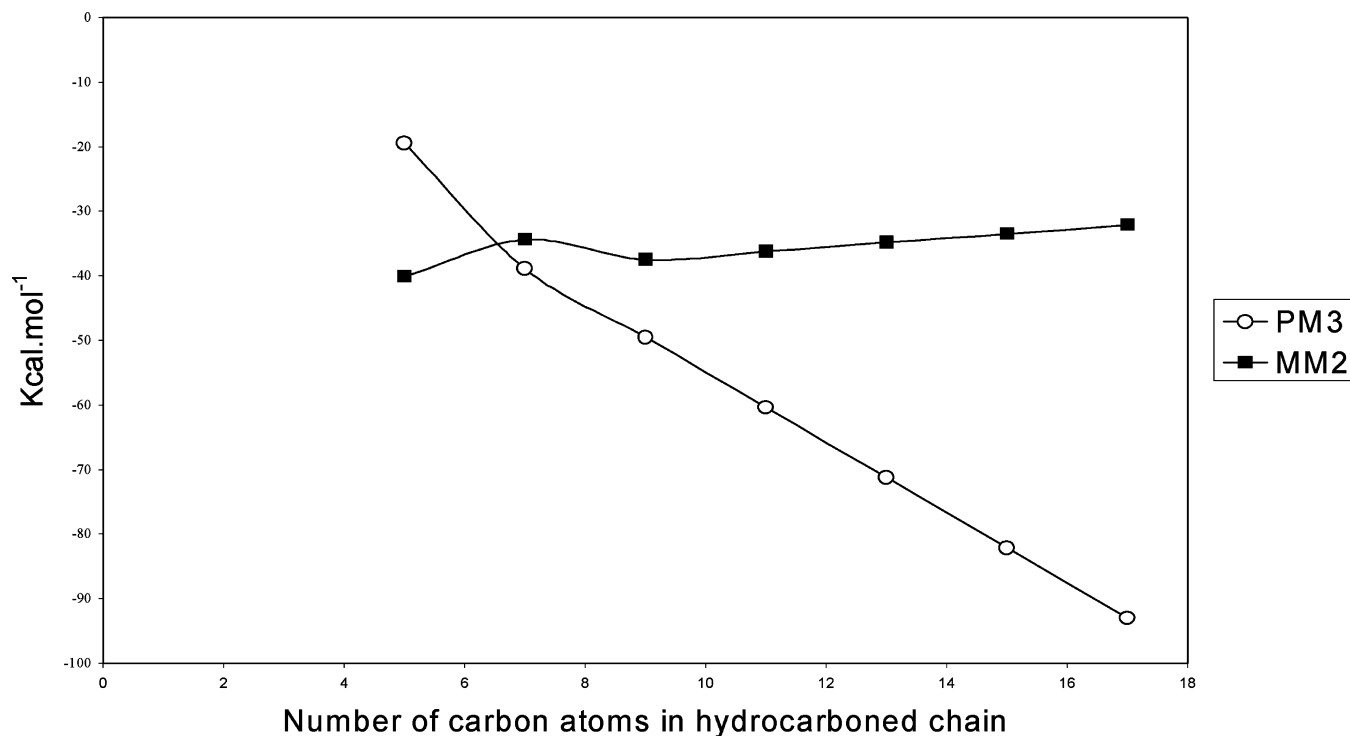


Figure 2. Steric energy (MM2) and the formation enthalpy (PM3) of the conformations of the RTAB with R from C₅ to C₁₇ for nonmicellized molecules.

energy, in their case with an enormous number of water molecules included. This kind of result is minimized if folding is allowed.

Jalili et al.³⁷ performed molecular dynamics simulations for a sodium dodecyl sulfate micelle in water using a coarse-grained model. The authors found that the interior of the micelle is completely void of solvent, as observed in other experiments^{38,39} and dynamics simulations.^{40–42}

Figure 2 presents the steric energy and the formation enthalpy of the conformations of the RTAB with R from C₅ to C₁₇. It may be seen that the steric energy slightly increases for the molecule isolated; however, the formation enthalpy (or ΔH°_f) is more and more negative from C₅ to C₁₇. This trend was found for an isolated molecule. In this sense, this may be related to an increase in the hydrophobic interactions of the “core” of the alkyl chains of the surfactants.

However, when micelles are considered, the energetic may be completely different. Configurational arrangements of different kinds of molecular structures may provide different results for calculations. The number of molecules per micelle (aggregation number) is very different. For example, dodecyltrimethylammonium bromide (DTAB) includes 60 molecules per micelle,⁴³ whereas hexadecyltrimethylammonium bromide includes 60 to 80, and decyltrimethylammonium includes 50 molecules per micelle.¹⁰ Aswal et al.⁴⁴ have studied the structures of mixed micelles of alkyltrimethylammonium where the constituent monomers differ in either their length or the headgroup size. Grossly speaking, the structural parameters of mixed micelles have values that are in between those for pure surfactants. The aggregation number depends on molecular length and the headgroup size and increases with increasing chain length or with decreasing headgroup size.

Haile et al.⁴⁵ have used the molecular dynamics method in a preliminary computer simulation study of intramolecular structure. Their first micelle model had 40 skeletal alkane chains, each composed of 13 soft spheres, mimicking a dodecyl surfactant.

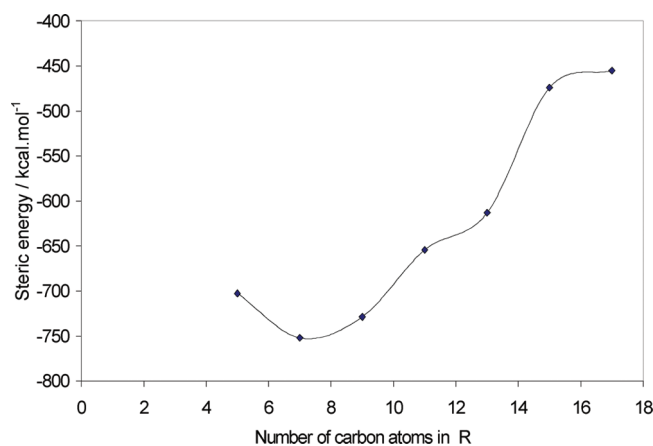


Figure 3. Steric energy for bidimensional model of a homogeneous micelle composed of 10 molecules as a function of number of carbon atoms in the hydrocarbon chain.

Unlike a traditional description of intramolecular structure, they find that only a very small fraction of chains are in an all-trans conformation, and even these are not, on the average, aligned along a micelle radius. Whereas a concentration of tails exists near the micelle center, the density of groups is not higher in the center than in outer shells.

Now, considering four bidimensional cuts in a sphere-like micelle, the total amount is near 10 to 20 molecules per bidimensional cut. Consequently, our model with 10 molecules is widely justified, especially because the main interest is to analyze conformational differences in the hydrophobic chains.

Figure 3 shows a less exothermic conformation in a homogeneous micelle when the number of carbon atoms in the hydrocarbon chain increases. Looking at the homogeneous micelle composed of 10 molecules, the steric energy also follows the trend found for the isolated molecules. C₇TAB shows a minimum energy point in its steric energy for the overall homogeneous micelles versus the number of carbon atoms in

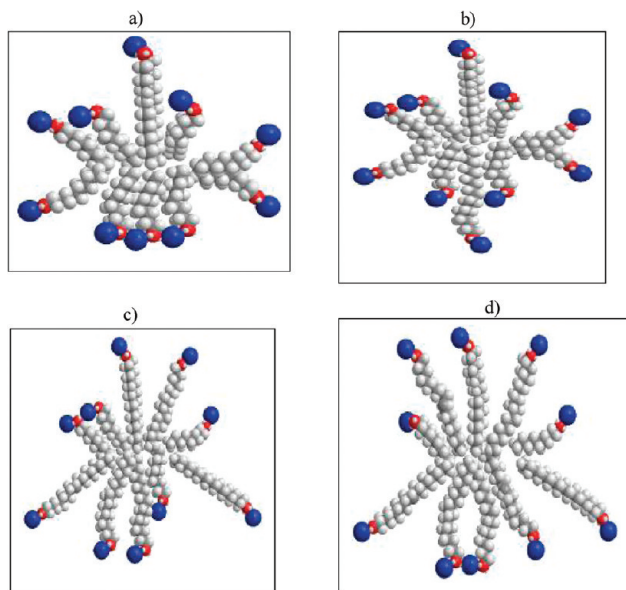


Figure 4. View of bidimensional cut of a spherical heterogeneous micelle for different surfactant proportion with linear chains. X_S = (a) 0.1, (b) 0.8, (c) 0.4, and (d) 0.2.

R. This could be due to possible extra stabilization for the chain conformation of the modeled micelles inside.

The most favorable ordering of the long chain molecules is with their axes parallel in average. This situation is not possible in micelles composed of only one kind of surfactant molecules because of the constraint produced by the spherical geometry of the micelle. Some of the surfactant chains must be folded to fulfill the spaces between other molecules. This also produces some water–hydrocarbon contact, a result in accordance with the work of Maillet et al.³⁶ Therefore, considering that our media is water with a high dielectric constant, the effect of the solvent is included implicitly in the shape analyzed for the micelle in our simulation as the initial structure, which was experimentally validated in our previous paper.⁹

Heterogeneous Systems. The heterogeneous systems studied are listed in Table 1. Considering the shorter surfactant, four groups of calculation were performed. Also, two different conformations for the longer hydrocarbon chain were considered in the heterogeneous micelles: linear and twisted chains. Figures 4 and 5 show the view of bidimensional cut of a spherical heterogeneous micelle for different surfactants proportion with linear and twisted chains, respectively. There is a tendency to avoid a “vacuum” in the core of the micelle leading to a linear form of the longest component of the pair in the case of heterogeneous micelles. Figure 4 clearly shows this tendency. Figure 5 shows that the inclusion of a shorter molecule may be intercalated between the extreme of the folded chain of the longest component and the micelle surface, replacing part of the hydrocarbon/water interface by a polar headgroup; then, “vacuum” is reduced.

The analysis of heterogeneous micelles can be done considering several aspects: (1) linear or twisted longer hydrocarbon chains, (2) effect of chain length on the final structure of the micelle and effect of twisting of the long chain on it, (3) impact of the difference in R chain length on the final structure of the micelle, and (4) impact of composition on the percentage of twisted and nontwisted micelles.

The analysis of bidimensional configurations of 10 linear chains with $\Delta n_C = 2$ for the systems C_{13} – C_{11} , C_{11} – C_9 , and C_9 – C_7 shows that the steric energy is more exothermic when

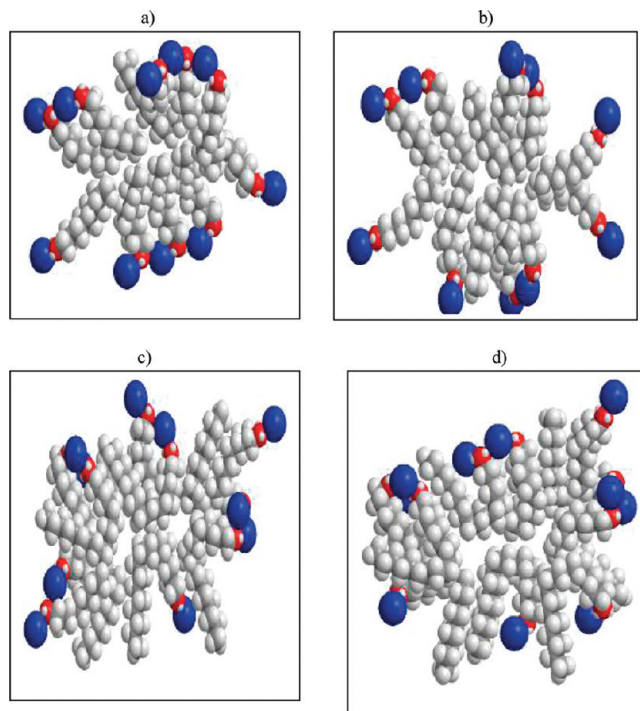


Figure 5. View of bidimensional cut of a spherical heterogeneous micelle for different surfactant proportion with twisted chains of the longer surfactant. X_S = (a) 0.1, (b) 0.8, (c) 0.4, and (d) 0.2.

the shorter component proportion increases. For the system C_7 – C_5 , it may be seen that it is less exothermic when the shorter component proportion increases. Between X_S 0.6 and 1, the steric energy becomes nearly stable, as shown in Figure 6. This implies a preferential composition of mixed micelles, the effect which was experimentally found in a previous paper.⁹

Figure 7 depicts the steric energy obtained from the analysis of bidimensional configurations of 10 linear chains with $\Delta n_C = 4$. It is clearly visible that for systems C_{13} – C_9 and C_{11} – C_7 the steric energy of formation is more exothermic when the shorter component proportion for the modeling conformation increases. Between X_S 0.8 and 1, the steric energy becomes nearly stable.

Figure 8 shows the steric energy obtained of the analysis of bidimensional configurations of 10 linear chains with $\Delta n_C = 6$. The micelle generation is more exothermic for the modeling conformation when the shorter component proportion increases; between X_S 0.8 and 1, the steric energy becomes nearly stable. For the system C_{11} – C_5 , the steric energy of formation is less exothermic when the C_5 is in greater proportion; the C_5 destabilizes the system when it is present in high proportion.

Spherical micelles are formed by a mixture of molecules having stretched chains and others having their chains folded to fill the spaces near the surface created by the radial disposition of the stretched molecules. This packing reduces the hydrocarbon/water contact at the micelle surface. Then, the inclusion of a shorter surfactant in a micelle of a longer homologous surfactant may produce stabilization because the shorter surfactant may fill these spaces with a reduced folding. The advantage must be small if Δn_C is small but must increase with increasing Δn_C . This is the behavior observed in the interaction parameter β_M ; it depends linearly on the difference in chain length Δn_C , and the interaction is more attractive when Δn_C increases.⁹

The analysis of bidimensional configurations of ten linear chains with $\Delta n_C = 8$ shows that the steric energy is more exothermic in the micelle generation for the modeling confor-

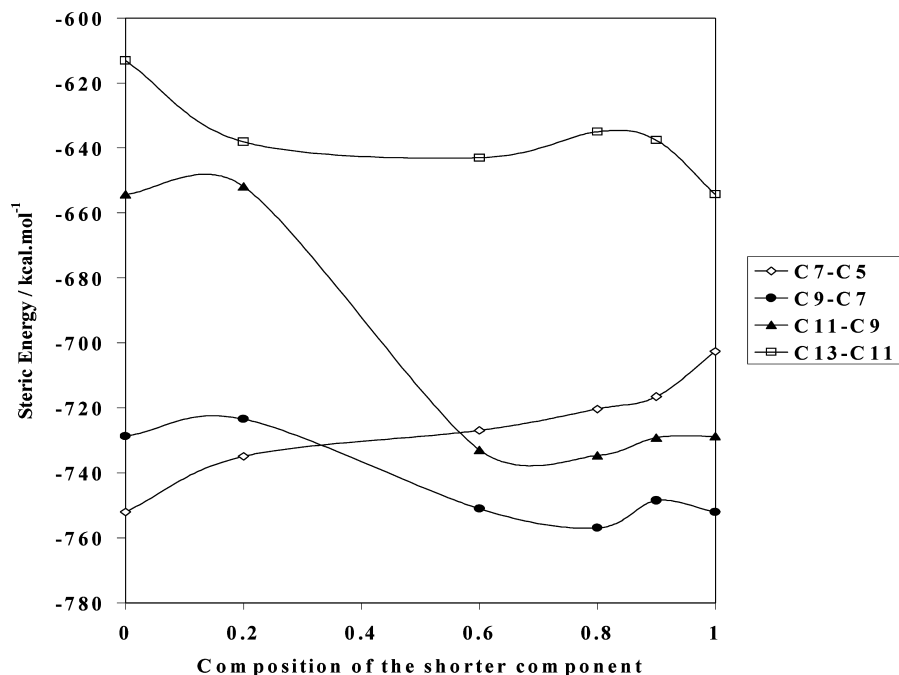


Figure 6. Steric energy as a function of the composition of the shorter component for $\Delta n_C = 2$.

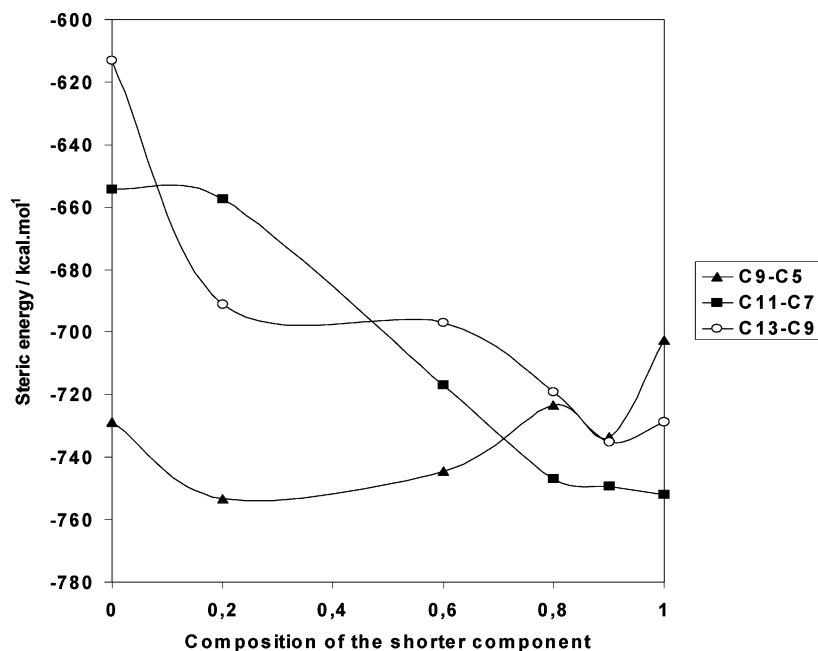


Figure 7. Steric energy as a function of the composition of the shorter component for $\Delta n_C = 4$.

mation when the shorter component proportion increases. For the system $C_{13}-C_5$, the steric energy is less exothermic when the C_5 is in greater proportion, as shown in Figure 9. It may be seen in Figure 9 that for $\Delta n_C > 6$ the C_5 destabilizes the system when it is present in high proportion.

From Figures 6–9, the surfactant chains are all linear.

The inclusion of a short homologous surfactant in a micelle produces a reduction in the folding of the longer component. If the difference in chain length is not high, then the shorter surfactant must also fold to fulfill the spaces left by the longer surfactant.⁹ The increase in stabilization above $\Delta n_C > 5$ probably reflects the fact that the need of folding of the shorter surfactant is reduced when the difference in chain length exceeds this value. Because the micelle core is of liquid nature, the folding of a chain must reduce its freedom of motion in comparison with the stretched ones.²⁷

Figure 10 shows a cut for the mixture with the proportion: $0.2C_{13}-0.8C_5$. The longer chain also folds preferentially to accommodate the shorter ones, giving extra stability to the micelles.

The role of twisting of the hydrocarbon chains in the steric energy in bidimensional heterogeneous configurations with $\Delta n_C = 8$ is shown in Figure 11. The twisted conformation implies that the chains are folded to be accommodated to fill the empty spaces within the micelle (100% of the corresponding chains). For systems $C_{15}-C_7$ and $C_{17}-C_9$, the comparison of linear configurations with twisted configurations shows that the micelle generation is more exothermic when the longer surfactant is twisted and the shorter surfactant is in high proportion and not twisted. The greater stabilization is observed when the shorter surfactant proportion is 0.6. For the systems $C_{13}-C_5$, the micelle generation is more exothermic when the conformation is linear

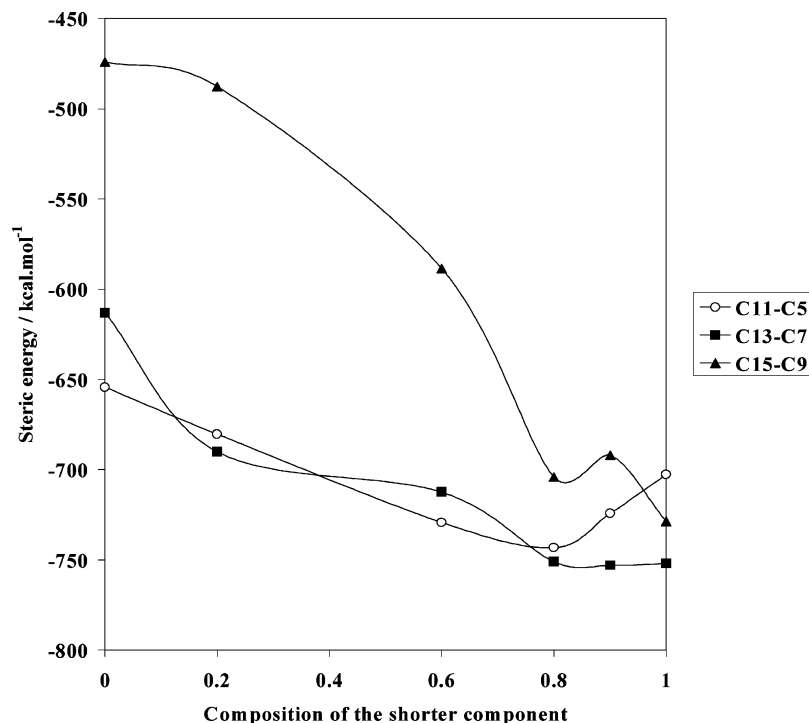


Figure 8. Steric energy as a function of the composition of the shorter component for $\Delta n_C = 6$.

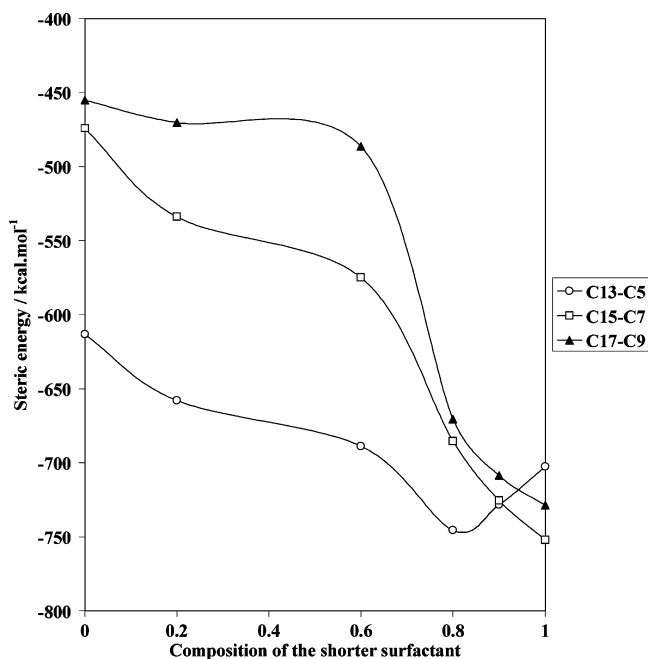


Figure 9. Steric energy as a function of the composition of the shorter component for $\Delta n_C = 8$.

and the proportion of C_5 is increased. This conclusion supports the explanation given to the experimental results shown in the previous works on homologous mixtures.⁹ In Figures 10 and 11, the surfactant with the long chain is twisted.

In the light of this interpretation, both components are affected by the inclusion in the mixed micelles. As said above, in a pure surfactant micelle, some of the chains are extended while others must be folded to fulfill the spaces between the extended surfactant molecules to reduce the hydrocarbon/water interface. However, some part of the chain, about three to four methylene groups by each micellized surfactant molecule, remains in contact with water.^{26–35} This is because it is impossible to cover

the entire micelle surface with the polar headgroups. The inclusion of a shorter molecule may be intercalated between the extreme of the folded chain of the longest component and the micelle surface, replacing part of the hydrocarbon/water interface by a polar headgroup. This situation reduces the surface free energy of micelles. The energetic advantage must increase with Δn_C because when Δn_C is large, the longest component can fold its distal end more easily in the space within the center of the micelle and the end of the shorter component chain. This situation must be more favorable when that space is of five methylene groups or more (i.e., ~ 0.66 nm length or more). Both the longer and the shorter chains in the mixed micelle expose less hydrocarbon surface to water than in the respective pure surfactant micelles and can be less folded.⁹

The free energy in excess $\Delta\mu_{\text{mix}}^{\text{excess}}$ is calculated as the difference between the partial molar free energy of the mixed micelles and that calculated according to the ideal behavior. Negative value indicates an attractive interaction between the two different surfactant molecules and the probability of the existence of synergism between them. (See Figure 12.) This could be interpreted considering that the free energy in excess is more exothermic when the shorter component proportion and Δn_C increase, which is in agreement with previous results of steric energy.

Figure 13 depicts the dependence of the micelle composition (X_{C10TAB} = mole fraction of the shorter component in the micelle) as a function of the total surfactant mixture composition (α_{C10TAB} = mole fraction of the shorter surfactant in the mixture) and the difference in length of the hydrocarbon chains between the two surfactants of the mixture, Δn_C .⁹ It shows that the larger the value of Δn_C the lower the proportion of the shorter surfactant in the mixed micelle. This means that the inclusion of the longer surfactant molecules in the mixed micelles is favored by the presence of a shorter homologous surfactant, and that effect increases with the difference in chain length. See ref 9.

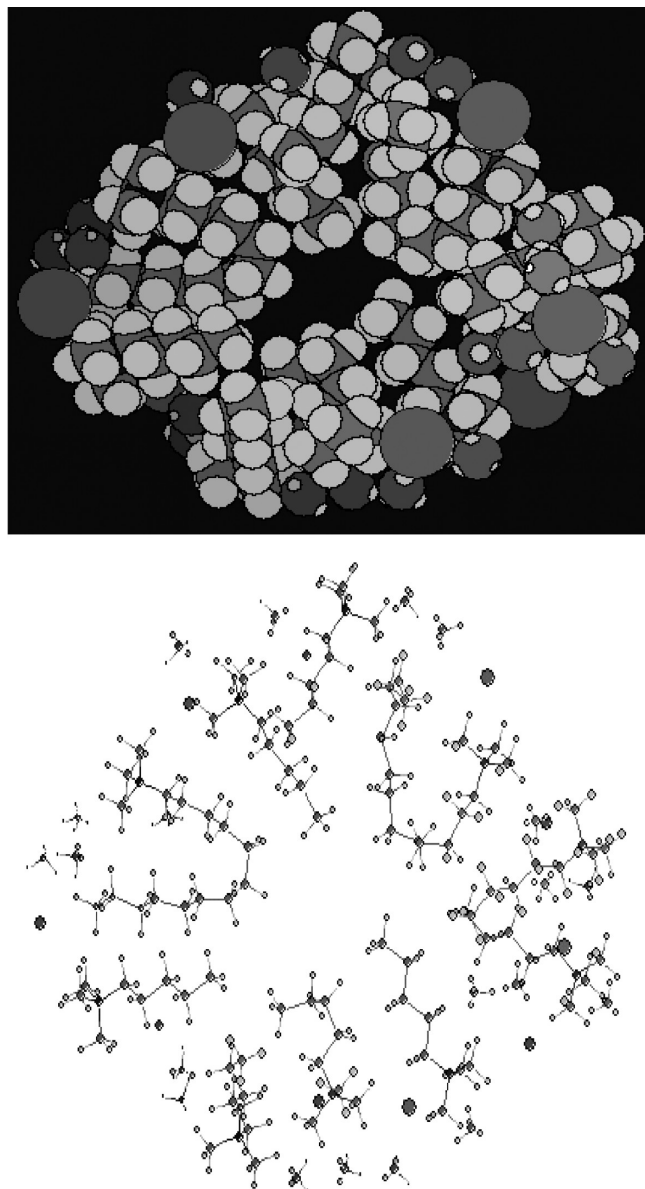


Figure 10. Cut for the mixture with the proportion: $0.2C_{13}-0.8C_5$.

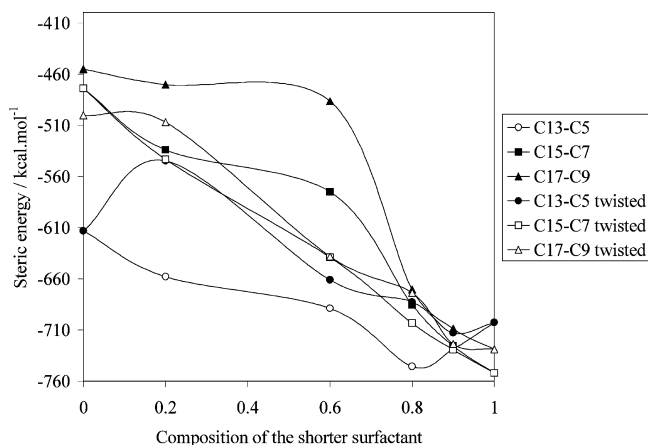


Figure 11. Steric energy as a function of the composition of the shorter component for $\Delta n_C = 8$ for linear and twisted configurations.

The final structure of the heterogeneous micelles may be conditioned by these factors: (1) difference in the number of carbon atoms between hydrocarbon chains, (2) tendency to twist or not of the longer surfactant to form the micelle, and (3) impact

of the length of the hydrocarbon chain and the difference in the number of carbon atoms in the stability of the final form of the micelle.

These characteristics may be related to our findings in such a way that several conclusions may be presented: (1) We confirmed that there is a tendency to avoid a "vacuum" in the core of the micelle, leading to a linear form of the longest component of the pair in the case of heterogeneous micelles. Figure 4 clearly shows this tendency. This fact is known, but Figure 4 shows that to avoid the formation of voids, the shorter component will be immersed in the micelle when all components are not folded. This is an energetically unfavorable situation because polar head groups are immersed in a polar medium (the micelle core), and water-filled pockets created at the micelle–water interface increase the hydrocarbon–water contact. (2) There is a tendency to accommodate shorter chains with interactions, mainly hydrophobic forces with twisting of the longer component of the surfactant pair (inside the micelle). On the surface, hydrophobic forces are very important. There are different local balance of van der Waals and hydrophobic forces to create the final micelle structure. (3) There would be a distribution inside the micelle of twisted and linear forms considering local conformational minima, as suggested in a previous article.⁹ (4) Deformations of the spherical form are expected in these systems. This was detected in the aqueous mixed system decyltrimethylammonium bromide ($C_{10}TAB$)–hexadecyltrimethyl ammonium bromide ($C_{16}TAB$).¹⁰ (5) The dependence on composition cannot be related to the shortest surfactant because the shortest is not thought to have different conformational species at once. The shorter surfactant is very difficult to twist; conversely, the longer surfactants are much easier to twist. Therefore, C_7 is hardly twisted, but C_{11} can twist without energetic problems (results not shown, comparing twisted vs linear forms of surfactants). At least, a string of four CH_2 by side (with a pivotal CH_2 in a point) is a needed structure to think of a symmetric twisted chain. Therefore, the total number of methylene groups is nine. In a micelle composed of surfactants with nine CH_2/CH_3 groups, there would probably be more linear than twisted chains. The twisted chain generates a vacuum between the "sides" of the chain. This vacuum is filled with a shorter chain, for example, when the difference between surfactants in mixed micelles is four, six, or eight in number of carbon atoms. (6) The solvent effect of water surrounding micelles is not significant enough to affect the validity of the simulation results, which did not take into account the effect of the polar solvent.

This simple modeling would predict a wide dispersion of structures, especially when the differences are six or eight carbon atom numbers and one of the components of the pair is shorter than C_9 .

We tested in one of our configurations with higher levels of theory using 16 chains for the system: $C_{17}-C_5$ with $X_S = 0.5$ and comparing linear conformation with twisted conformation with 50% of the C_{17} twisted chains. We applied MOPAC2009 p.m.3 and MOPAC2009 p.m.6 for the comparison of both configurations. The results of the MM2 calculations indicate that the configuration with 25% of twisted chains is more stable in 17 kcal/mol, whereas considering the MOPAC2009 p.m.3, the configuration C_5-C_{17} with 25% of the C_{17} twisted is more stable by 32 and by 28.3 kcal/mol for MOPAC2009 p.m.6.

These results with higher levels of theory (PM3 and PM6 for this particular configuration), even when they are not quantitatively similar as expected, are in the same line as our former results with MM2: partial twisting of long chain

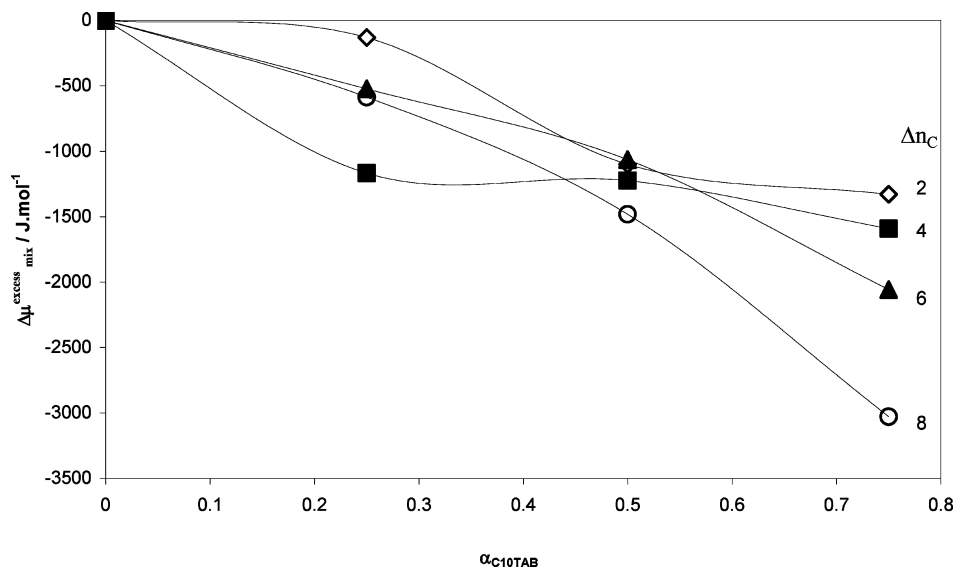


Figure 12. Free energy in excess for different C₁₀TAB proportion and the difference in chain length Δn_C .

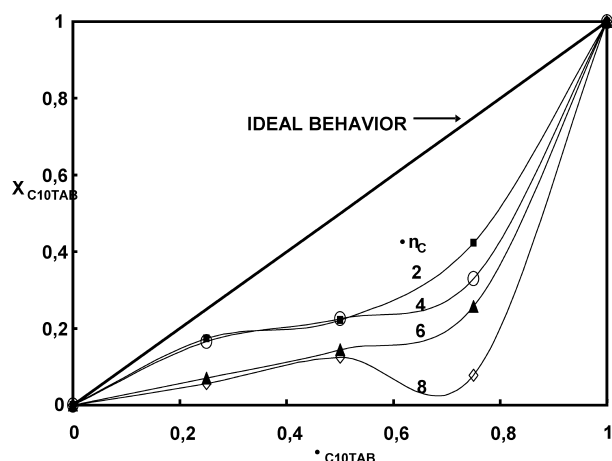


Figure 13. Dependence of the micelle composition X_{C10TAB} as a function of the total surfactant mixture composition α_{C10TAB} and the difference in length of the hydrocarbon chains between the two surfactants of the mixture, Δn_C . See ref 9.

surfactant stabilizes the structure of the micelles in comparison with the all linear structure.

The testing of this hypothesis using the higher levels of theory previously mentioned is a different approach than a semiempirical method plus molecular mechanics, as presented here. However, the results for a particular case are similar to the one obtained with PM3 with MOPAC2009 and in agreement with the results of MM2, qualitatively.

Conclusions

In micelles composed of different homologous surfactants, one with a shorter and the other with a longer hydrocarbon chain, a shorter molecule may be intercalated between the extreme of the folded chain of the longest component and the micelle surface, replacing part of the hydrocarbon/water interface by a polar headgroup. This situation reduces the surface free energy of micelles. The energetic advantage must increase with Δn_C because when Δn_C is large, the longest component can fold its distal end more easily in the space within the center of the micelle and the end of the shorter component chain. This situation is more favorable when $\Delta n_C > 5$, being the shorter chain in the range of C₅–C₇.

The exothermic values of the found steric energy evidence a stronger attraction between components of homologous surfactants mixtures. When one surfactant of the binary mixture has a long chain, micelle formation is favored.

It was demonstrated that the inclusion of a shorter surfactant in the mixture and the twisting of the longer surfactant makes more exothermic the modeling conformation than in the case when all homologous component are not twisted.

It is noticeable that the trend found in aqueous phase (as found experimentally) and in the gas-phase modeling (though simulation) is the same. This shows that the solvent effect of water surrounding micelles is not significant enough to affect the validity of the simulation results, which did not take into account the effect of the polar solvent. This was initially thought to be the case because our system of study was the interior of the micelle, where the effect of the polar solvent is already shielded by the polar groups. The micelle volumes were imposed data in the model and taken from experimental data, and thus the effect of the solvent in determining the micellar volume is already taken into account in this way.

All preceding findings agree with the experimental results in micelles formed by a mixture of surfactant homologous⁹ including the dependence of the micelle stabilization on Δn_C . Then, this work gives theoretical support to the explanations on the origin of this behavior given in that work.

This Article is intended to be a first step in the evaluation of bidimensional interactions, with the aim of extending the strategy to other kind of mixtures of anionic and cationic surfactants, and also in the analysis of tridimensional structures with higher levels of theory (such as tridimensional spherical/cylindrical or wormlike structures of micelles).

Acknowledgment. This work was financed by a grant of the Universidad Nacional del Sur and another from the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET). M.L.F. is an independent researcher, M.A.M. is an adjunct researcher and M.B.S. is an assistant researcher of the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET).

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