

Phase Behavior of Fatty Acid/Oil/Water Systems: Effect of the Alkyl Length Chain Acid

B. Bravo^{a,*}, N. Márquez^a, F. Ysambertt^a, G. Chávez^a, A. Cáceres^a, R. Bauza^a,
A. Gracia^{a,b}, J. Lachaise^b, and J.L. Salager^c

^aLab. Petroquímica y Surfactantes, Facultad de Ciencias, Universidad del Zulia, Maracaibo, Venezuela; ^bLab. Fluides Complexes, Université de Pau, Pau, France, and ^cLab. FIRP, Ingeniería Química, Universidad de los Andes, Mérida, Venezuela

ABSTRACT: The phase behavior of different fatty acids (FA) in pseudo-ternary mixtures [(water)/(FA) + (alcohol)/(oil)] was studied. The Winsor I-III-II transitions of ionized compounds were attained by varying the FA composition through the formulation scan. The middle-phase volume, the pH of the optimum system, and the partition coefficient increased with the chain length of FA. Conversely, the acid partition coefficient allows calculation of the Gibbs free energy of transfer of a CH₂ group from oil to water, which is found to be +0.87 J/mol.

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KEYWORDS: Fatty acid, formulation, middle phase, partition coefficient, pH, phase behavior.

Lipids, including fatty acids (FA), are important groups of amphiphilic molecules that are used in stabilizing oil/water (o/w) interfaces. These molecules may self-assemble into a variety of aggregates ranging from micelles to bilayers and lamellar multilayers or other forms of liquid crystalline structures (1–3).

Low molecular weight amphiphiles such as phospholipids are capable of forming vesicles from both their aqueous solutions and o/w emulsions. Strong evidence of the presence of FA vesicles in o/w emulsions was provided by Ferezou et al. (4), Hajri et al. (5), and Westsen and Wehler (6), who reported that in most FA-stabilized commercial o/w formulations, lipids co-exist as a dispersed phase with emulsified droplets.

Conversely, reports often suggest that vesicles are usually produced spontaneously from surfactant solution without the application of any external stimuli. Aqueous FA solutions are able to spontaneously exhibit vesicles, which are formed as the pH is changed by deprotonation of FA molecules (7). In these systems, carboxylate anions are regarded as (hydrophilic) surfactants while the corresponding FA is

considered as a (lipophilic) co-surfactant. Therefore, the formation of vesicles in these systems strongly depends on the carboxylate anion–carboxylic acid mixture ratio. A higher fraction of undissociated FA generally leads to a more lipophilic mixture and vice versa. When the proper acid/salt mixture is attained, a natural curvature of almost zero is reached and lamellar structures are likely to develop. Pautot et al. (8) reported that, provided the correct initial composition is chosen, ternary systems consisting of FA, oil, and water are capable of spontaneously generating both the emulsified droplets and multilamellar aggregates of the vesicle type under most experimental conditions.

Since the phase behavior of ternary surfactant/oil/water systems was first elucidated by Winsor (9) 50 years ago, there has been considerable research to understand increasingly complex situations. In the 1970s, the oil price surged and the prospect of enhanced oil recovery drove scores of industrial and university research teams to focus on these topics. As a consequence, the formulation variables were recognized and their influence was established in a quantitative fashion for many systems. The phase behavior of surfactant/oil/water systems is usually referred to via the Winsor model. When the surfactant affinity for the water phase dominates, a so-called Winsor Type I (WI) phase behavior takes place in which an aqueous surfactant-rich phase is in equilibrium with an excess oil phase. The analogous situation, in which the surfactant affinity for the oil phase dominates, is referred to as Winsor Type II (WII) phase behavior. When the affinity of the surfactant for the oil phase exactly equilibrates its affinity for the water, a so-called Winsor Type III (WIII) system is attained in which a microemulsion containing most of the surfactant is in equilibrium with both water and oil excess phases. As the formulation is changed progressively, a phase behavior transition takes places in the direction WI→WIII→WII or vice versa.

A deeper insight into water/oil/surfactant/alcohol quaternary systems has been gained (10–15), particularly in relation to enhanced oil recovery (16–17). These studies have led to a good understanding of the relationships between the nature of the surfactant, oil, alcohol, and composition parameters and the phase behavior (especially the multi-

*To whom correspondence should be addressed at Laboratorio de Petroquímica y Surfactantes, Departamento de Química, Facultad Experimental de Ciencias, Universidad del Zulia, Apartado 526, Maracaibo, Venezuela.
E-mail: belgicabravo@yahoo.es, bbravo@luz.ve

Abbreviations: CMC, critical micelle concentration; CN, chain length; FA, fatty acid; HPLC, high-performance liquid chromatography; o/w, oil/water; WI, Winsor Type I phase behavior; WII, Winsor Type II phase behavior; WIII, Winsor Type III phase behavior.

phase behavior, often named the Winsor III→II transition) within pseudo-ternary diagrams. In order to obtain three-phase systems (WIII) to detect the optimal formulation (Winsor $R = 1$), the effect of the FA chain length on the phase behavior was studied for FA/oil/water systems.

EXPERIMENTAL PROCEDURES

Materials. The following acids were studied: caprylic (C_8), capric (C_{10}), lauric (C_{12}), myristic (C_{14}), palmitic (C_{16}), and stearic (C_{18}), all provided by Merck. They are referred to as C_n , where n indicates the number of carbon atoms in the acid molecule. NaOH (99.9% pure) and NaCl (99.9% pure) were provided by Merck. The oil phase was *n*-heptane, purchased from J.T. Baker. Methanol (MeOH, 99.9% pure, Merck) and acetonitrile (ACN, 99.9% pure, Merck) were used as mobile phase for high-performance liquid chromatography (HPLC). *n*-Butanol (Merck) was used as co-surfactant.

FA/oil/water system preparation. FA/oil/water systems are studied according to the so-called one-dimensional scan technique. For each of the series, a dozen test tubes are prepared, each containing oil and water in identical amounts and the respective acid, with acid concentration changing progressively from one test tube to the next. Test tubes typically contain 10 mL of *n*-heptane (oil phase), 10 mL of distilled water (with NaOH and NaCl as indicated in Table 1) as water phase, and x grams of commercial FA. The FA are introduced as an oil solution. The tubes are closed with a screw cap and placed in a vertical position to equilibrate at 25°C. They are gently stirred once a day for a period of 1 wk to improve the contact between phases; then they are left to rest for at least

2 wk to fully equilibrate. After equilibration, the oil and aqueous phase volumes are observed and registered. The acid concentration in the different phases is determined using an HPLC method, as described elsewhere (18).

RESULTS AND DISCUSSION

Enhanced oil recovery by alkaline flooding was proposed some years ago as an inexpensive way to take advantage of the acid components that occur naturally in some crude oils (19–20). The stabilization of *o/w* emulsions can also be attained in this way. In these cases the carboxylic acids contained in the crude oil adsorb at the *o/w* interface, where they are neutralized to form carboxylic salts with surfactant properties such as tension-lowering or emulsion stabilization. To observe the phase behavior of FA in an *o/w* system, a concentration scan with a different FA was performed. The phase behavior diagram of the FA/water/*n*-heptane system was explored at points containing 0.4 g to 2.0 g per 100 mL of FA in the systems. When the acid concentration was increased from this point, the number, volume, and composition of phases were registered for each system. The systems were described according to the Winsor classification of multiphase systems.

Figure 1 shows the general map of Winsor transitions for lauric, myristic, and palmitic acid. The results show it is possible to obtain a wide range of WIII systems. The optimum formulation (three-phase system where the middle phase is in equilibrium with the same volume of water and oil excess phases) was reached at 1.4 g, 1.2 g, and 1.0 g per 100 mL for the lauric (C_{12}^*), myristic (C_{14}^*), and palmitic (C_{16}^*) acid,

TABLE 1
FA Concentration in the Three Phases of the O/W Optimum System

Acid	$K_{r(o \rightarrow w)}$	Oil phase (%) ^a	Water phase (%) ^a	Middle phase (%) ^a
Lauric	107	58.96	0.55	41.04
Myristic	215	43.02	0.20	56.98
Palmitic	439	31.61	0.07	68.39

^aPercentage of total volume occupied by this phase.

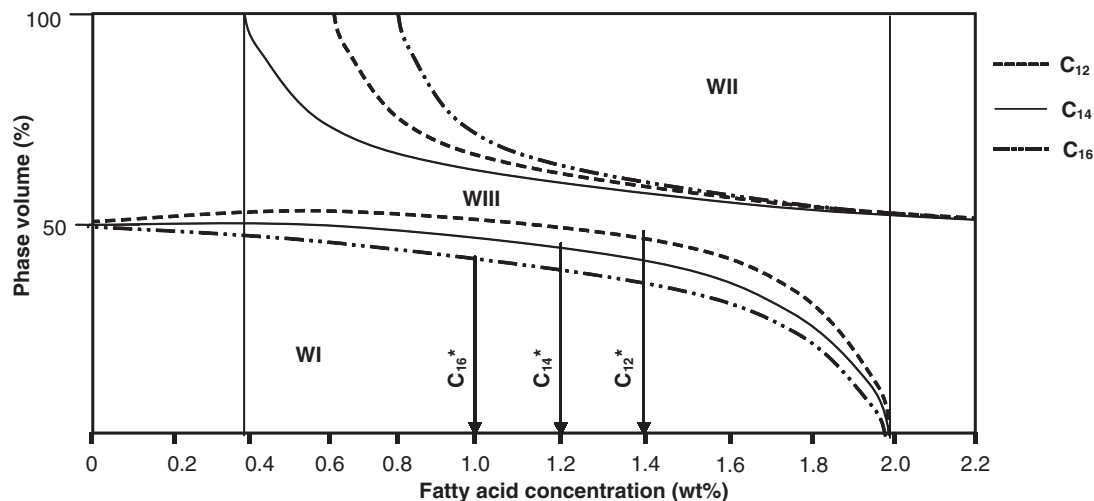


FIG. 1. Map of the phase behavior of systems containing (lauric, myristic, and palmitic) acid/heptane/water.

respectively. Figure 1 shows that a WI \rightarrow WIII \rightarrow WII transition takes place as concentration increases.

Conversely, the middle-phase volume variation of the WIII system is shown in Figure 2 for each acid at different concentrations. Figure 2 shows the linear relationship of the middle-phase volume of the acid concentration in the system. The intercept point of these curves (where the middle-phase volume is zero) corresponds to the concentration of acid in excess phases. Because there is essentially no acid in water, it indicates the acid concentration in the oil phase.

It is worth remarking that the middle-phase volume for the palmitic acid was always larger for lauric acid, which indicates the better solubilization attained with the former on a weight basis, as well as on a molar basis, since the molecular weight is relatively close.

The pH of the optimum system was measured for each acid scan. Figure 3 shows the linear relationship between the optimum pH and the chain length of the FA, as expected from previous studies (21). Moreover, the optimum pH system is independent of the acid concentration, probably because of a buffer system that results from the acid-base equilibrium (21).

Another difficulty arises when the pH-sensitive system contains both an aqueous phase and an oil phase. This is because the dissociated (ionic) and undissociated (nonionic) species are likely to selectively partition or fractionate between water and oil phases. However, it can generally be assumed that the amount of dissociated salt in oil is negligible, whereas the amount of undissociated acid in the water phase must be taken into account because it appears in the dissociation equilibrium (21–22). The partition coefficient (K_r) of the undissociated acid between oil and water phases is the ratio of the FA concentration in the oil excess phase ($[HA_o]$) and the concentration in the water excess phase ($[HA_w]$), as indicated in Equation 1.

$$K_r = \frac{[HA_o]}{[HA_w]} \quad [1]$$

Many HPLC methods are available for the analysis of FA (18, 23–27). In the present case, the acid content in the oil, middle, and water phases was determined using a reverse-phase HPLC method discussed elsewhere (18).

The variation of the partition coefficient is plotted in Figure 4A as a function of the alkyl chain length (symbolized

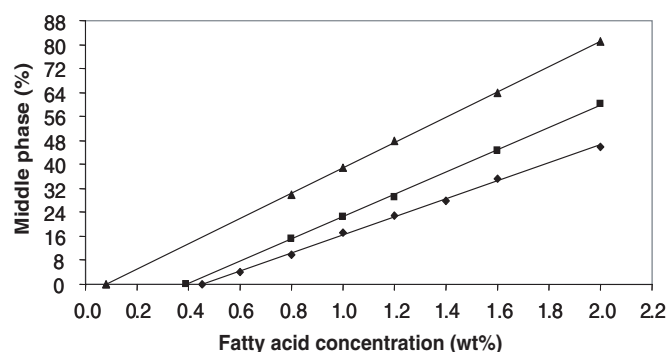


FIG. 2. Middle-phase volume versus acid concentration (wt%) for (◆) lauric, (■) myristic, and palmitic (▲) acids in the heptane/water system.

by “CN”). Figure 4 data show that the logarithm of the partition coefficient follows a linear increase versus the alkyl-group length. The overall mole inventory of the FA in the three-phase optimum system is shown in Table 2. These data show the fractionation of the more lipophilic acid in the middle phase. This behavior can be seen more clearly in Figure 4B, where the logarithm of $[HA_o]$ decreases linearly with the chain length of the acid. Therefore, for long-chain FA, K_r is larger than 100.

On the other hand, it is known that the addition of alcohol produces a phase-behavior transition of WI \rightarrow WIII \rightarrow WII for the ethoxylated alkylphenol and sulfonated surfactants (28–30). Because soaps are anionic surfactants, alcohol is added in high-soap concentration systems to obtain a microemulsion instead of a gel mesophase (28). To study the effect of alcohol in a WIII system, an alcohol concentration scan is carried out by increasing amounts of *n*-butanol. Figure 4A shows a comparison between variation of the partition coefficient versus CN for a FA/*n*-heptane/water system with (□) and (■) without *n*-butanol. In both cases, the linear variation has the same slope (0.2). It is worth noting that the presence of alcohol decreases the partition coefficient of the acid by a factor close to 100, which is an indication that the butanol increases the affinity of the acid for the water phase. Figure 5 shows that, as more alcohol is added, the middle-phase volume of the WIII system decreases, because the alcohol partitions more in excess phases. This change essentially follows the variation in the middle-phase volume, so that the concentration of FA in the middle phase remains roughly constant.

A relationship between the partition coefficient and the chemical potential of the surfactant is required to thermodynamically describe the optimum system equilibrium. As initially suggested by Cratin (31), the variation in the partition coefficient can lead to interesting information from the formulation point of view. In the present case of a three-phase system, the chemical potential of the surfactant can be written as

$$\mu_w = \mu_w^* + RT \ln C_w \phi_w \quad [2]$$

$$\mu_o = \mu_o^* + RT \ln C_o \phi_o \quad [3]$$

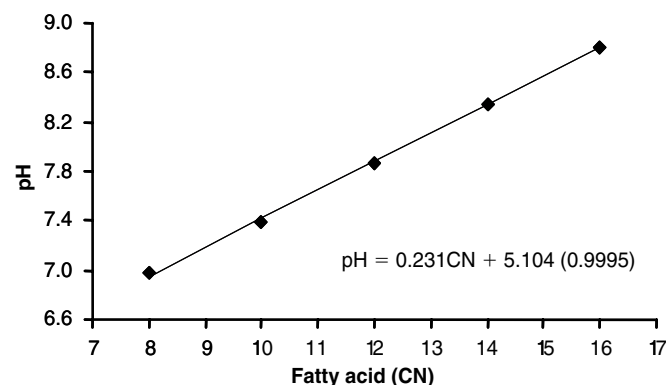


FIG. 3. Variation of the pH of the optimum system with chain length of FA.

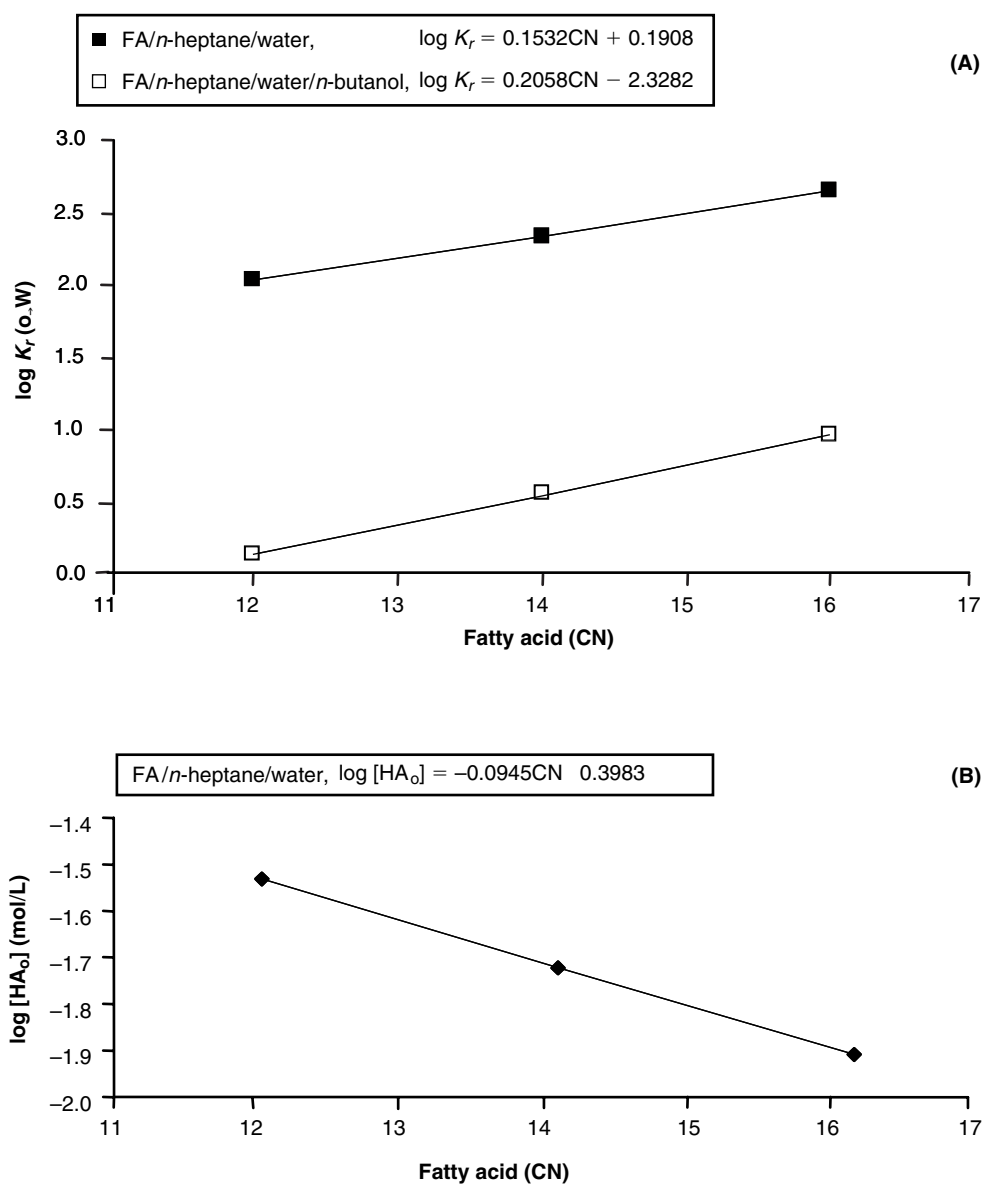


FIG. 4. (A) Partition coefficient of FA between oil and water, in the presence and absence of alcohol. (B) FA molar content in the oil phase.

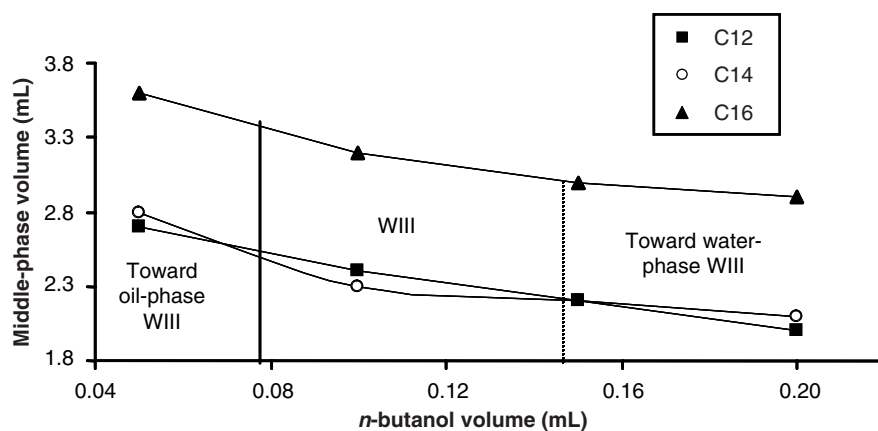


FIG. 5. Middle-phase volume variation by adding alcohol in the FA/water/heptane system.

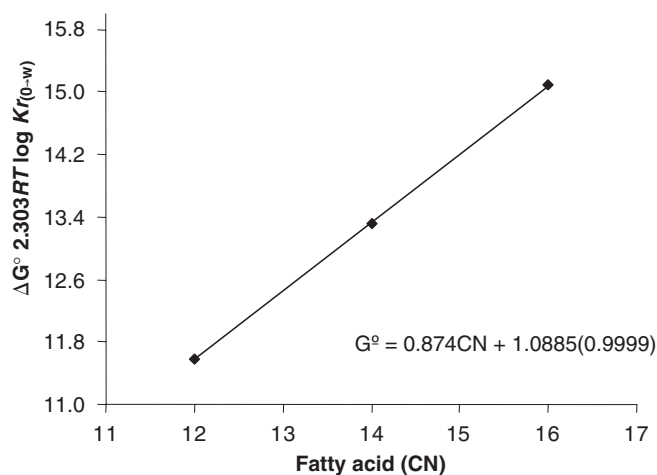


FIG. 6. Gibbs free energy of transfer of FA from oil to water phase.

TABLE 2
Composition of Phases

Acid	g Acid / 100 mL	mL NaOH (0.6 mol/L)	mL NaCl (0.6 mol/L)	Moles NaCl	Moles NaOH	Fi ^a
C ₁₂	1.4	0.8	9.2	0.00552	0.000480	0.400
C ₁₄	1.2	1.2	8.8	0.00528	0.000720	0.686
C ₁₆	1.0	1.6	8.4	0.00504	0.000960	0.768

^aFi = (moles of added NaOH) / (initial moles of acid)

where μ^* stands for the standard chemical potential in a given reference state, C is the dimensionless concentration, and ϕ is the activity coefficient. Superscripts “w” and “o” refer to the water and oil excess phases, respectively. Because the water and oil phases are at equilibrium in a three-phase system, their chemical potentials are the same. It can be assumed that the activity coefficients are unity because the surfactant concentration in the water excess phases is low (typically at the critical micelle concentration). As a consequence, the partition coefficient K_r of the surfactant between the water and oil phases may be written as

$$RT \ln K_r = RT \ln C_w / C_o = \mu_o^* - \mu_w^* \quad [4]$$

The standard chemical potential difference contains only energetic terms. According to Cratin it can probably be written as a summation of partial contributions according to the first law of thermodynamics. It is worth noting that a similar assumption led to the development of the surfactant affinity difference concept as a numerical expression of the generalized physicochemical formulation (32).

The Gibbs free energy of transfer of a methylene group from *n*-heptane to water can be calculated by the experimental coefficient values (slope and intercept) (31–34) shown in Figure 6. The value for $\Delta\mu^*(\text{CH}_2 \text{ group}) = \mu_o^* - \mu_w^*$ is found to be +0.87 J/mol at 25°C. As expected, the positive sign of the free energy variation indicates that the transfer from oil to water phase of a CH₂ group is unfavorable.

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Bélgica Bravo is an assistant professor of chemistry at the University of Zulia, Maracaibo, Venezuela. She received a B.S., an M.S.,

and a Ph.D. in chemistry from the University of Zulia. She worked on microemulsions as an exchange doctoral student at the University of Pau, France.

Nelson Márquez is a professor of chemistry at the University of Zulia, Maracaibo, Venezuela, where he founded LPS laboratory. He earned a B.S. in chemistry from the University of Zulia, an M.S. degree in analytical chemistry from the University of Georgia, USA, and a Ph.D. from the University of Pau, France. He has been working in HPLC analytical chemistry for the past 25 years.

Fredy Ysamberdt is a professor of chemistry at the University of Zulia, Maracaibo, Venezuela. He is the current director of LPS laboratory. He received a B.S. in chemistry and an M.S. in environmental science from the University of Zulia, and he received a Ph.D. from the University of Pau, France. He has been working in analytical chemistry of surfactants and polymers for the past 20 years.

Gerson Chávez is an assistant professor of chemistry at the University of Zulia, Maracaibo, Venezuela, where he earned a B.S., an M.S., and a Ph.D. in chemistry.

Ana Cáceres is a professor of chemistry at the University of Zulia, Maracaibo, Venezuela. She earned a B.S. in chemistry from the University of Zulia, a graduate diploma from the University of Cordoba, Spain, and a Ph.D. in chemistry from Sheffield Hallam University, UK.

Roberto Bauza is a professor of chemistry at the University of Zulia, Maracaibo, Venezuela. He received his B.S. and M.S. degrees in chemistry from the University of Zulia, and he received a Ph.D. from the University of Cordoba, Spain.

Alain Graciaa is a professor of physics at the University of Pau, France, where he is the current director of the Research Center. He earned a Ph.D. in physics from the University of Pau, and has been working in microemulsions for enhanced oil recovery and other applications for the past 30 years.

Jean-Bernard Lachaise is a professor of physics at the University of Pau, France. He received a Ph.D. in physics from the University of Pau, France, where he heads the colloid research group at LFC. He has been involved in the research and development of emulsions and microemulsions for the past 30 years.

Jean-Louis Salager is a professor of chemical engineering, and is the founder and director of the FIRP laboratory at the University of the Andes. He received a degree in chemical engineering from ENSIC, the University of Nancy, France, and a Ph.D. in chemical engineering from the University of Texas at Austin. He has been involved in research and consulting in the formulation of micro- and macroemulsions for the past 30 years.