

Phase behavior of fatty carboxylic acids in n-heptane/water systems

*Bélgica Bravo**, *Jhoana Sánchez*, *Gerson Chávez*, *Ana Cáceres*,
Fredy Ysambertt y *Nelson Márquez*

*Laboratorio de Petroquímica y Surfactantes, Dpto. de Química, Facultad de Ciencias,
Universidad del Zulia, Apdo. 526, Zulia-Venezuela.*

Recibido: 16-04-06 Aceptado: 26-04-07

Abstract

The phase behavior of different fatty carboxylic acids (FA) in oil/water system was studied. The Winsor I-III-II transitions of ionized compounds were attained by varying the FA composition through the formulation scan. The effect of adding an alcohol in the system was study. The middle-phase volume decreases with the chain length and alcohol concentration. On the other hand, FA partition in biphasic systems was study. The partition isotherm is obtained plotting the decimal logarithm of the acid concentration in the oil and water phase. The intercept of this graph is related with the critical micellar concentration (cmc) of each fatty acid. It was observed that the cmc decreases with the chain length of FA.

Key words: Cmc; fatty acid; formulation scan; phase behavior.

Comportamiento de fase de ácidos carboxílicos grasos en sistemas n-heptano/agua

Resumen

Se estudió el comportamiento de fase de diferentes ácidos carboxílicos grasos (FA) en sistemas aceite/agua. La transición Winsor I-III-II de compuestos ionizados se obtuvieron variando la concentración de FA a través de barridos de formulación. Se estudió el efecto de adición de alcoholes en el sistema. El volumen de fase media disminuye con la longitud de la cadena y la concentración del alcohol. Por otro lado, se estudió el reparto de FA en sistemas bifásicos. La isoterma de reparto se obtiene graficando el logaritmo decimal de la concentración de ácido en las fases oleica y acuosa. El punto de intercepción de este gráfico se relaciona a la concentración micelar crítica (cmc) de cada ácido graso. Se observó que la cmc disminuye con la longitud de la cadena del FA.

Palabras clave: Acidos grasos; barridos de formulación; comportamiento de fase; cmc.

Introduction

The phase behavior of ternary surfactant-oil-water systems was first elucidated by Winsor (1) 50 years ago. Since then

a lot of research has been carried out to understand more and more complex situations. As a consequence the formulation variables were recognized and their influ-

* Autor para la correspondencia. E-mail: belgicabravo@yahoo.es, bbravo@luz.ve

ence was established in a quantitative fashion for many systems (2, 3). The phase behavior of surfactant-oil-water systems is usually referred to the Winsor model (1, 3).

When the surfactant affinity for the water (respectively oil) phase dominates a so-called Winsor Type I (respectively II) phase behavior takes place in which an aqueous (respectively oil) surfactant-rich phase is in equilibrium with an excess oil (respectively water) phase. When the affinity of the surfactant for the oil phase exactly equilibrates its affinity for the water a so-called Winsor Type III system is attained in which a microemulsion containing most of the surfactant is in equilibrium with both excess water and excess oil. As the formulation is changed monotonously phase behavior transition takes places either in the direction I→III→II or vice versa (4-11).

Lipids, including fatty acids, are important group of amphiphilic molecules that are used in stabilizing oil-water (o/w) interfaces. Lipid as well as fatty acid as amphiphilic molecules may self-assemble into a variety of aggregates ranging from micelles to bi-layers to multilayered stacked of lamellar type to other form of liquid crystalline structures (12, 13). In any case vesicles in emulsion with these appealing feature finds potential applications in pharmaceutical and cosmetic industries due to their ability in releasing drugs and other biologically active substances encapsulated in a slow and controlled manner (14).

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 fatty acid vesicles in o/w emulsions was provided by Ferezou et al. (15), Hajri et al. (16) and Westsen and Wehler (17), reported that in most fatty acid stabilized commercial o/w formulations lipid vesicles coexist as dispersed phase with emulsified droplets. Aqueous fatty acid solutions are capable of forming vesicles spontaneously,

where vesicles are formed as a function of pH by deprotonation of fatty acid molecules (18). In these systems carboxylate anion are regarded as surfactant, whilst the corresponding fatty acid as a co-surfactant (19).

Wider knowledge has been developed on the quaternary systems water/oil/surfactant/alcohol (6-11), especially in application to enhanced oil recovery (20, 21). These studies have led to a good understanding of the relations between the nature of the surfactant, oil, alcohol and composition parameters and the phase pattern (especially the multiphase behavior often named Winsor II→III) within pseudo ternary diagrams. In the specific case of the polyethylene oxide surfactants, the simple variation of the temperature leads to the progressive change of the phase pattern. This behavior can be related to the change in the polar head hydration. On the other hand, 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 (22, 23).

The stabilization of oil-in-water emulsions can also be attained in this way. In these cases the carboxylic acid contained in the crude oil adsorbs at the O/W interface, where it is neutralized into a carboxylic salt with surfactant properties such as interfacial tension lowering or emulsification. In order to obtain three-phase systems (Winsor III) as a traces of the optimal formulation (R= 1), we studied the effect of FA length chain in the phase behavior of fatty acids in FA/oil/water systems.

Experimental Procedure

The studied amphiphiles were as follows: caprylic acid (C8), capric acid (C10), lauric acid (C12), myristic acid (C14), palmitic acid (C16) and stearic acid (C18), which behave as surfactants (all provided by Merck). They are referred to as CN, where N indicates the number of carbon atom in the acid molecule. 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, water, and acid in identical amounts, but with the nature of one of the components changing progressively from one test tube to the next. In the present study the fatty acid length chain and concentration are the studied variables.

Test tubes typically contain 10 mL of *n*-heptane, 10 mL of aqueous phase (dionized water with NaOH and NaCl at 0.6 mol/L, from Merck), and X grams of commercial fatty acid (0.4 to 2.0 % p/v). The FA is introduced as an oil solution. The tubes are closed with a screw cap and placed in a vertical position at constant temperature enclosure (25°C). They are gently stirred once a day for a period of one week to improve the phase contact; then they are left to fully equilibrate for at least 2 weeks. When the mass of acid was increased the number, volume and composition of phases were registered for each fatty acid surfactant.

The samples were described according to the Winsor classification of multiphase systems. Since in low concentration systems, the FA is not enough to produce a three-phase optimum system, a concentration scan of alcohol co-surfactant (*n*-propanol, *n*-butanol, and *n*-hexanol, from Merck) was made.

In the specific case of the partition isotherm study the biphasic systems was used, and the acid concentration is much lower. It was taken as close to the cmc of the salt in water and different NaOH concentration were used to produce a formulation scan. In the all cases, the concentration of acid in the different phases was determined by HPLC method using a Nucleosil C18 (25 cm x 4.6 mm, 5 µm) column and acetonitrile (Baker Chemicals) as mobile phase (24).

Result and Discussion

The pH-sensitive systems are best treated as containing a mixture of two amphiphilic species that occur in different pro-

portions depending on the pH. In order to observe the phase behavior of fatty acid in an oil/water system, a scan formulation with different fatty acid was performed. In this system the optimum pH is independent of the acid concentration. That is, does not depend on the initial acid concentration of the system due to the formation of a tampon. On the other hand, when sodium hydroxide is added in the three-phase region, a reaction take place with the acid specie and their soap appear in the interface due to its hydrophilic character and the acid-base equilibrium presented.

Figure 1 shows the concentration scan for C12 in an *n*-heptane/water system. The results showed that it is possible to obtain a wide range of WIII systems. The optimum formulation (three phase system where the microemulsion is in equilibrium with both water excess and oil excess phases) was reached at 1.4%, 1.2% and 1.0% p/v for the lauric (C12*), myristic (C14*) and palmitic (C16*) acid, respectively as shown in the Table 1.

Figure 2 shows that in these systems takes place a transition of type WII→WIII→WI. In WII (water-in-oil microemulsion) an excess water phase is in equilibrium with the microemulsion phase, i.e. water is solubilized into reverse micelles dispersed in the oil continuous phase. In WIII (middle phase) a microemulsion occurs between Winsor type II and type I. This phase is thermodynamically stable and contains virtually all of the surfactant, and a mixture of oil and water. This middle phase coexists with excess oil and water phases. WI (oil-in-water, microemulsion) contains an excess oil phase and surfactant micelles in the microemulsion phase. In this phase, the oil solubility is enhanced by partitioning into surfactant micelles dispersed in water continuous phase).

Table 1 also shows the impact of fatty acid chain length on the phase behavior of the microemulsion: the longer the chain length and the lower concentration of the

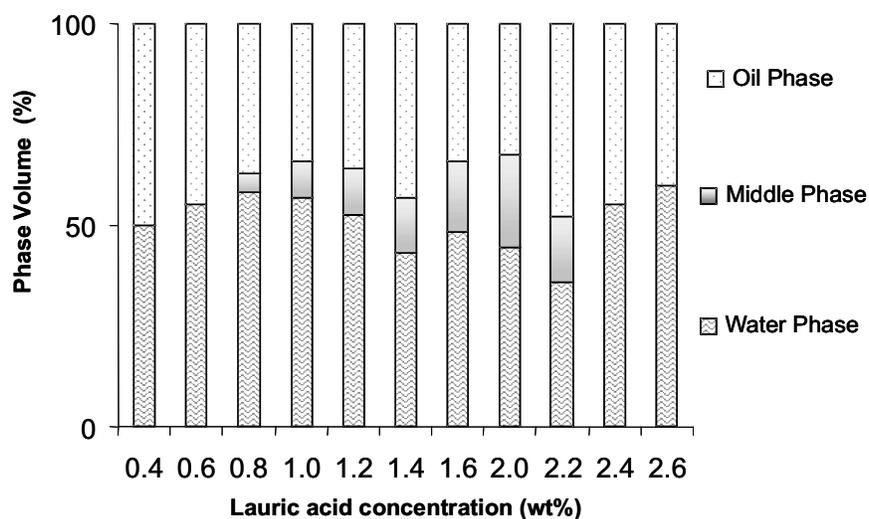


Figure 1. Formulation scans for C12 acid in an n-heptane/water system.

fatty acid (C16) required for achieving the phase transition. This result is as expected

Table 1

Characteristics of the fatty acid in the optimum formulation systems.

Acid	g Acid/ 100 mL	Middle phase volume (mL)	pH
C12	1.4	2.8	7.87
C14	1.2	3.0	8.35
C16	1.0	3.9	8.86

Water phase: NaOH and NaCl at 0.6 M.

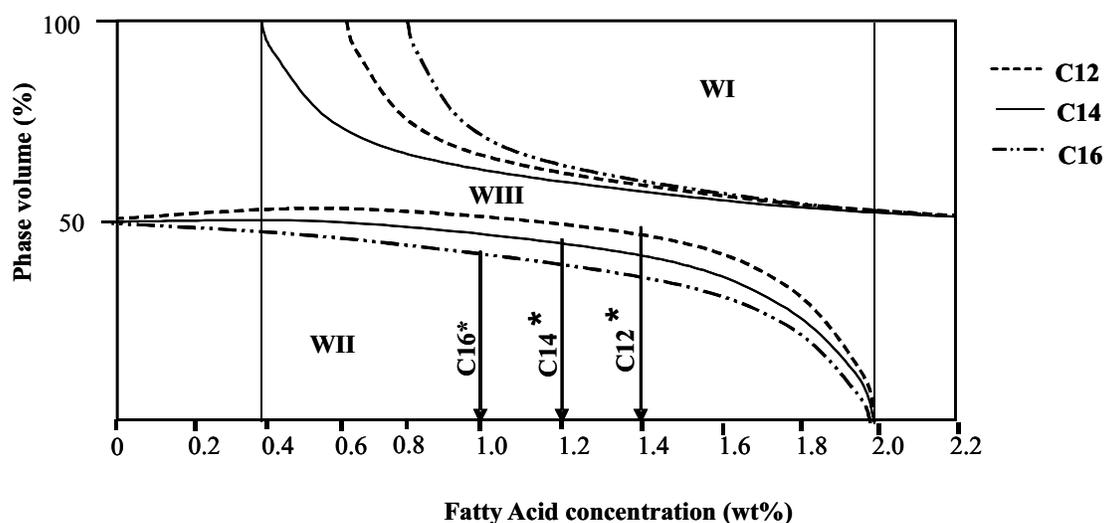


Figure 2. Variation of the phase volume along the FA formulation scan.

and can be described on the basis of modified Winsor's *R*-ratio (Equation 1) (1):

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \quad [1]$$

Term *A* represents the interaction energy per unit interfacial area. Subscripts *C*, *W* and *O* are interfacial surfactant, water, and oil molecules, respectively, whereas subscripts *L* and *H* represent the lipophilic and hydrophilic parts of the surfactant. A Winsor type II system has an *R*-ratio greater than unity because the interaction energy between the surfactant and the oil is larger than that between the surfactant and the water (3, 25-26) due to the lipophilic character of these fatty acids. As the *R*-ratio approaches one, conditions are favorable to form a Winsor III or IV system (3). System containing short-chain fatty acids (*n*= 8, 10) formed a clear solution whereas the system containing long-chain fatty acids (*n* = 12, 14) resulted in gel formation. This could be due to the lack of solubility of long-chain fatty

acids and consequently a liquid crystal/gel formation occurs (3, 25, 27).

On the other hand, a lineal relationship of the volume of middle phase with the concentration of the FA in the system was observed; this indicates that this phase contains the biggest concentration of surfactant. The microemulsion volume in the Winsor III system for C16 was always larger than for C12, which indicates the better solubilization attained with the former on a weight basis.

As the concentration of a surfactant in an aqueous or oil solution is increased, the so-called micellization takes place at a concentration referred to as the critical micelle concentration or cmc. The cmc is not exactly a value but certain concentration interval that can be relatively wide if the surfactant is a mixture of notably different chemical species. The partition isotherm of the carboxylic acid in the oil-water system was determined over the concentration range and above the cmc of the corresponding soap solution. Figure 3 shows the partition of C8, C10, C12 and C14 in the

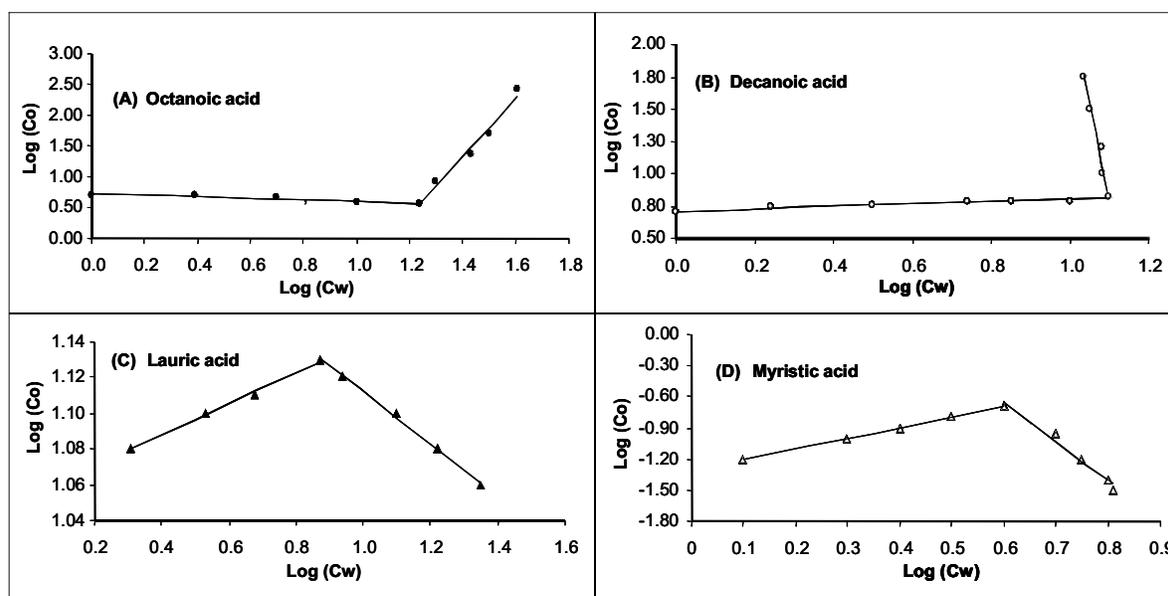


Figure 3. Partition of (A) C8, (B) C10, (C) C12, and (D) C14 acid; obtained by HPLC on a Nucleosil C18 (25 cm x 4.6 mm, 5 μ m) column and acetonitrile as mobile phase.

n-heptane-water biphasic system at 25°C. As seen in this figure, the partition of a surfactant in *n*-heptane-water system exhibits an abrupt change of slope when the equilibrium concentration of the surfactant attains the cmc. This crossing point allows calculated a estimate value of the cmc for each fatty acid studied.

A decrease of the cmc value as the number of carbon atoms in the hydrophobic group increases was observed. The cmc (mM) calculated was: 17.37 (C8), 11.22 (C10), 7.41 (C12) and 4.82 (C14). A widely used rule for straight-chain ionic surfactants is that the cmc is halved by the addition of one methylene group to its hydrophobic group. However, when the number of carbon atoms in a straight-chain hydrophobic group exceeds 16, the cmc no longer decreases so rapidly with an increase in the chain length. This may be due to the coiling of these long chains in water (26, 28-31).

On the other hand, the addition of alcohol is known (3, 32, 33) to cause a phase behavior transition of the Winsor I-Winsor III-Winsor II kind for ethoxylated alkylphenols. Moreover, since soaps are anionic surfactants, alcohol is added in systems of high soap concentration so that a microemulsion

forms instead of a solid mesophase (3). In low FA concentration system alcohol is not necessary. However in the referred case there is not enough surfactant to produce a three-phase behavior. To study the effect of alcohol in these systems to obtain Winsor III (three-phase) behavior, an alcohol concentration scan was carried out by increasing amounts of *n*-butanol in a FA/*n*-heptane/water system with different NaOH concentration. Figure 4 show this effect. It can be observed that for a system with low NaOH concentration (0.2 M) a high alcohol concentration is necessary to attain the three-phase system, due to negligible ionic strength brought by the presence of sodium hydroxide. In these systems the acid is solubilized in the aqueous phase thanks to the alcohol that partitions into it.

Furthermore, when the Winsor III is attained and more alcohol is added to the three-phase system, the middle phase volume is reduced. This change essentially follows the variation in the middle phase volume, so that the concentration of FA in the middle phase remains roughly constant. The middle phase volume for C16 acid was higher due their more lipophilic character. This effect was also studied for

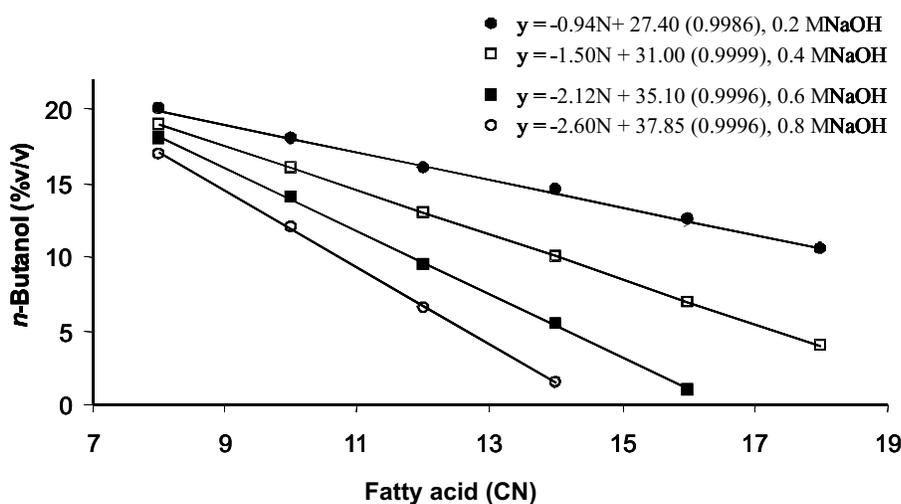


Figure 4. Concentration of *n*-Butanol necessary for obtain three-phase system in the acid/*n*-heptane/water system with different NaOH concentration.

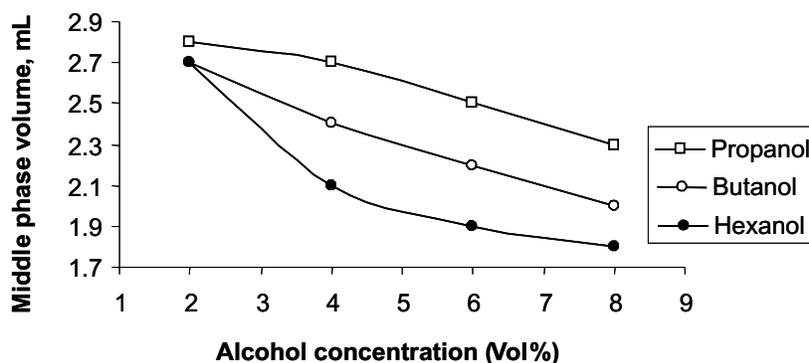


Figure 5. Variation of the middle phase volume with different alcohol in the *n*-heptane/water system.

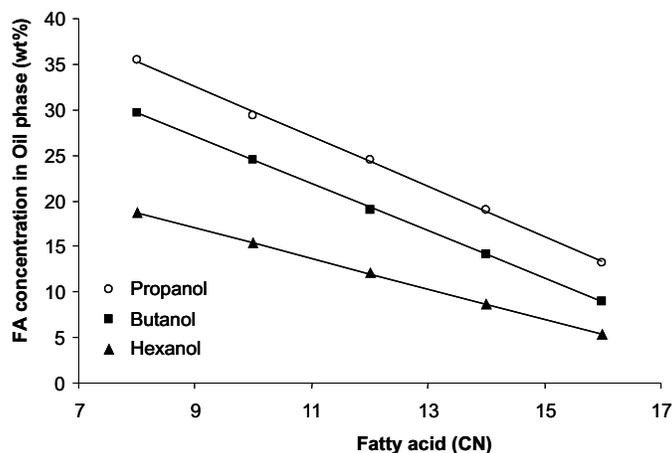


Figure 6. Effect of adding alcohol on the FA concentration in the oil phase.

n-propanol and *n*-hexanol. In all cases the middle phase volume decreases with the alcohol concentration (Figure 5). Figure 6 shows a decrease in the FA concentration in the oil phase with the chain length, which indicates that the more lipophilic acid is distributed mostly in the middle phase.

Conclusions

The concentration for attaining the optimum formulation decreases with the chain length of the fatty acid due to the lipophilic character of these surfactants. In the oil/water system the cmc value of these acids decreases with the

length of the chain acid. On the other hand, for the system with NaOH 0.2 M a high *n*-butanol concentration (more than 10 % v/v) was necessary, due to negligible ionic strength brought by the sodium hydroxide to produce a Winsor III system.

Acknowledgments

This work was financially supported by various projects from the Venezuelan Ministry of Science and Technology (FONACIT G-2005000428) and from Zulia University of Research Council, (CONDES-LUZ CC-0322-06 and CC-0957-06).

References

1. WINSOR P. **Solvent Properties of Amphiphilic Compounds**, Butterworths, London, pp. 1396-1415, 1954.
2. SHAH D., SCHECHTER R. Eds., **Improved Oil Recovery by Surfactants and Polymer Flooding**, Academic Press: New York (USA), pp. 396-415, 1977
3. BOURREL M., SCHECHTER R. **Microemulsions and Related Systems**, Marcel Decker, Inc., New York (USA), p. 504-515, 1988
4. SALAGER J.L. **Handbook of Detergents part A**; Marcel Dekker, New York (USA), pp 253-285, 1999.
5. BOURREL M., SALAGER J.L., SCHECHTER R., WADE W. **J Colloid Interface Sci** 75: 451-460, 1980.
6. SCHUNK A., MENERT A., MAURER G. **Fluid Phase Equilibria** 224: 55-72, 2004.
7. SILVA C., MOR M., VACONDIO F., ZULIANI V., VINCENZO P. **Il Farmaco** 58: 989-993, 2003.
8. LEE J.F., HSU M.H., CHAO H.P., HUANG H.C., WANG S.P. **J Hazardous Materials B** 114: 123-130, 2004.
9. STANDNES D., AUSTAD T. **Colloids Surfaces A** 216: 243-259, 2003.
10. WANG W., NANDAKUMAR Z., XU Z., MASLIYAH J. **J Colloid Interface Sci** 274: 625-630, 2004.
11. KARAPANAGIOTIA H., SABATINIB D., BOWMAN R. **Water Research** 39: 699-709, 2005.
12. LASIC D., **Liposomes: From Physics to Applications**, Elsevier B.V., Amsterdam, pp. 196-215, 1993.
13. NIKOLAU C., PARAF A. **Liposomes, Drugs and Immunocompetent Cell Functions**, Academic Press, pp. 296-310, 1981.
14. BARRY B., ECCLESTON G. **J Texture Study A** 4: 53-62, 1973.
15. FEREZOU J., LSI N., LERAY C., HAJRI C., FREY A., CABARET Y., COURTIEU J., LUTTOON C., BACH A. **Biochem Biophys Acta** 1213: 149-158, 1994.
16. HAJRI T., FEREZOU J., LUTTOON C. **Biochem Biophys Acta** 1047: 121-130, 1990.
17. WESTSEN K., WEHLER T. **J Pharma Sci** 81: 777-786, 1992.
18. HARGREAVES J., DEAMER D. **Biochemistry** 17: 3759-3768, 1978.
19. PAUTOT S., FRISKEN B., WEITZ D. **Langmuir** 19: 2870-2879, 2003.
20. ZHANG L., LUO L., ZHAO S., XU Z., AN J., YU J. **J Petrol Sci Eng** 41: 189-198, 2004.
21. GU G., ZHOU Z., XU Z., MASLIYAH J. **Colloids Surfaces A** 215: 141-153, 2003.
22. MUNGAN N. **World Oil** 6: 209-215, 1981.
23. HOLM L., ROBERTSON D. **J Petrol Technol** 33: 161-168, 1981.
24. BRAVO B. Reparto preferencial de ácidos carboxílicos en sistemas surfactante/agua /aceite por HPLC (Dr. These). Universidad del Zulia (Venezuela), pp. 152-178, 2004.
25. SHARMA M., SHAH, D. **Introduction to macro and microemulsions** edited by Shah, D.O., ACS Symposium Series 272, Am Chem Soc, Washington, DC, pp. 1, 1985.
26. ROSEN M. **Surfactants and interfacial phenomena**. John Wiley-Sons LTD, New York (USA), pp. 83-122, 1978.
27. GRACIAA A., LACHAISE J., CUCUPHAT C., BOURREL M., SALAGER J.L. **Langmuir** 9: 3371-3379, 1993.
28. BLANCO E., GONZALEZ A., RUSO J., PEDRIDO R., PRIETO G., SARMIENTO F. **J Colloid Interface Sci** 288: 247-260, 2005.
29. GONZALEZ A., RUSO J., ROMERO M., BLANCO E., PRIETO P., SARMIENTO F. **Chem Phys** 313: 245-249, 2005.
30. MUKERJEE P. **Adv Colloid Interface Sci** 1:241: 255, 1967.
31. SCHICK M. **Nonionic Surfactants**. Marcel Decker, Inc., New York (USA), pp.1062, 1967.
32. SALAGER J.L., MORGAN J., SCHECHTER R., WADE W., VASQUEZ E. **Soc Petrol Eng J** 19: 107-112, 1979.
33. HARUSAWA H., NAKAJIMA H., TANAKA M. **J Soc Cosmet Chem** 33: 115-121, 1982.