Inversion Properties of n-Alkane Phosphonic Acids Stabilized Emulsions: HLB Dependence

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The emulsifier properties of n-alkane phosphonic acids (C10H21PO3H2; C12H25PO3H2 and C13H27PO3H2) and their mono- and di-sodic salts were studied, with emphasis on the morphological and dynamical inversion properties as a function of their neutralization degree. Maximum stabilization properties were appreciated for C10PO3H2 and C12PO3H2 while not for C13PO3H2. Such fact is associated to their odd number of carbon atoms chain, which is the origin of the intrachain constraints on the tail-chain flexibility.

1. INTRODUCTION

The main problem in emulsion studies is the preparation of stable emulsions of a predefined type. The system of hydrophile-lipophile balance (HLB) numbers was intended to facilitate the appropriate selection of emulsions. When mixing oil, water, and surfactant, the type of the formed emulsions depends not only on the stabilizing ability of the surfactant with respect to certain type of the emulsion, but also on the relative volume of the phases, surfactant concentration, temperature, etc. Many surfactants are capable of stabilizing both direct (O/W) and inverse (W/O) emulsions (while de stability of one of these types is usually higher) in such cases it is especially important to take precautions for the preparation of an emulsion of the desired type, because the disperse phase and dispersion media can easily exchange their roles, leading to a phase inversion.

Inversion of phases means transformations of a direct emulsion into an inverse one, or vice versa, caused by some external factor (addition of a surfactant or salt, variation in the volume fraction of the phases, etc.). One should distinguish between a phase inversion caused by the variation of HLB of the surfactant (or surfactant mixture), that is,

transition inversion[1–3] and a phase inversion by changing the disperse phase volume, the catastrophic inversion.[1,4,5]

In early publications[6,7] phase inversions from a direct emulsion into inverse ones caused by the addition of electrolyte were mainly studied. In these studies no attention was paid to the fact that the types of stabilization of direct and inverse emulsions were different.[8,9] In these cases, it is difficult to formulate a criterion of the phase inversion, and such criterion is unlikely to be related unambiguously with the HLB of the surfactant.

To determine the conditions necessary for the phase inversion, from a physicochemical point of view one should first study the transition from one emulsion type to the opposite one with the same stabilization mechanism (by adsorption layers of a surfactant with the formation of thin films of certain type), caused by the variation of the parameters determining the film stabilization (surfactant concentration, temperature, added electrolytes, etc.). For example, when hydrophilic surfactants (SDS, CTAB, etc.) are added to stable inverse emulsions prepared from organic solutions of hydrophobic surfactants (ethers of oleic acids and triethanol amine), a phase inversion takes place at certain proportion between the hydrophilic and hydrophobic component.[10] This means that the phase inversion takes place due to the variation in the properties of the equilibrium thin films, related to a change of the HLB surfactant mixture towards the hydrophobicity. Thus, it is the HLB of the surfactant which acts as the factor which controls the phase inversion. Other cases, which demonstrate phase inversion without changing the stabilization type, occurred with nonionic surfactants like oxyethylene derivatives or some ionic surfactants as AOT.[1,11]

A research effort that started two decades ago has provided the two-dimensional and three-dimensional description,[12] the categorization[13] and the theoretical interpretation of the different kinds of emulsions inversions.[14–17]

A clear-cut phenomenological approach is currently available for understanding its characteristics, the factors that influence and control it,[18–20] and the importance of fine-tuning the emulsification protocol, and the crucial occurrence of organized structures such as liquid crystals or multiple emulsions.[21–23] The current know-how is used to analyze some industrial process involving emulsion inversions.[24]

Here, we present a study of emulsifier properties of n-alkane phosphonic acids (C10PO3H2; C12PO3H2, and C13PO3H2) and their sodium salts. In a previous work we have studied the HLB properties of such surfactant by the employment of two different methods.[25] Phosphonic amphiphiles derivative from n-alkane phosphonic acids are diprotic substances from which a variety of properties are dependence from their neutralization degree.

Hence, the aim in this article is to evaluate the dependence of n-alkane phosphonic acids stabilized emulsions inversion properties with the surfactant HLB. The information derived from such study would be useful in practical applications, that is, in petroleum industry, a desirable emulsion that must be carefully stabilized to assist a stage of an oil production process may be undesirable in another stage and necessitate a demulsification strategy.[26]

2. MATERIALS AND METHODS

2.1. Materials

All reagents were 99% pure and used as received. Phosphonic acids, C10PO3H2 (HLB = 15.4); C12PO3H2 (HLB = 15.2); C13PO3H2 (HLB = 13.3), and their salts, C10PO3HNa (HLB = 18.4); C12PO3HNa (HLB = 16.1); C13PO3HNa (HLB = 13.6); C10PO3Na2 (HLB = 19.0); C12PO3Na2 (HLB = 17.8); C13PO3Na2 (HLB = 16.8) were synthesized in our laboratory by the Roos and Kossalapoff method.[27] The obtained products were recrystalized four times in petroleum ether (Cicarelli Laboratories, 60–80°C) until constant melting point was reached. HLB values for acids and theirs salts were determined in a previous work.[25] The HLB values of mixtures were calculated by the employ of the following relationship $HLB_{mix} = HLB_A \times X_A + HLB_B \times X_B$, where A and B are the different components in the mixture; HLB_A, HLB_B, X_A and X_B are their respective pure substance HLB and molar fraction values.[28]

2.2. Methods

2.2.1. Emulsion Systems

Experiments were performed on surfactant-oil-water (SOW) systems. The oil phase tested was petroleum ether 60–80°C (composed by a linear hydrocarbon mixture with boiling point in the 60–80°C temperature range, required HLB ≈ 14.0[25]) as a model for aliphatic Argentinean petroleum. The composition of the emulsion is given here in terms of W_0, the ratio of water to surfactant concentration, and S_0, the ratio of oil to surfactant concentration.[29]

Emulsions for centrifuge test were prepared by mixing the appropriate quantities of oil and surfactant aqueous solution of a concentration equal to twice the critical micelle concentration (CMC) to complete a total volume of 40 mL for C10PO3H2; C10PO3HNa; C12PO3H2, and C12PO3HNa stabilized emulsions and a volume of 13 mL for those that content C10PO3Na2, C12PO3Na2, C13PO3H2, C13PO3HNa, and C13PO3Na2. The mixture was sonicated in a laboratory ultrasound generator (MADA no. 6000) for about 5 minutes. The resulting emulsions were then placed in stopped test tubes and left to pre-equilibrate at room temperature (such circumstances guarantee that systems with identical formulation and composition are in identical state at the moment of measurement) for approximately 24 hours before the experimental measurements. This precaution allows rationalization of the formulation effects.[9]

For conductivity measurements, the samples were prepared with a quantity of surfactant that lead to the major emulsion volume (determined by centrifuge test, Table 1). Different amounts of NaOH (0.192 M) solution were added to obtain emulsions stabilized by pure phosphonic acid, acid-monosodic salt mixture, pure monosodic salt, monosodic–disodic salts mixture and finally pure disodic salt. The same procedure was doing beginning with disodic salt stabilized emulsion and adding HCl (0.1098 M) solution.

2.2.2. Centrifuge Test

Experiments were carried out in an ACL PK 120 centrifuge. The samples were centrifuged during 10 minutes, accelerated from 0 to 3000 rpm and the emulsifier volume was measured.

2.2.3. Conductivity Measurements

The emulsions conductivity was measured as a function of W_0 with a CRIBABB SELECTED CON-04 conductivimeter and an ORION conductivimeter cell. The system was calibrated with KCl as usual. The test tube with a certain amount of sample (prepared as mentioned above) was placed in a thermostated bath at 25.0 ± 0.2°C and titrated with double-distilled water. The sample was maintained under permanent stirring and was equilibrated for at least 10 minutes after any conductivity reading was done. All measurements were repeated almost twice.

2.2.4. Optical Microscopy

To evaluate emulsion morphology the samples were observed at a Nikon Polarizing Microscope (Eclipse E200 POL).

TABLE 1

Maximum stabilization conditions for n-alkane phosphonic acids and their salts. S_0: oil to surfactant ratio, W_0: water to surfactant ratio

Surfactant	S_0	W_0	% of surfactant[*]	Total[a] volume/mL	Emulsion volume/mL
C10PO3H2	725	1356	0,05	40	33
C10PO3HNa	150	74	0,40	40	33
C10PO3Na2	132	34	2,03	13	2.75
C12PO3H2	1221	1958	0,04	40	25
C12PO3HNa	265	326	0,42	40	13
C12PO3Na2	8	13	12,83	13	3.75
C13PO3H2	3149	1269	19,70	13	0.10
C13PO3HNa	541	831	2,40	13	0.30
C13PO3Na2	241	311	2,40	13	0.80

[*]Grams of surfactant required to obtain 100 mL of emulsion.

[a]Total volume = (oil + water) phase volume before emulsification.

3. RESULTS AND DISCUSSION

The effect of n-alkane phosphonic acids and their salts in emulsion stability was studied. Emulsion stability is a measure of the rate at which an emulsion creaming (separation of the dispersed phase due to the difference in density without a change in drop size), flocculation (clustering of the dispersed droplets without a change in drop size), or coalescence (formation of larger drops from small drops). The rates of these changes are measured by determined the size and distribution of the oil droplets in the material. This can be done by photography and image analysis, pulsed nuclear magnetic resonance, a coulter counter, ξ-potential measurements, turbidity, and other light-scattering methods,[9] Nevertheless, centrifugation is a useful tool to obtain a rapid evaluation of emulsion stability. Such method provides a quick scanning of products. During the centrifuge test, droplets were accelerated beyond earth acceleration, g, to raise their mobility.

The surfactant concentration variation on the emulsion stability to sedimentation was analyzed by measurement of the emulsion volume formed after 24 hours. Figure 1 shows the effect of centrifuge speed on the emulsifier volume after 10 minutes of centrifugation vs. S_0 (petroleum ether to surfactant ratio) for C12PO3HNa, similar results were obtained for all tested systems. The stability to sedimentation decreased with centrifugal acceleration.

At light of the obtained results it was possible to infer that the maximum of emulsified volume and sedimentation stability was obtained for those emulsions that contained decanephosphonic acid (C10PO3H2) and its monosodium salt, followed by those with dodecanephosphonic acid (C12PO3H2) and its monosodium salt. A minimum emulsion volume was presented by the systems that contained C10PO3Na2, C12PO3Na2 as well as tridecanephosphonic acid (C13PO3H2) and its mono and disodium salts.

Maximum stability emulsion conditions for all tested surfactants are summarized in Table 1.

Since emulsions present a large interfacial area, any reduction in interfacial tension must reduce the driving force toward coalescence and showed promote stability.

Except for tridecanephosphonic acid and it salts, phosphonic acids lead to a larger stabilization than their mono-sodium or disodium salts. Particularly, there is a larger difference between the acid and its monosodium salt and the respective disodium one. This fact is related to differences in the water/oil interface structure when a phosphonic acid or a monosodium salt is present instead of the disodium salt. C10PO3H2 and C12PO3H2 can strongly
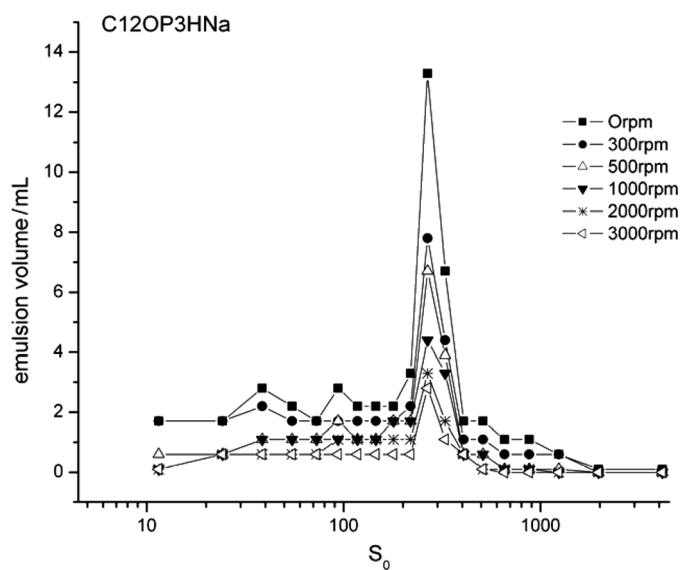

FIG. 1.   Emulsified volume after 10 minutes of centrifugation versus S_0 (ether to surfactant ratio) for C12PO3HNa.

interact by H-bonds at the water/oil interface, these interactions remaining in C10PO3HNa and C12PO3HNa while there are not possible in C10PO3Na2 and C12PO3Na2. The possibilities of H-bond formation at the water/oil droplets interface give an extra stabilization of the emulsion.

Figure 2 shows the variation of emulsion formation vs. neutralization degree. As it was previously inferred by the analysis of centrifuge test results, high content of emulsion was presented by C10PO3H2, and the amount of emulsion diminished in the order C12PO3H2 and C13PO3H2. The volume of emulsion decreased notably as the neutralization degree increased.

The anomalous behavior of tridecanephosphonic acid and their salts is associated to their odd number of carbon atoms chain. In a homologue series, the length of the chain decides on the surface activity of a given component. The unrestricted hydrocarbon chain is quite flexible and, therefore, can assume conformations when exposed into a liquid–liquid interface. When adsorption progresses and the interface become crowded with surfactant, less area is accessible for a single chain. Therefore, some conformations with highest area are strongly restricted. The chain containing n carbons atoms can assume $3n-3$ conformations of dihedral angles.[30] There are three rotational energy minima for a given carbon–carbon bond in these tail chain: one trans rotational state and two gauche rotational states. The net energy differences between the *trans* state and either of the two gauche states (with the gauche states having the higher energy) are the origin of the intrachain constraints on the tail-chain flexibility. Due to the existence of such intrachain constraints effects,

even–odd effects in the conformation distribution are suggested.[31] At the interface, hydrocarbon chains with odd number of carbon atoms tend in average to assume more expanded conformations than chains with even number of carbons.

Due to the intrachain constraints that exist between the C13PO3H2 tails at the oil/water droplet interface, such acids and its mono and disodium salts are compelled to adopt an expanded and nonflexible conformation. So, as the hydrocarbon chains in such systems have a minor capacity to accommodate at the interface, a minor capacity of interfacial tension reduction is possible and as a consequence a minor emulsion stabilization. Also, an expanded monolayer has low elasticity and cohesion which favors coalescence. A rigid and less dense packing of hydrocarbon chains at interface also favors droplet content exchange and coalescence.

Formulation composition maps for the systems containing C10PO3H2, C12PO3H2 and C13PO3H2 are shown in Figures 3 through 5. In all cases physicochemical formulation was altered changing the neutralization degree by addition of concentrated NaOH aqueous solution.

To determine the border line between different kinds of emulsion, the electrical conductivity was measured. There is a significant difference in conductivity between O/W and W/O emulsions since the conductivity is largely determined by the continuous phase. Thus, conductometry has been used to follow phase inversion.[32] Since pure water and the brine conductivity are about $250\,mS\,cm^{-1}$ and $900\,mS\,cm^{-1}$ respectively, while the petroleum ether conductivity is less than $10\,\mu S\,cm^{-1}$, the type of emulsion

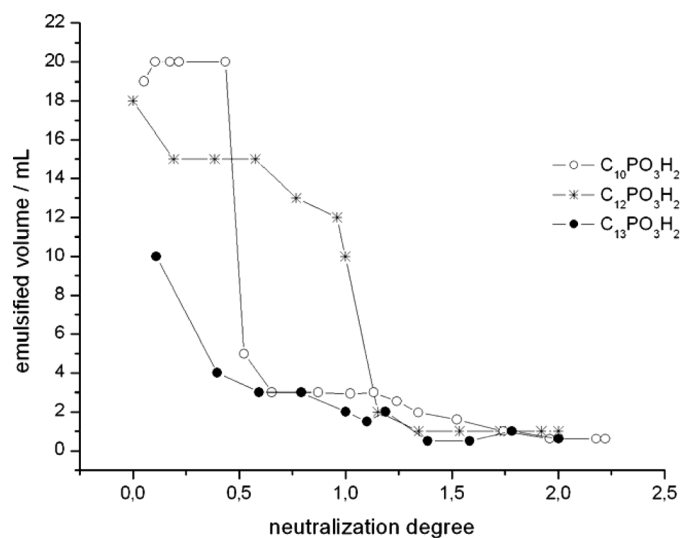FIG. 2. Variation of emulsified volume versus neutralization degree for the emulsion systems that contain: C10PO3H2 ($S_0 = 725$; $W_0 = 1356$), C12PO3H2 ($S_0 = 1221$; $W_0 = 1958$) and C13PO3H2 ($S_0 = 3149$; $W_0 = 1269$).

FIG. 3. Formulation composition map for the systems containing C10PO3H2. W/O: water-in-oil emulsion; O/W: oil-in-water emulsion; w/O/W: multiple water-in-oil-water emulsion.
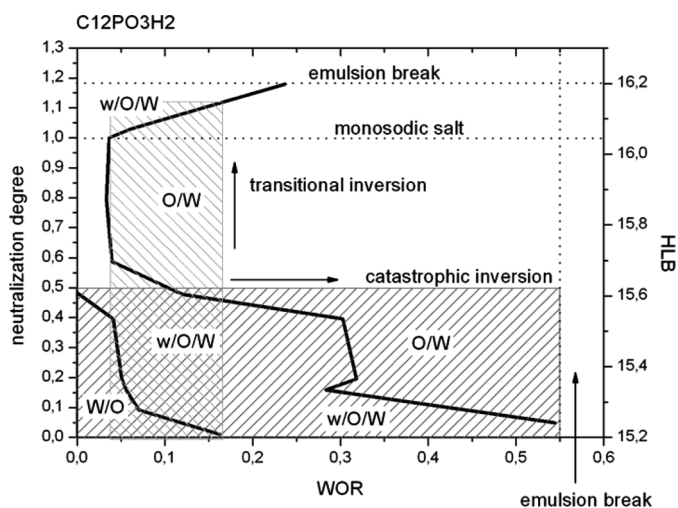
FIG. 4.   Formulation composition map for the systems containing C12PO3H2 **W/O**: water-in-oil emulsion; O/W: oil-in-water emulsion; w/O/W: multiple water-in-oil-water emulsion.

is readily determined as O/W (or respectively W/O) whenever the conductivity is higher (or respectively lower) than $10\,\mu S\,cm^{-1}$.

Figure 6 show the variation of emulsion conductivity by addition of double distilled water for system containing C10PO3H2 until inversion to an O/W emulsion took place. The sudden increase in conductivity corresponds to a swap in the external phase that is an oil external emulsion to a water external one. This morphological switch was corroborated by optical microscopy. Similar results are obtained for all tested SOW systems.

Inversion patterns, illustrated in Figures 3 through 5, shows the type of emulsion at a given formulation and
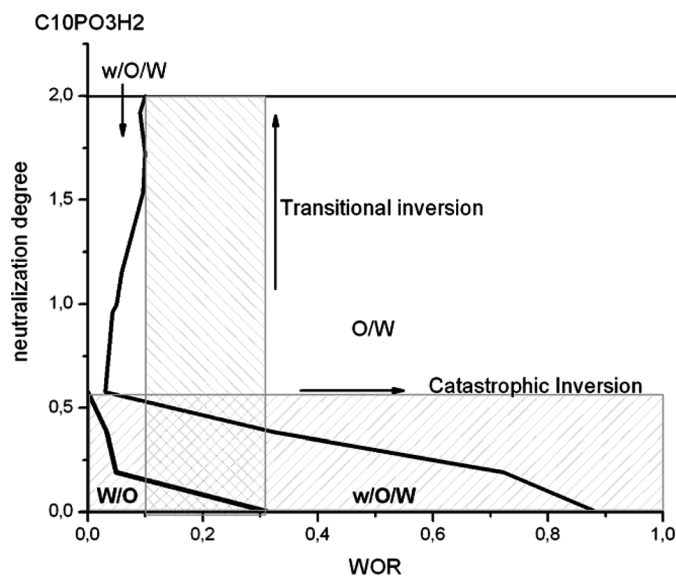

FIG. 5.   Formulation composition map for the systems containing C13PO3H2. W/O: water-in-oil emulsion; O/W: oil-in-water emulsion; w/O/W: multiple water-in-oil-water emulsion.
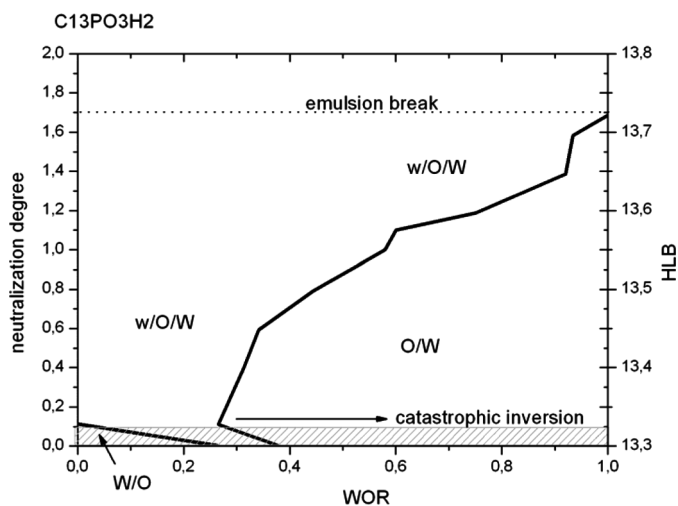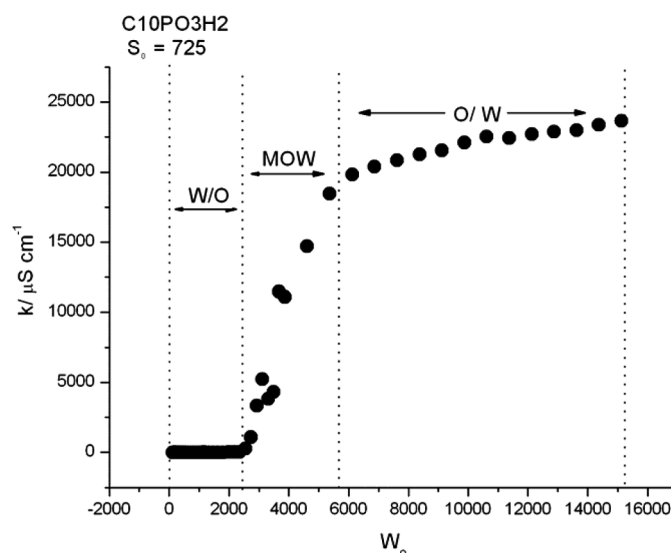

FIG. 6.   Emulsion conductivity variation versus W_0 (water to surfactant ratio) for the system that contain C10PO3H2 ($S_0 = 725$; $W_0 = 1356$) as emulsifier. W/O: water in oil emulsion; MOW: multiple oil in water emulsion; O/W: oil in water emulsion.

water/oil content. The formulation/composition map is divided into different zones according of the emulsion type: W/O; O/W and an intermediate region, which corresponded with a transition region where multiple w/O/W emulsions are formed.

The line that separates W/O emulsion from O/W emulsion is called the inversion line.[33] The crossing over through the horizontal branch of the inversion line, indicated by a vertical arrow, corresponds to the transitional inversion from a normal W/O to a normal O/W emulsion or vice versa. This process is caused by physicochemical factors and is generally reversible.[9] The other type of inversion, the so-called catastrophic inversion, is produced by trespassing the inversion line, as indicated by the horizontal arrow.

The existence of different emulsion types in inversion maps was confirmed by optical microscopy (Figure 7).

Figure 3 indicates a bidimensional formulation WOR composition map for the C10PO3H2 system. At low water content (WOR < 0.03) and neutralization degree inferior to 0.56 a W/O emulsion existed. An augment of the neutralization degree (superior to 0.5) generated multiple w/O/W emulsions. No direct (O/W) emulsion appeared at low water content by increasing the neutralization degree. When WOR > 0.3, the W/O emulsions disappeared at every neutralization degree. Only w/O/W emulsions could be recognized which transformed in O/W emulsion as the water content or the neutralization degree augment.

Two zones which corresponded to catastrophic and transitional inversions could be identified in the inversion map.

Catastrophic inversion occurred when the water/oil ratio was increased in a 0–0.56 neutralization degree range, or
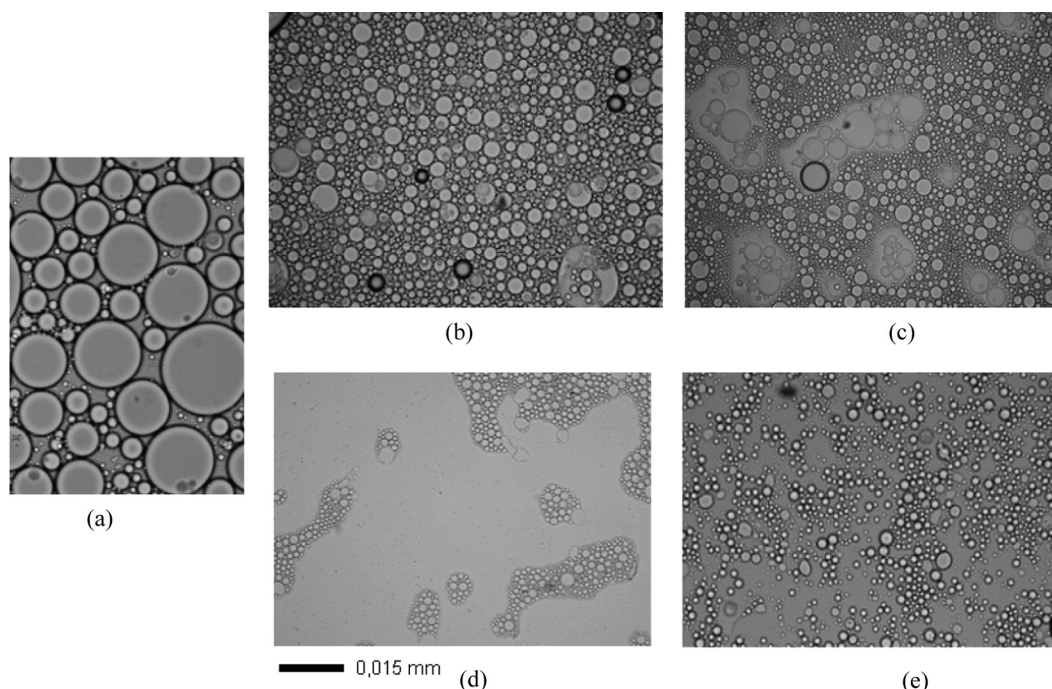
FIG. 7. Optical microphotograph of the emulsions stabilized by C12PO3H2; neutralization degree 0.1 (HLB = 15.34) as the water content was increased to obtain catastrophic inversion. (a) WOR = 0 (water in oil emulsion); (b) WOR = 0.1, multiple emulsion; (c) WOR = 0.25, multiple emulsion; (d) WOR = 0.4 (water channels between multiple emulsions); (e) WOR = 0.5 (oil in water emulsion).

what is the same in a 15.4–17.0 emulsifier HLB range. In such conditions we have varied the emulsifier composition from pure acid (neutralization degree = 0; HLB = 15.4) to a 1:1 acid: monosodium salt mixture (neutralization degree = 0.56; 0.56; HLB = 17.0). If the neutralization degree augments with respect to the mentioned value, the inverse emulsion zone is replaced by multiple w/O/W emulsions, an increment in the water content lead to a very unstable O/W emulsions.

The WOR values needed for catastrophic inversion are dependent on the neutralization degree. For such systems, it can be seen that the catastrophic inversion line appeared at high water content as the neutralization degree diminished. This fact is consistent with Bankroft rule. As the surfactant became more and more water soluble (when the neutralization degree augments) the O/W is favored instead of W/O emulsion. Then a minor water amount is necessary to add for obtain emulsion inversion.

Transitional inversion can be achieved by an increase of the neutralization degree if water/oil ratio in emulsion is maintained superior to 0.1 and inferior to 0.3 (0.1 < WOR < 0.3). The inversion occurred at emulsifier HLB values between 16.4 and 17.0 (0.35–0.5 neutralization degree range) and depended on the emulsion water content.

The formulation-composition map for systems containing C12PO3H2 is shown in Figure 4. A similar behavior than C10PO3H2 stabilized emulsions can be seen. A zone with O/W emulsions appeared at low water content (WOR < 0.03) and at low neutralization degree (less than 0.5). An increment of neutralization degree in such WOR conditions transformed inverse emulsion in a multiple w/O/W emulsion but not inversion was seeing. From WOR > 0.16 only multiple w/O/W and O/W emulsions could be observed.

Similarly as happened with C10PO3H2, catastrophic inversion occurred by the augment of emulsion water content in a 0–0.5 neutralization degree range, which correspond to the emulsifier HLB values between HLB = 15.2 (pure C12PO3H2) to HLB = 15.6 ((1:1) C12PO3H2: C12PO3HNa mixture). WOR values needed to cause catastrophic inversion depended on the neutralization degree and diminished as the content of C12PO3HNa in the emulsifier mixture increased. Nevertheless, for such phosphonic acid WOR would be always inferior to 0.55 because an extra addition of water to the systems caused emulsion break.

Transitional inversion occurred in the formulation map at 0.03 < WOR > 0.16 zone by the increment of neutralization degree from 0 to 1–1.1. A new increment of neutralization degree caused the existence of multiple unstable emulsions and then emulsion break. Transitional inversion occurred when the emulsifier HLB is about 15.6.

For C13PO3H2 stabilized systems (Figure 5) W/O emulsions existed at low water content (WOR < 0.27) and low neutralization degree (inferior to 0.11). A small increment in either of both factors caused multiple emulsions formation.

When water content was increased such emulsions transformed in O/W ones. In such case, at difference of what

happened with C10PO3H2 and C12PO3H2 stabilized emulsions, as neutralization degree augment and the surfactant became more and more soluble, more water is needed to transform multiple in O/W emulsions. This fact is supposed related to an odd–even effect between the hydrocarbon chains and the differences in the conformations that the surfactants can adopt at the water-oil interface.

For this system catastrophic inversion was possible while transitional one was not. Nevertheless, inversion occurred in a narrow zone of neutralization degree inferior to 0.11.

To evaluate the reversibility of phosphonic acid behavior, similar formulation – composition maps were constructed beginning with the disodium salt and adding HCl solution, results not shown. Results showed that no reversibility exists, and that emulsions prepared in such conditions were less stable.

Since a variation of the emulsifier neutralization degree implies a change in the HLB value of the emulsifier, it follows that the phase inversions occur due to the dissimilarities in the properties of the equilibrium thin films, which are related to change of the surfactants mixtures HLB towards the hydrophilicity changes.

4. CONCLUSION

High content of emulsion was presented by C10PO3H2 followed by C12PO3H2. The volume of emulsion decreased notably as the neutralization degree increased, which is related to the capacity of phosphonic acids to give a cohesive monolayer at the water-oil droplet interface through H-bonds between polar headgroups. An anomalous behavior was presented by tridecanephophonic acid (C13PO3H2) and their salts, which is associated to their odd-number of carbon atoms chain, giving rise to intrachain constraints to the chain flexibility.

For C10PO3H2 stabilized emulsions, catastrophic inversion occurred when the water/oil ratio was increased in a 0–0.56 neutralization degree range, that is, a (15.4–17.0) emulsifier HLB range. Transitional inversion is produced by a neutralization degree increase for emulsions with $0.1 < WOR < 0.3$. The inversion occurred at emulsifier HLB values of 16.4 to 17.0 and depended on the emulsion water content.

A similar behavior was obtained for systems that contain C12PO3H2. For emulsions stabilized with C13PO3H2 only catastrophic inversion was observed while transitional one was not seen. Nevertheless, inversion occurred in a narrow zone of neutralization degree inferior to 0.11.

REFERENCES

[1] Binks, B.P. (1998) *Modern Aspects of Emulsion Science*; Cambridge, UK: Royal Societ of Chemistry.

[2] Salager, J.L., Miñana-Perez, M., Perez-Sanchez, M., Ramirez-Gouveia, M., and Rojas, C.I. (1983) *J. Dispersion Sci. Technol.*, 4 (3): 313.

[3] Brooks, B.W. and Richmond, H.N. (1994) *J. Colloid Interface Sci.*, 162: 67–74.

[4] Dickinson, E. (1981) *J. Colloid Interface Sci.*, 84: 284–287.

[5] Smith, H. and Johnson, G.K. (1995) *J. Phys. Chem.*, 99: 10853–10857.

[6] Sherman, P. (1968) *Emulsion Science*; London: Academic Press.

[7] Clayton, W. (1943) *The Theory of Emulsions and Their Technical Treatment*, 4th ed., London: Chapman and Hall.

[8] Binks, B.P. (1993) *Langmuir*, 9: 25.

[9] Becher, P. (1985) *Encyclopedia of Emulsion Technology*; New York: Marcel Dekker, Vols. pp. 1–3.

[10] Kuznetsova, L.L., Kruglyakov, P.M., Mikina, T.V., Koretski, A.F., and Izvestiya, S.O. (1977) *AN SSSR; Seria Khim.*, 3: 167.

[11] Binks, B.P. (1993) *Colloid Surf. A*, 71: 167.

[12] Tapas, K. and De, M.A. (1995) *Adv. Colloid Interface Sci.*, 59: 95–193.

[13] Bourrel, M., Garciaa, A., Schechter, R.S., and Wade, W.H. (1979) *J. Colloid Interface Sci.*, 72: 161–163.

[14] Antón, R.E. and Salager, J.L. (1986) *J. Colloid Interface Sci.*, 111: 54–59.

[15] Hazlett, R.D. and Schechter, R.S. (1988) *Colloid Surf. A*, 29: 53–69.

[16] Kabalnov, A. and Wennerström, H.J. (1996) *Langmuir*, 12: 276–292.

[17] Ruckenstein, E. (1999) *Adv. Colloid Inter. Sci.*, 79: 59–76.

[18] Suzuki, T., Takei, H., and Yamazaki, S. (1989) *J. Colloid. Interface Sci.*, 129: 491–500.

[19] Sagitani, H. (1988) *J. Dispersion Sci. Technol.*, 9: 115–129.

[20] Rouvière, J. (1991) *Inform Chimie*, 325: 158.

[21] Rouvière, J., Razakarison, J.L., Marignan, J., and Brun, B. (1989) *J. Colloid Interface Sci.*, 133: 293–301.

[22] Forgiarini, A., Esquema, J., Gonzales, C., and Solans, C. (2001) *Prog. Colloid Polym Sci.*, 118: 184–189.

[23] Friberg, S.E., Mandell, L., and Larsson, M. (1969) *J. Colloid Interface Sci.*, 29: 155–156.

[24] Salager, J.L., Forgiarini, A., Márquez, A.L., Peña, A., Pizzino, A., Rodríguez, M.P., and Rondón-Gonzalez, M. (2004) *Adv. Colloid Inter. Sci.*, 108–109: 259–272.

[25] Verdinelli, V., Messina, P.V., Schulz, P.C., and Vuano, B. (2008) *Colloid Surf. A*, 316: 131–135.

[26] Schramm, L.L. (1992) *Emulsions: Fundamentals and Applications in the Petroleum Industry*; Washington, DC: American Chemical Society.

[27] Kossalapoff, G. (1951) *Organic Reactions VI*; New York, Wiley, pp. 273.

[28] Griffing, W.C.J. (1949) *Soc. Cosmetic Chemist*, 1: 311–326 and (1954) 5: 249–256.

[29] Alexandridis, P., Holzwarth, J.F., and Hatton, T.A. (1995) *J. Phys. Chem.*, 99: 8222–8232.

[30] Flory, P.J. (1971) *Principles of Polymer Chemistry* (Russian ed.); Moscow: MIR.

[31] Dowell, F. (1988) *Phys. Rev. A*, 38 (1): 382–393.

[32] Allouche, J., Tyrode, E., Sadler, V., Choplin, L., and Salager, J.L. (2004) *Langmuir*, 20: 2134–2140.

[33] Silva, F., Peña, A., Miñana-Pérez, M., and Salager, J.L. (1998) *Colloid Surf. A*, 132: 221–227.