

# Influence of the Mixed Propoxy/Ethoxy Spacer Arrangement Order and of the Ionic Head Group Nature on the Adsorption and Aggregation of Extended Surfactants

Ana M. Forgiarini · Cesar Scorzza ·  
Josmary Velásquez · Francia Vejar ·  
Emérita Zambrano · Jean-Louis Salager

Received: 7 March 2010 / Accepted: 25 May 2010 / Published online: 23 June 2010  
© AOCs 2010

**Abstract** Two families of extended surfactants were prepared with the same head groups (carboxylate, sulfate, disodium phosphate) and different intermediate spacer structures. In one there was an average of 7 propylene oxide groups on the side of the tail and an average of 7 ethylene oxide groups on the side of the head, to produce a sequence of two different polarity segments. In the other case the spacer contained the same average numbers of propylene and ethylene oxide groups but in some homogeneous arrangement. The intermediate spacer structure, without ionic head group and in the cases of the carboxylate and sulfate extended surfactants, had a packing density reduction which is associated to the homogeneously alkoxide arrangement in the spacer. Such an arrangement was found to produce about 20% more surface area at the interface, apparently because it results in some plumpness due to the spacer folding to remain close to the interface. Both the critical micelle concentration and occupied interfacial area of the extended surfactant increased with the ionization of the anionic group associated with the electrostatic repulsion effect.

**Keywords** Extended surfactant · Adsorption · Micellization · Intermediate spacer structure

## Introduction

So-called extended surfactants contain an intermediate polarity spacer between the conventional hydrophilic head

and lipophilic tail groups. This structure was introduced about 15 years ago [1] to mimic the effect of the surfactant and lipophilic linker [2–6] combination in increasing solubilization in bicontinuous microemulsions [7]. Extended surfactants were found to be able to produce a low interfacial tension and a high solubilization with polar oils such as fatty acid esters, diglycerides and even natural triglycerides [1] to an importance not attained by conventional surfactants [8, 9]. The current state of the art attributes these outstanding properties to a smooth transition from a polar to an apolar environment at the interface over a considerable thickness [10].

Only a few experimental species of the alkyl polypropylene oxide sulfate type have been made available by surfactant manufacturers and have been tested in applications such as detergency or solubilization of polar oils [11–16]. Extended surfactants behave in some aspect as conventional ones and may be mixed with other surfactants with fairly linear mixing rules [17, 18]. Some species with other head groups such as carboxylate, C5 and C6 glucosides have been prepared [19–22] but there is not yet a clearly established relationship between the extended surfactant structure and the properties beyond the fact that the alkyl polypropylene oxide sulfate species behave in some aspects as conventional surfactants, with some additional features that seem to depend on the (polypropylene oxide) spacer size. It was found that such an intermediate spacer is part of the hydrophobe and that its size is of paramount importance to solubilize some oils [8, 9]. Additionally it was recently found that the portion of it which is close to the sulfate group, is probably slightly hydrated by water and confers on them a temperature dependency closer to polyethoxylated nonionics rather than to anionics [23].

The present investigation reports on the influence of two structural characteristics not yet studied, i.e. the effect of

A. M. Forgiarini (✉) · C. Scorzza · J. Velásquez · F. Vejar ·  
E. Zambrano · J.-L. Salager  
Lab. FIRP, Universidad de Los Andes, Mérida, Venezuela  
e-mail: anafor@ula.ve

the anion head group nature, particularly its ionization level, and the influence of the intermediate polarity spacer ordering, on the interfacial adsorption packing and on the association in micelles. A companion paper will deal with the effect of these structural characteristics on the physicochemical formulation aspects of surfactant-oil-water systems.

### Synthesis of Different Species: C12/PO7/EO7/HEAD and C12/PO + EO[H7 + 7]/HEAD

#### Synthesis of Alkoxyated Dodecanol Intermediates

*N*-dodecanol, synthesis grade from Merck was alkoxyated by Lipesa (San Tomé, Venezuela) according to a standard synthesis method [24–27] and the products were used as received. The basic method involves dissolving a KOH catalyst in a mixture of water and isopropyl alcohol, which is then evaporated. Ethylene oxide and propylene oxide are introduced as gaseous aliquots, which are each a small fraction of the total amount, i.e. 10% for the ethoxylation and propoxylation, and 5% for the mixed alkoxides addition. Each aliquot introduction slightly increases the reactor pressure, and the conversion is followed by the pressure decay. The next aliquot is introduced when the pressure has come to normal and so forth.

Two kinds of products were prepared with the same total amount of an average of 7 propylene oxide and 7 ethylene oxide groups per dodecanol molecule, but with different addition procedures. The first product type so-called “sequential” intermediate was prepared by first adding to dodecanol an average of 7 propylene oxide molecules, and next an average of 7 ethylene oxide molecules. It was labeled C12/PO7/EO7 to indicate that the polypropylene oxide group is located between the alkyl chain and the polyethylene oxide block (Scheme 1).

The second one referred to as a “homogeneous” intermediate was prepared according to the same method but by introducing very small aliquots (1/20th of the total amount) containing a gas mixture with equimolecular proportions of propylene oxide and ethylene oxide. The polyalkoxide block thus contained ethylene and propylene oxides, somehow homogeneously distributed over the spacer because of the

introduction of the gas mixture as 20 consecutive small aliquots. The compound was labeled C12/PO + EO[H7 + 7] to indicate the homogeneous distribution of an average of 7 propylene oxide and 7 ethylene oxide groups in the spacer, with essentially no segregation (Scheme 2).

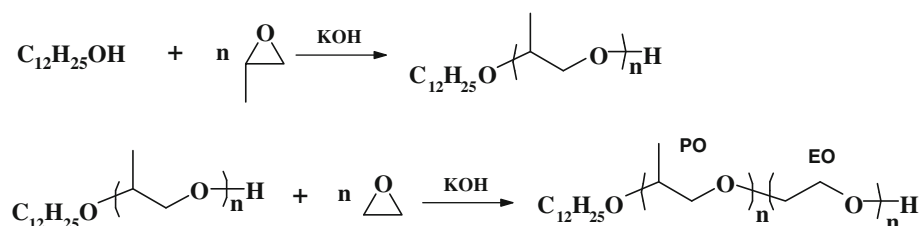
#### Addition of Ionic Head Group

The sulfate head extended surfactants were synthesized according to the method described elsewhere [21]. Depending of the alkoxyated structure of the intermediate they were labeled C12/PO7/PO7/S or C12/PO + EO[H7 + 7]/S.

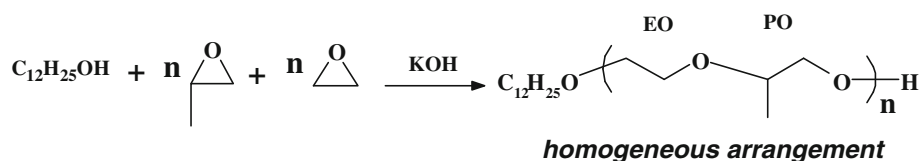
The carboxylate head extended surfactants were prepared in a similar way by diluting the corresponding alkoxyated dodecanol intermediate in a mixture of toluene and dimethylsulfoxide (1:1) containing KOH, which was then reacted with sodium chloroacetate for 24 h at ambient temperature under constant stirring. The filtered product was acidified with sulfuric acid and the resulting alkoxyated dodecanol carboxylic acid was extracted with toluene. The toluene was then evaporated and the acid was neutralized with a solution of NaOH in methanol. The final carboxylate head group extended surfactants was obtained by evaporation of the methanol. They were labeled C12/PO7/EO7/C and C12/PO + EO[H7 + 7]/C depending on the sequential or homogeneous nature of the alkoxide intermediate spacer (Scheme 3).

The disodium phosphate extended surfactants were prepared according to the literature to insure the formation of mono-alkyl phosphates [28] by first diluting the alkoxyated intermediate into toluene, which was then reacted with a 10 vol% polyphosphoric acid solution in toluene (added drop by drop) at ambient temperature under constant stirring during 72 h. The aqueous phase was removed and the organic phase was washed with 20 wt% NaCl brine and 2 N hydrochlorohydric acid. The organic phase was then treated with a 5 wt% sodium hydroxide aqueous solution to extract the disodium phosphate species in the aqueous phase. The aqueous phase was acidified again to restore the acid species which were extracted with ethyl ether. The extract was neutralized with a sodium hydroxide solution in methanol until pH 11 was attained, to warranty the formation of the disodium salt as recently shown [29]. Finally, the solvent

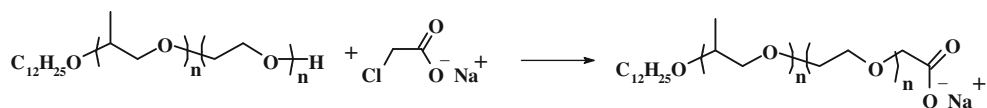
**Scheme 1** Synthesis of alkyl polypropylene oxide—polyethylene oxide intermediate C12/PO7/EO7 with sequential order



**Scheme 2** Synthesis of alkyl—poly(propylene oxide)—ethylene oxide) intermediate C12/PO + EO[H7 + 7] with homogeneous arrangement of alkoxides



**Scheme 3** Synthesis of alkyl polypropylene oxide—polyethylene oxide sodium carboxylate



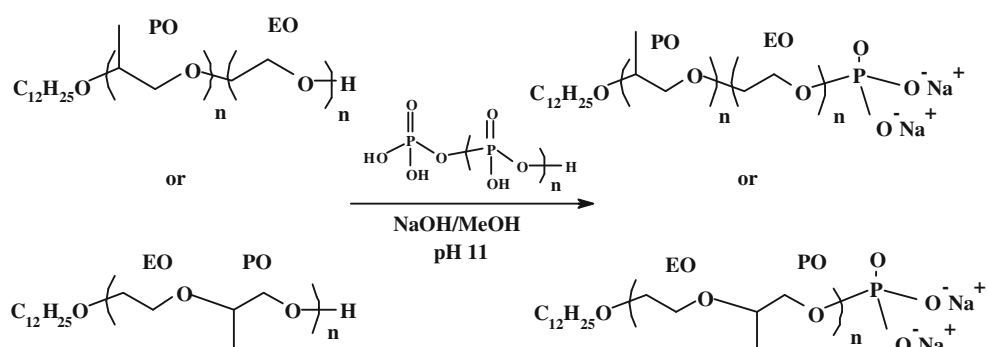
was evaporated under a vacuum. The final disodium phosphate head group extended surfactants were labeled C12/PO7/PO7/DSP and C12/PO + EO[H7 + 7]/DSP depending on the intermediate spacer structure (Scheme 4).

## Results

**Alkoxylated dodecanol intermediates** C12/PO7/EO7 and C12/PO + EO[H(7 + 7)] are slightly hydrophilic nonionic surfactants, and hence have a cloud point, which happens to be close to ambient temperature as seen in Table 1.

**The cloud point** was essentially the same for both substances, i.e. it is independent of the arrangement of the EO and PO groups in the polyalkoxide chain. However, a slight cloud point decrease was observed as expected [30] as salinity was increased. The sequential arrangement intermediate was found to be very slightly more hydrophilic at zero salinity with a cloud point at 27 °C versus 25.5 °C for the homogeneous arrangement one, which is a difference at the limit of significance, and even less when salt is added. It may be said that the ethylene oxide and propylene oxide contributions to the cloud point, i.e. the tendency to be less water soluble, is basically quite insensitive to the alkoxide species arrangement in the spacer. The cloud point temperature in pure water was similar to the one found for the dodecanol with approximately 4 ethylene oxide groups (C12EO4) [31] which is known to be a nonionic surfactant with balanced hydrophilic-lipophilic tendencies. Hence adding 7 PO groups increases the lipophilicity and needs

**Scheme 4** Synthesis of alkyl polypropylene oxide polyethylene oxide disodium phosphate by adding a polyphosphoric acid



**Table 1** Cloud point temperature of alkyl alkoxide intermediates (at 1 wt%)

	Cloud point temperature (°C) ± 1 °C					
NaCl wt% in water	0	1	2	3	4	5
C12/PO7/EO7	27.0	23.5	21.5	19.0	16.5	14.5
C12/EO + PO[H(7 + 7)]	25.5	22.5	20.0	18.5	16.5	14.5

the addition of about 3–4 EO groups to compensate. This kind of equivalence will be discussed in the next report on phase behavior and optimum formulation.

## Tension Variations

The plots of surface tension versus (log) concentration (Fig. 1) allowed us to calculate the critical micelle concentration CMC (from the breaking point) and the maximum adsorption density  $\Gamma_m$  or molecular packing (from the slope just before the CMC) indicated as the interfacial area occupied per adsorbed molecule  $a^S$  calculated in  $\text{\AA}^2$  according to the following relationships [31].

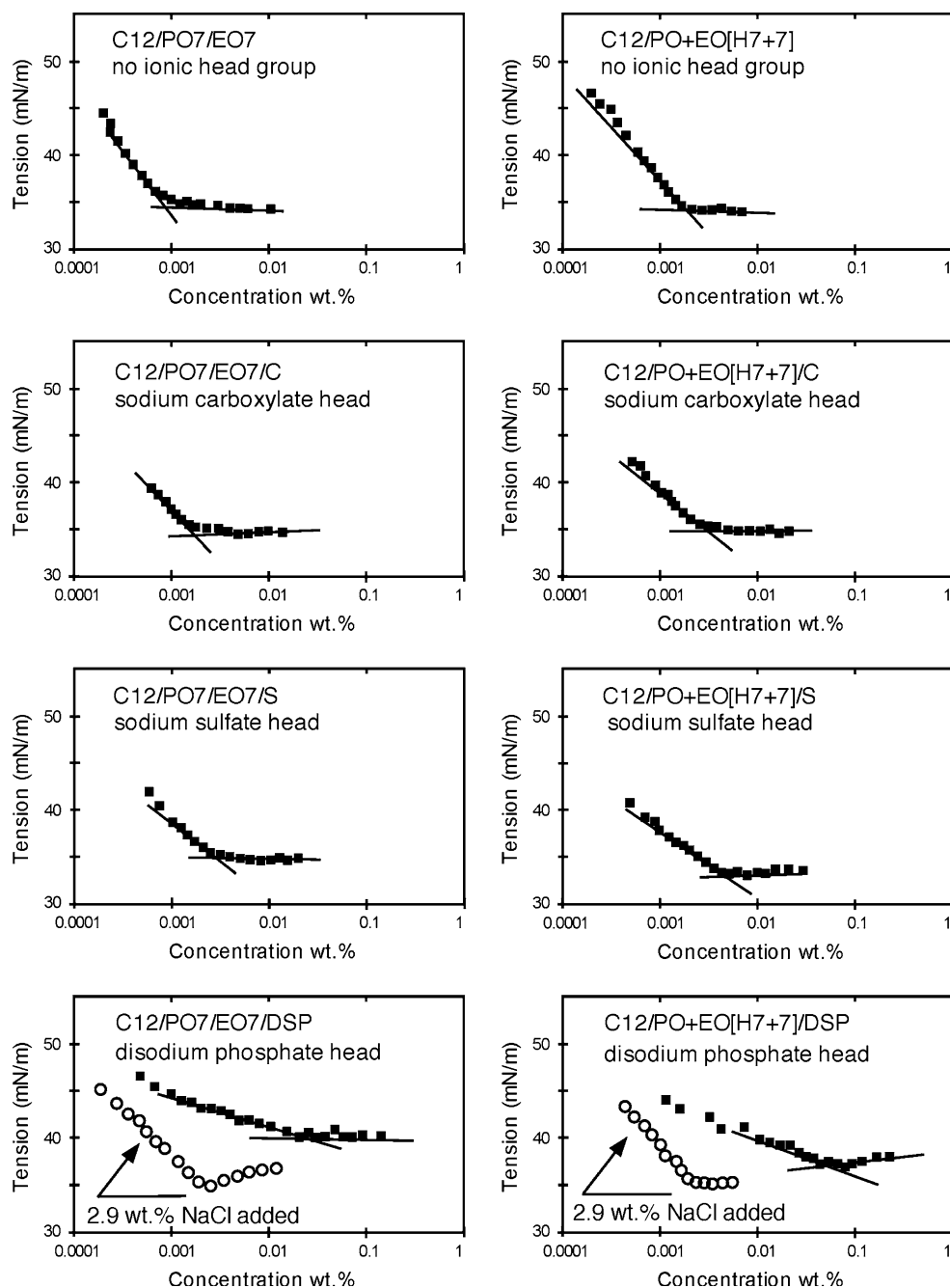
$\Gamma_m = -(1/2.3 RT) (\partial\gamma/\partial\log C)$  at the CMC and when  $\Gamma_m$  is in mol/1,000 m<sup>2</sup>, as in  $\text{\AA}^2$  equals  $a^S = 10^{23}/N_A \Gamma_m$ .

At 25 °C (298.16°K) the interfacial area in  $\text{\AA}^2$  per molecule may be calculated as

$$a^S = 946.32 n/\text{slope} (\partial\gamma/\partial\log C \text{ in mN/m})$$

where  $n$  is 1 for the nonionic species, 2 for the 1:1 anionic sulfate and carboxylate head products, and 3 for the disodium phosphates [31, 32]. In the case of adding 2.9

**Fig. 1** Variation of surface tension (mN.m) versus (log) concentration (in wt%)



wt% (0.5 mol/liter) NaCl in the solution of disodium phosphates,  $n = 1$  because the sodium ion concentration was essentially constant and only the phosphate concentration varied. The CMC and area per adsorbed molecules for the different cases are indicated in Table 2.

#### Effect of Intermediate Spacer Structure on Adsorption at the Interface

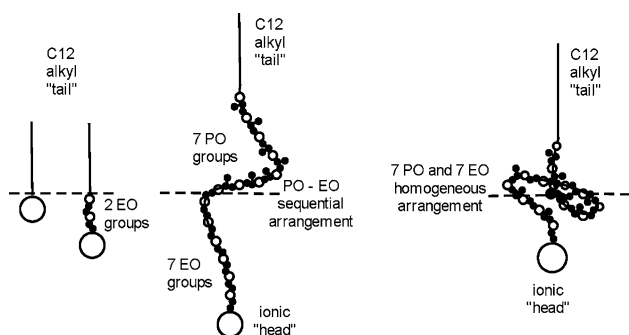
In the cases of the intermediate without an ionic head group, and of the carboxylate and sulfate extended surfactants, a

packing density reduction is associated to the homogeneously alkoxide arrangement in the spacer. Such arrangement was found to produce about 20% more surface area at interface, presumably because it resulted in some plumpness at the surfactant interfacial “waist” as illustrated in the Fig. 2, and thus induced more steric repulsion between neighboring molecules. Consequently the adsorbed molecule with the homogeneous arrangement in the spacer was less stretched than the one with a sequential arrangement spacer.

It should be remembered that a recent study has reported that the alkyl polypropylene oxide sulfate type extended

**Table 2** CMC in wt% (and mol/liter) and interfacial adsorption of extended surfactants (in Å<sup>2</sup> per molecule) with different spacers and ionic heads

	CMC	a <sup>S</sup> (Å <sup>2</sup> )
C12/PO7/EO7	0.0010 wt% (0.000011 mol/liter)	65
C12/PO7/EO7/C	0.0018 wt% (0.000019 mol/liter)	170
C12/PO7/EO7/S	0.0030 wt% (0.000030 mol/liter)	230
C12/PO7/EO7/DSP	0.020 wt% (0.00020 mol/liter)	720
C12/PO7/EO7/DSP with 2.9 wt% (0.5 mol/liter) NaCl	0.0022 wt% (0.000022 mol/liter)	85
C12/PO + EO[H7 + 7]	0.0020 wt% (0.000023 mol/liter)	80
C12/PO + EO[H7 + 7]/C	0.0029 wt% (0.000030 mol/liter)	200
C12/PO + EO[H7 + 7]/S	0.0045 wt% (0.000046 mol/liter)	270
C12/PO + EO[H7 + 7]/DSP	0.040 wt% (0.00040 mol/liter)	710
C12/PO + EO[H7 + 7]/DSP with 2.9 wt% (0.5 mol/liter) NaCl	0.0020 wt% (0.000020 mol/liter)	83

**Fig. 2** Position of a surfactant molecule adsorbed at interface: Dodecyl and dodecyl ether sulfate (*left*), and dodecyl alkoxide sulfate extended surfactants with sequential (*center*) and homogeneous (*right*) PO/EO arrangement spacer

surfactant (see Fig. 2 center) is not completely stretched [23] as the dodecyl sulfate or ethoxy sulfate (Fig. 2 left), because of the evidence that the first 2–3 propylene oxide groups in the spacer which are close to the head group are likely to be slightly hydrated. As a consequence the polypropylene oxide part of the spacer is probably slightly bent to accommodate some proximity of the interface for the first propylene oxide groups, as shown in Fig. 2 (center) sequential spacer molecule.

This interpretation explains why the C12/PO7/EO7/S occupies 230 Å<sup>2</sup> per molecule, compared with 53 Å<sup>2</sup> for

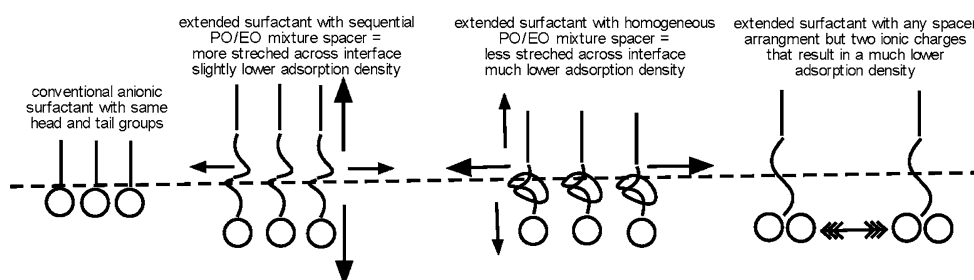
dodecyl sulfate (C12/S) or 60 Å<sup>2</sup> dodecyl ether sulfate (C12/EO2/S) [31].

Following this trend, the intermediate spacer made by homogeneous arrangement mixture of ethylene and propylene oxides would be even more hydrated and thus more bent to stay closer to interface (Fig. 2 right), as corroborated by the 270 Å<sup>2</sup> occupied by each molecule. This sequence is illustrated by the three left drawings in Fig. 3 in which the adsorption characteristics are illustrated.

In the case of the disodium phosphate specie, the packing appeared to be extremely loose, with an area per molecule (720 Å<sup>2</sup>) which was more than two times larger than in other cases (see Fig. 3 right drawing). Moreover there was essentially no difference in packing between the molecules containing sequential and homogeneous arrangements of the alkoxide groups in the spacer. This may be easily interpreted as the dominating influence of the double ionic charge in the head group which produced an electrostatic repulsion, that determined the packing and offset any steric repulsion effect produced by the spacer folding.

#### Effect of the Ionic Head Group on Adsorption at Surface

The effect of the ionic group was first analyzed by comparing the CMC and area per molecule with the case of the

**Fig. 3** Adsorption characteristics versus the spacer arrangement in different cases

dodecyl alkoxide intermediate C12/PO7/EO7 with no ionic head, which has a low CMC (0.0010 wt% or 0.000011 mol/liter) and occupies  $65 \text{ \AA}^2$  per molecule. The introduction of the carboxylate group raised the area to  $170 \text{ \AA}^2$ . The sulfate group generally exhibited slightly more charge because it comes from a stronger acid, and thus the CMC and area per molecules increased slightly more.

This is in agreement with the literature for the non-extended species, e.g.,  $53 \text{ \AA}^2$  for the  $\text{C}_{12}\text{SO}_4^-\text{Na}^+$  that is slightly more than  $40\text{--}48 \text{ \AA}^2$  for  $\text{C}_{11}\text{H}_{23}\text{COO}^-\text{Na}^+$  and the  $\text{C}_{11}\text{--O--CH}_2\text{COO}^-\text{Na}^+$  depending on conditions.

The disodium phosphate exhibited 2 charges and thus the increase in repulsion was considerably higher and resulted in a large increase in the CMC and in the surface area per molecule, which reached  $700 \text{ \AA}^2$ . It may be concluded that the effect of the head group is essentially related to the ionization, the carboxylate being slightly less dissociated than the sulfate, and the disodium phosphate having essentially two times more charges.

The same ranking and progression was found in the homogeneous alkoxide spacer species, with a slightly higher surface area per molecule with none or with a single ionic charge. The explanation is that the alkoxide (sequential or homogenous) spacer was not fully stretched to be positioned perpendicular to interface, and that there was some additional repulsive interaction of steric nature, e.g. some “tail whipping” or “playing elbow” effect, with the carboxylate and sulfate ionic heads. This effect was, however, completely offset by the electrostatic repulsion in the case of the divalent phosphate species whose properties are the same whatever the spacer.

#### Influence of the Alkoxide Spacer Arrangement on the CMC

It is sometimes difficult to determine the CMC very accurately at the breaking point of the tension—log concentration plot, but it is in general easy to find out which of two plots exhibits a higher or lower CMC, by just overlapping them. Hence, the values shown in Table 2 may be somehow inaccurate, but the ranking of the CMCs according to the surfactant species is unquestionable.

For the nonionic intermediates, the two times lower CMC for C12/PO7/EO7 indicates that the sequentially arranged spacer is more likely to gather in micelles. This may be interpreted as a better segregation between head and tail, and probably a lower interaction with water of the 7 EO and 2–3 PO close to water when compared with the homogeneous arrangement  $\text{EO} + \text{PO}/\text{H7} + 7$ . The bulkier “waist” group results in some steric repulsion that opposes micellization in particular because it weakens the interaction between the tails.

For the two monovalent anionic head group species, again the sequentially arranged spacer systematically exhibited a two-three times lower CMC than the homogeneously arranged spacer counterpart, thus corroborating that the presence of the homogeneous alkoxide spacer tends to increase the interaction with water, independently of the anionic head group.

Of course the occurrence of a double charge in the disodium phosphate species considerably increase the CMC, and the electrostatic effect seems to be much more important that the spacer structure, which has, however, still some minor effect on the CMC.

#### Influence of the Head Group on the CMC

When the CMCs were compared according to the nature of the head group, it was seen that for both sequential and homogeneous spacers, it was slightly raised by the introduction of the carboxylate, even more with the sulfate, and considerably more with the divalent phosphate. This ranking exactly corroborates the increased hydrophilicity associated with the head group ionization, just in the same way as it was found to influence the repulsion between neighboring adsorbed molecules at the interface.

#### A Summing up of the General Trends

The comparison of the area per adsorbed molecule at the air-water interface and of the CMC in aqueous solution, indicated that the extended surfactant species may be ranked according to their head group ionization, which increases from the nonionic group to carboxylate, sulfate and disodium phosphate. The more ionized the head group, the higher the CMC and the higher the surface area per adsorbed molecule. On the other hand, the replacement of the polypropylene oxide—polyethylene oxide sequence by an homogeneous mixing of the alkoxides in the spacer tends to increase the surface area per adsorbed molecule and the CMC, with an increased hydrophilicity probably due to a better interaction with water of the uniformly mixed alkoxide spacer, because its closer position with respect to the interface.

**Acknowledgments** The authors thank their industrial associate LIPESA ([www.Lipesa.com](http://www.Lipesa.com)) for taking care of the propoxylation and ethoxylation reactions to produce intermediate substances.

#### References

1. Miñana-Pérez M (1993) Contribution à la microémulsification d'huiles polaires de synthèse ou naturelles [in French], Ph.D. Dissertation, University of Pau PA, France

2. Graciaa A, Lachaise J, Cucuphat C, Bourrel M, Salager JL (1993) Improving solubilization in microemulsion with additives-part 1: the lipophilic linker role. *Langmuir* 9:669–672
3. Graciaa A, Lachaise J, Cucuphat C, Bourrel M, Salager JL (1993) Improving solubilization in microemulsion with additives-part 2: long chain alcohols as lipophilic linkers. *Langmuir* 9:3371–3374
4. Salager JL, Graciaa A, Lachaise J (1998) Improving Solubilization in microemulsion with additives-part III: lipophilic linker optimization. *J Surf Deterg* 1:403–406
5. Sabatini DA, Acosta E, Harwell JH (2003) Linker molecules in surfactant mixtures. *Current Opin Colloid Interface Sci* 8:316–326
6. Acosta E, Mai PD, Harwell JH, Sabatini DA (2003) Linker-modified microemulsions for a variety of oils and surfactants. *J Surf Deterg* 6:353–363
7. Salager JL, Antón RE, Sabatini DA, Harwell JH, Acosta EJ, Tolosa LI (2005) Enhancing solubilization in microemulsions—State of the art and current trends. *J Surf Deterg* 8:3–21
8. Miñana-Pérez M, Graciaa A, Lachaise J, Salager JL (1995) Solubilization of polar oils with extended surfactants. *Colloids Surf A* 100:217–224
9. Miñana-Pérez M, Graciaa A, Lachaise J, Salager JL (1995) Solubilization of polar oils in microemulsion systems. *Prog Colloid Polym Sci* 98:177–179
10. Salager JL, Scorzza C, Forgiarini A, Arandia MA, Pietrángeli G, Manchego L, Véjar F (2008) Amphiphilic mixtures versus surfactant structures with smooth polarity transition across interface to improve solubilization performance. Paper A-17. 7th World Surfactant Congress CESIO, Paris, June 23–25
11. Smith GA, Hand KR (2006) Enhanced solubilization using extended chain surfactants. US Patent 2006/0211593 A1. 21 Sept 2006
12. Tongcumpou C, Acosta EJ, Quencer LB, Joseph AF, Scaemhorn JF, Sabatini DA, Yanumet N, Chavadej S (2005) Microemulsion formation and detergency with oily soils. III performance and mechanisms. *J Surf Deterg* 8:147–156
13. Withayapanyanon A, Acosta E, Harwell JH, Sabatini DA (2006) Formulation of ultralow interfacial tension systems using extended surfactants. *J Surf Deterg* 9:331–339
14. Do L, Withayapanyanon A, Harwell JH, Sabatini DA (2009) Environmentally friendly vegetable oil microemulsions using extended surfactants and linkers. *J Surf Deterg* 12:91–99
15. Withayapanyanon A, Phan TT, Heitmann TC, Harwell JH, Sabatini DA (2010) Interfacial properties of extended surfactant based microemulsions and related macroemulsions. *J Surf Deterg* 13:127–134
16. Phan TT, Harwell JH, Sabatini DA (2010) Effects of triglyceride molecular structure on optimum formulation of surfactant-oil-water. *J Surf Deterg* 13:189–194
17. Miñana-Pérez M, Graciaa A, Lachaise J, Salager JL (1996) Systems containing mixtures of extended surfactants and conventional nonionics. Phase behavior and solubilization in microemulsion. 4th World Surfactants Congress (Barcelona, Spain, June 3–7, 1996) Proceedings vol. 2, 226–234. Edited by R. de Lluria for AEPSAT, Barcelona, Spain
18. Withayapanyanon A, Harwell JH, Sabatini DA (2008) Hydrophilic-lipophilic deviation (HLD) for characterizing conventional and extended surfactants. *J Colloid Interface Sci* 325:259–266
19. Scorzza C, Godé P, Martin P, Miñana-Pérez M, Salager JL, Villa P, Goethals G (2002) Synthesis and surfactant properties of a new “extended” glucidoamphiphile made from D-Glucose. *J Surf Deterg* 5:331–335
20. Scorzza C, Godé P, Goethals G, Martin P, Miñana-Pérez M, Salager JL, Usubillaga A, Villa P (2002) Another new family of “extended” glucidoamphiphiles. Synthesis and surfactant properties for different sugar head groups and spacer arm lengths. *J Surf Deterg* 5:337–343
21. Fernandez A, Scorzza C, Usubillaga A, Salager JL (2005) Synthesis of new extended surfactants containing a carboxylate or sulfate polar group. *J Surf Deterg* 8:187–191
22. Fernandez A, Scorzza C, Usubillaga A, Salager JL (2005) Synthesis of new extended surfactants containing a xylitol polar group. *J Surf Deterg* 8:193–198
23. Velázquez J, Scorzza C, Véjar F, Forgiarini A, Anton RE, Salager JL (2010) Effect of the temperature and other variables on the optimum formulation of anionic extended surfactants-alkane-brine systems. *J Surf Deterg* 13:69–73
24. Cox MF, Weerasooriya U (1999) Enhanced propoxylation of alcohols and alcohols ethoxylates. *J Surf Deterg* 2:59–68
25. Di Serio M, Vairo G, Iengo P, Felippone F, Santacesaria E (1996) Kinetics of ethoxylation and propoxylation of 1- and 2-octanol catalyzed by KOH. *Ind Eng Chem Res* 35:3848–3853
26. Santacesaria E, Di Serio M, Garaffa R, Addino G (1992) Kinetics and mechanisms of fatty alcohol polyethoxylation. 1. The reaction catalyzed by potassium hydroxide. *Ind Eng Chem Res* 31:2413–2418
27. Santacesaria E, Di Serio M, Garaffa R, Addino G (1992) Kinetics and mechanisms of fatty alcohol polyethoxylation. 2. Narrow range ethoxylation obtained with barium catalysts. *Ind Eng Chem Res* 31:2419–2421
28. Tracy DJ, Reieson RL (2002) Commercial synthesis of monoalkyl phosphates. *J Surf Deterg* 5:169–172
29. Osanai S, Yanada G, Hidano R, Beppu K, Namiwa K (2010) Preparation and properties of phosphate surfactants containing ether and hydroxy groups. *J Surf Deterg* 13:41–49
30. Mahajan RK, Vohra KK, Kaur N, Aswal VK (2008) Organic additives and electrolytes as cloud point modifiers in octylphenol ethoxylate solutions. *J Surf Deterg* 11:243–250
31. Rosen M (2004) Surfactants and interfacial phenomena, 3rd edn. Wiley-Interscience, Hoboken
32. Adamson A, Gast AP (1997) Physical chemistry of surfaces, 6th edn. Wiley, New York

## Author Biographies

**Ana M. Forgiarini** earned a BS in Chemical Engineering from the Technological Institute in Barquisimeto (Venezuela) and an MS in Chemical Engineering from University of the Andes. She received her Ph.D. from University of Barcelona (Spain) and spent a year as a postdoctoral fellow at North Carolina State University (USA). Over the past 20 years she has been involved in teaching and research at the University of the Andes, where she is currently deputy director of Lab. FIRP, and heads the micro and nanoemulsions R&D group.

**Cesar Scorzza** holds a BS in Pharmacy, an MS in Drug Chemistry, and a Ph.D. in Applied Sciences from the University of the Andes (Mérida, Venezuela) and was awarded a FONACIT Postdoctoral Fellowship. He is currently a Senior Research Scientist at Lab. FIRP, working on the synthesis of surfactants and their physico-chemical properties.

**Josmary Velasquez** earned a BS in Chemistry from the Central University of Venezuela in Caracas. During the past 2 years she has been working in surfactant formulation projects as a Research Assistant in Lab. FIRP at University of the Andes (Mérida Venezuela).

**Francia Vejar** received a BS in Chemical Education from the University of the Andes (Mérida-Venezuela). She has been working in laboratory teaching and research in the Chemical Engineering

School for the past 29 years, where she has been head of Lab. FIRP technical staff since 1992.

**Emérita Zambrano** earned a BS in Chemical Engineering from the University of the Andes (Venezuela) in Mérida. For the past 2 years she has been working in surfactant formulation projects as a Research Assistant in Lab. FIRP at the University of the Andes (Mérida Venezuela).

**Jean-Louis Salager** earned a BS in chemistry and a BS in chemical engineering from the University of Nancy (France) and a Ph.D. from the University of Texas at Austin (USA). For the past 30 years he has been involved in teaching and research at the University of the Andes where he is the founder and former director of Lab. FIRP. He is a consultant in petroleum production, health care, hygiene and detergent products.