

New oligomeric surfactants with multiple-ring spacers: Synthesis and tensioactive properties

Marcelo C. Murguía, María I. Cabrera, Javier F. Guastavino, Ricardo J. Grau *

*Laboratorio de Química Fina., Instituto de Desarrollo Tecnológico para la Industria Química-INTEC,
Universidad Nacional del Litoral (UNL) and Consejo
Nacional de Investigaciones Científicas y Técnicas (CONICET), Güemes 3450, 3000 Santa Fe, Argentina*

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Abstract

New anionic oligomeric (tetrameric) surfactants with different spacing architecture based on dioxane rings were synthesized, and their surface-active properties were studied. The synthesis of these compounds involves a three-step procedure comprising tetraglycidyl ethers as key intermediates for connecting four amphiphilic moieties. Critical aggregation concentration (CAC), surface tension at the CAC (γ_{CAC}), ability of these compounds to lower surface tension by 0.02 N/m (C_{20} and pC_{20}), estimated values of the surface area occupied by the surfactant headgroups (a), and packing parameter (P) values are reported at 20 and 40 °C. The molecular architecture of these compounds influences strongly the values of these physicochemical parameters. It was found that the ability of these compounds to lower surface tension is good, but the high relative propensity to form aggregates is their distinctive feature. This ability of aggregation is favored as the number of dioxane rings in the spacer group increases and the spacer group is less flexible.

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1. Introduction

The development of new surfactants displaying greater propensity to reduce surface tension efficiently and to form new modes of self-assembly is experiencing rapid academic and technological advances. Most of these compounds belong to the type named gemini surfactants, which comprises dimeric surfactants having two amphiphilic moieties linked together at the level of the headgroup by a spacer group of varying nature [1–5]. The unusual properties exhibited by dimeric surfactants have stimulated the synthesis of oligomeric surfactants [6]. Even though the properties of oligomeric surfactants have been found to be better than those corresponding to dimeric homologues, only a limited number of trimeric surfactants have been synthesized and studied so far, and still less attention has been paid to tetrameric surfac-

tants. For example, typical colloidal properties of multiarmed and multicationic surfactants having different spacers have been recently reported [1–5].

In a previous report, we described the synthesis of double-chain and quadruple-chain anionic surfactants having C_{10} saturated hydrocarbon tails and pentaerythritol as spacer group [7]. They exhibit an excellent performance to lower the surface tension in aqueous solutions. Indeed, the critical micelle concentration (CMC) and the concentration of surfactant required to reduce the surface tension by 20 mN/m (C_{20}) were found to be in the 10^{-5} and 10^{-6} mol/L range, respectively (surfactant **A**, Scheme 1). In view of this high effectiveness and in continuation of our program to develop novel surfactants, we now report the facile synthesis of new tetrameric anionic surfactants with different spacing architecture (**B–D**) as shown in Scheme 1. The spacers are flexible (**B**), semi-flexible (**A** and **C**), or rigid (**D**), and possess dioxane groups that confer wet-ability. We also report a study of their surface-active properties and discuss the effect of their

* Corresponding author. Tel.: +54 342 4511 539; fax: +54 342 4511 597.
E-mail address: cqfina@ceride.gov.ar (R.J. Grau).

structural differences on behavior of these oligomeric surfactants.

2. Material and methods

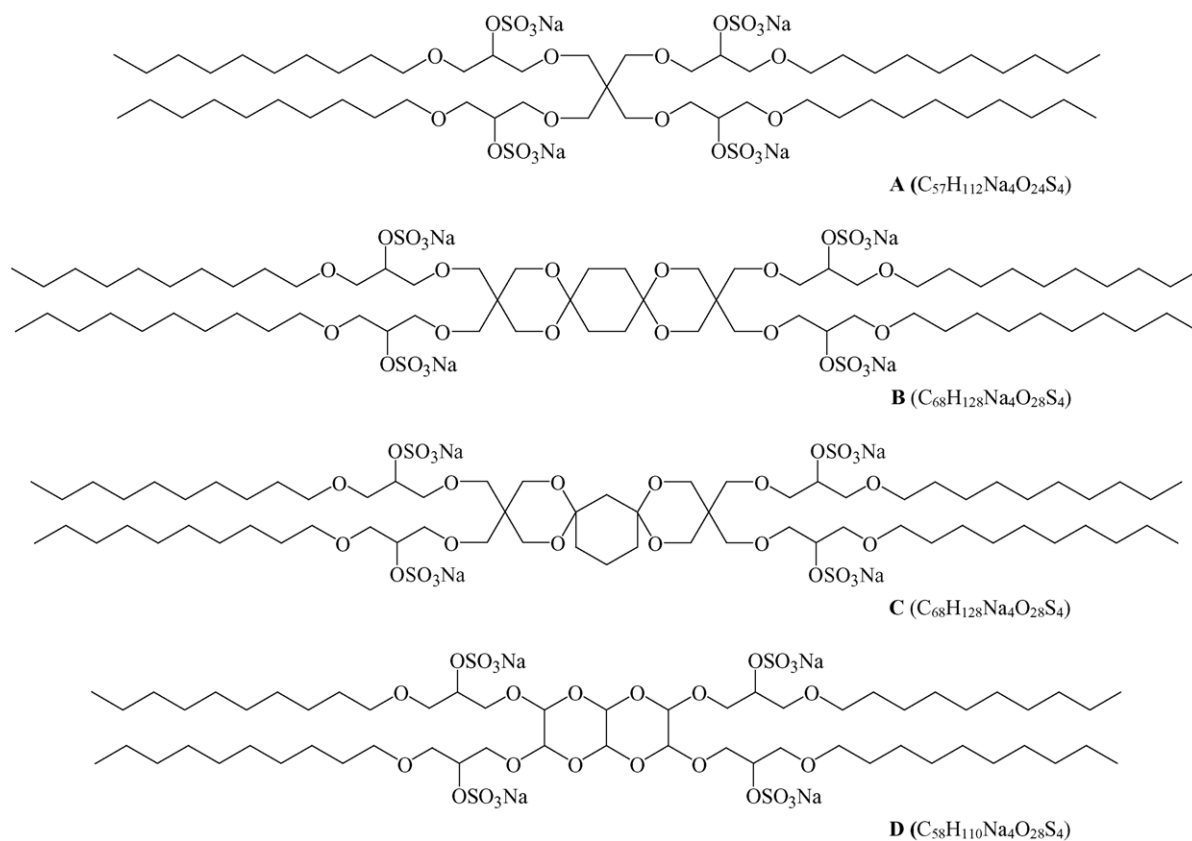
2.1. General experimental procedure

Surfactant **A** was synthesized as previously reported [7]. The preparation of new surfactants **B–D** is outlined in Scheme 2. The synthetic strategy involves a three-step procedure comprising tetraglycidyl ethers as key intermediates for connecting four amphiphilic moieties. The reaction of symmetric tetraols **1a–d** with (\pm)-epichlorohydrin in the presence of potassium hydroxide in DMSO gave tetraglycidyl ethers **2a–d** in 78, 89, 74, and 65% yields, respectively. Further basic solvolysis of the oxirane with *n*-decanol in the presence of metallic potassium afforded the hydrophobized intermediates **3a–d** in 74, 84, 79, and 74% yields, respectively. After the complete sulfonation of the hydroxy groups with chlorosulfonic acid in dichloromethane, compounds **A–D** were obtained in about 70% yields. All yields reported are for isolated products. The purification of compounds was performed by TLC and column chromatography. The structures of all synthesized compounds were satisfactory confirmed by spectra (IR, ^1H and ^{13}C NMR)

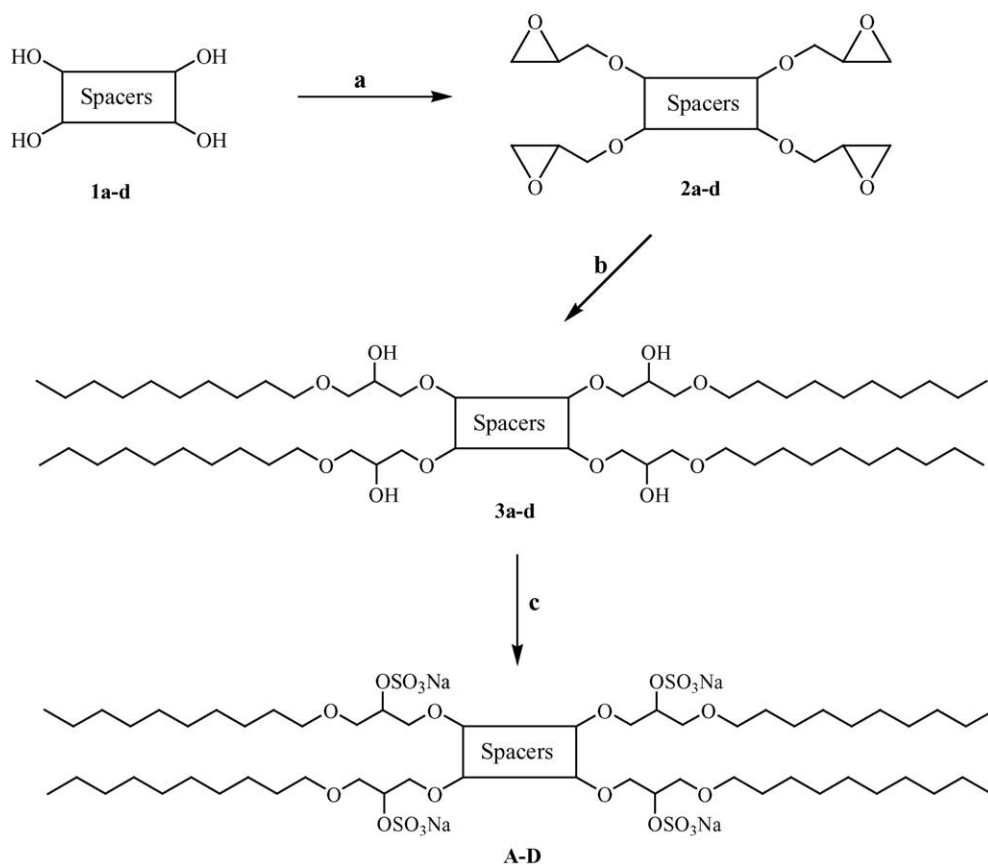
and elemental analyses. In all cases, the spectra and elemental analyses acquired were consistent with the assigned structures of the compounds. Purity of surfactants **A–D** was also checked from the observed clear break point in their surface tension versus concentration (on log scale) curves.

2.2. Procedure for the preparation of tetraglycidyl ethers **2b–d**

A stirred solution of **1b**, **1c** or **1d** (4.3 mmol) and KOH (17.1 mmol) in DMSO (15 mL) was heated until complete dissolution at 35 °C, and the (\pm)-epichlorohydrin (25.71 mmol) was then added dropwise for 30 min. After complete addition, stirring was continued for 7 h. The solid material was filtered and washed with CH_2Cl_2 (150 mL). The organic solvent was removed under vacuum and the residue was partitioned between Et_2O (2×150 mL) and brine (80 mL). The organic extract was dried (MgSO_4), filtered and concentrated. The purification was performed by column chromatography on silica gel with acetone–hexane (30–70, v/v) as eluent. It afforded compounds **2b–d** in good yields (89, 74 and 65% yield, respectively) as oil pale yellow. The details of the spectral characterizations and elemental analysis are summarized in Table 1.



Scheme 1. Molecular structure of the tetrameric surfactants **A–D**.



Scheme 2. Reagents and conditions: (a) \pm -Epichlorhydrin/KOH/DMSO, 35 °C; (b) C₁₀H₂₁OH/K, 80 °C; (c) (i) ClSO₃H/dichloromethane, <0 °C, (ii) NaOH/EtOH.

Table 1
Spectral and elemental analysis data for the compounds **2b–c**

Compound	IR spectra ^a ν_{\max} (/cm)	MS spectra m/z (% rel. int.)	¹ H NMR (CDCl ₃) δ	¹³ C NMR (CDCl ₃) δ (ppm)	Elemental anal. found (calc'd)
2b	1100.0	572 (M^+ , 3)	1.72–1.90 (m, 8H)	33.09	H, 7.74 (7.59)
	1460.0	299 (4)	2.42–2.62 (m, 8H)	42.11	C, 58.73 (58.62)
	2980.0	285 (12)	2.94–2.98 (m, 4H)	44.47	O, 33.53 (33.79)
		113 (10)	3.43–3.66 (m, 8H)	49.91	
		83 (42)	3.74–3.84 (m, 8H)	63.07	
		55 (95)	4.13 (s, 4H)	63.15	
		31 (100)	4.23 (s, 4H)	72.63	
				95.90	
2c	1095.0	572 (M^+ , 3)	1.28–1.72 (m, 6H)	17.58	H, 7.74 (7.61)
	1461.0	299 (4)	1.75–2.01 (m, 2H)	35.86	C, 58.73 (58.68)
	2978.0	285 (13)	2.42–2.62 (m, 8H)	43.21	O, 33.53 (33.71)
		113 (10)	2.94–2.98 (m, 8H)	49.91	
		83 (40)	3.43–3.66 (m, 8H)	63.07	
		55 (97)	3.74–3.84 (m, 8H)	63.15	
		31 (100)	4.13 (s, 4H)	72.63	
			4.24 (s, 4H)	106.23	
2d	1110.0	434 (M^+ , 5)	2.45–2.62 (m, 4H)	44.47	H, 6.03 (6.29)
	1463.0	298 (4)	2.86–2.92 (m, 4H)	54.59	C, 49.77 (49.97)
	2985.0	285 (12)	3.47–3.58 (m, 8H)	69.97	O, 44.20 (43.74)
		113 (10)	4.64 (s, 2H)	96.08	
		83 (42)	4.66 (s, 4H)	100.30	
		55 (95)			
		31 (100)			

^a Film on KBr.

Table 2
Spectral and elemental analysis data for the compounds **3b–c**

Compound	IR spectra ^a ν_{\max} (/cm)	¹ H NMR (CDCl ₃) δ	¹³ C NMR (CDCl ₃) δ (ppm)	Elemental anal. found (calc'd)	
3b	1100.0	0.82–0.85 (m, 12H)	14.07, 22.80	H, 11.03 (11.25)	
	1461.0	1.17–1.35 (m, 56H)	28.93, 29.23	C, 67.74 (67.80)	
	2980.0	1.59–1.65 (m, 8H)	29.55, 29.60	O, 21.23 (20.95)	
	3500.0	1.76–1.84 (m, 8H)	29.88, 29.90		
		2.78 (m, 4H)	33.09, 41.11		
		3.32–3.51 (m, 24H)	63.07, 63.16		
		3.73–3.83 (m, 12H)	70.11, 71.14		
		4.13 (s, 4H)	72.71, 73.77		
		4.23 (s, 4H)	95.90		
3c	1095.0	0.82–0.85 (m, 12H)	14.05, 17.58	H, 11.03 (11.22)	
	1460.0	1.18–1.36 (m, 60H)	22.80, 28.93	C, 67.74 (67.82)	
	2876.0	1.58–1.66 (m, 10H)	29.23, 29.55	O, 21.23 (20.96)	
	3500.0	1.97–2.01 (m, 2H)	29.60, 29.88		
		2.78 (m, 4H)	29.90, 32.20		
		3.31–3.44 (m, 24H)	43.21, 63.07		
		3.48–3.52 (m, 12H)	63.16, 70.11		
		4.13 (s, 4H)	71.14, 72.71		
		4.23 (s, 4H)	73.77, 106.23		
3d	1091.0	0.80–0.87 (m, 12H)	14.01, 22.80	H, 10.76 (10.79)	
	1460.0	1.16–1.37 (m, 56H)	25.95, 28.93	C, 65.26 (65.10)	
	2875.0	1.55–1.69 (m, 8H)	29.23, 29.55	O, 23.98 (24.11)	
	3500.0	2.78 (m, 8H)	29.60, 29.90		
		3.28–3.78 (m, 24H)	32.20, 68.09		
		4.64 (s, 2H)	70.11, 71.14		
		4.69 (s, 4H)	72.71, 96.08		
		98.90			

^a Film on KBr.

2.3. Procedure for the preparation of hydrophobic adducts **3b–d**

Metallic potassium (6 mmol) was dissolved into *n*-decanol (48 mmol) at 60 °C. Compounds **2b–d** (2.45 mmol) were dropped carefully into the resulting alkoxide solution. The reaction mixture was then stirred for 12 h at 80 °C. After neutralization with 10% hydrochloric acid at ambient temperature, the reaction mixture was extracted with a methylene chloride (3 × 50 mL):water (1 × 50 mL) solvent system. After the organic extracts were combined and dried with magnesium sulfate, any excess of *n*-decanol was distilled off under reduced pressure by Kugelrohr distillation. Compounds **3b–d** were isolated by silica gel chromatography of the residue with a hexane:acetone (3:1, v/v) as eluent. This procedure afforded **3b–d** in good yields (84, 79 and 74%, respectively) as white waxy products. The details of the spectral characterizations and elemental analysis are summarized in Table 2.

2.4. Procedure for the preparation of surfactants **B–D**

Chlorosulfonic acid (6 mmol) in dichloromethane (2.5 mL) was dropped carefully into a stirred solution of **3b–d** (0.6 mmol) in dichloromethane (5 mL) below 0 °C. The reaction was continued until the TLC peak based on **3a–c** disappeared (4 h) at ca. 0 °C. The reaction mixture was changed to pH 10 with alcoholic sodium hydroxide solution. After evaporation and subsequent extraction of the reaction

mixture with a *n*-BuOH (3 × 45 mL):water (100 mL) solvent system, the combined organic extracts were evaporated. The crude product was dissolved in dichloromethane and dried with magnesium sulfate, and then the insoluble solids were filtered off by passage through a Celite short column. After evaporation of the filtrate, compounds **B–D** were isolated as a white waxy product by silica gel chromatography of the residue with the following gradient elution system: dichloromethane:ethanol (10:1, v/v) subsequent to hexane:dichloromethane (1:1, v/v) afforded **B–D** in good yields (71, 72 and 70% yields, respectively) as white waxy products. The details of the spectral characterizations and elemental analysis are summarized in Table 3.

2.5. Analytical methods

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were measured in CDCl₃ or D₂O with a Bruker FT-200 spectrometer. Chemical shifts (δ) were reported in ppm related to tetramethylsilane (TMS) as an internal standard. The infrared (IR) spectra and mass spectra were recorded on a Shimadzu 8201 PC spectrometer and a Shimadzu GCMS-QP 5000 spectrometer, respectively. Elemental analyses were performed at Galbraith Laboratories, Inc., Knoxville, United States. TLC was carried out on precoated aluminum plates (0.1 mm) of silicagel 60 F-254; detection was performed by exposure to UV light and by spraying the plates with 5% (v/v) H₂SO₄ in ethanol followed by heating.

Table 3
Spectral and elemental analysis data for the compounds **3b–d**

Compound	IR spectra ^a ν_{\max} (/cm)	¹ H NMR (D ₂ O) δ	¹³ C NMR (D ₂ O) δ (ppm)	Elemental anal. found (calc'd)
B	1045.0	0.82–0.85 (m, 12H)	14.05, 22.80	H, 7.99 (8.01)
	1225.0	1.24–1.35 (m, 56H)	25.95, 28.93	C, 50.60 (50.43)
	2920.0	1.47–1.53 (m, 8H)	29.23, 29.55	Na, 5.70 (5.62)
	3382.9	1.80–1.84 (m, 8H)	29.60, 29.90	O, 27.76 (27.68)
		3.28–3.37 (m, 12H)	33.09, 41.11	S, 7.95 (8.26)
		3.66–3.84 (m, 24H)	63.07, 63.16	
		4.13 (m, 4H)	71.14, 72.74	
		4.23 (m, 4H)	72.92, 73.80 95.90	
C	1044.5	0.82–0.86 (m, 12H)	14.05, 17.58	H, 7.99 (8.01)
	1225.4	1.18–1.37 (m, 60H)	22.80, 25.95	C, 50.60 (50.63)
	2921.0	1.47–1.56 (m, 10H)	28.93, 29.23	Na, 5.70 (5.72)
	3383.1	1.84–2.00 (m, 2H)	29.60, 29.90	O, 27.76 (27.78)
		3.28–3.37 (m, 12H)	32.20, 35.86	S, 7.95 (7.86)
		3.66–3.84 (m, 24H)	43.21, 63.07	
		4.13 (m, 4H)	63.16, 71.14	
		4.23 (m, 4H)	71.74, 72.92 73.80, 106.23	
D	1041.0	0.82–0.85 (m, 12H)	14.05, 22.80	H, 7.51 (7.55)
	1222.0	1.15–1.35 (m, 56H)	25.95, 29.23	C, 47.21 (47.24)
	2919.0	1.36–1.56 (m, 8H)	29.55, 29.60	Na, 6.23 (6.36)
	3383.0	2.76 (m, 6H)	29.90, 32.20	O, 30.36 (30.39)
		3.29–3.38 (m, 12H)	70.91, 71.14	S, 8.69 (8.46)
		3.68–3.96 (m, 8H)	71.74, 96.08	
		4.64 (s, 4H)	98.90	
		4.69 (s, 4H)		

^a Film on KBr.

2.6. Surface tension measurements

Air–water surface tensions were measured at 20 and 40 °C by the Du Nuoy ring method. Calibration was performed against a range of standard liquids: excellent agreement with the literature values was found [8]. The critical aggregation concentrations (CAC) were determined using a series of aqueous solutions at various concentrations, and estimated from the break point of each surface tension versus concentration (on log scale) curve. The values of the surface tension of solutions of **A–D** compounds as a function of concentration are shown in Fig. 1.

3. Results and discussion

The critical aggregation concentration, the surface tension at the CAC (γ_{CAC}), the ability of these compounds to lower surface tension by 0.02 N/m (C_{20} and pC_{20}), the estimated values of the surface area occupied by the surfactant head-groups (a), and the packing parameter (P), at 20 and 40 °C, are summarized in Table 4.

Surfactant **D** having the most rigid spacer displays a minor surface activity at 20 °C, since the corresponding plot of surface tension versus log concentration does not display a dramatic change in slope of the curve as obtained

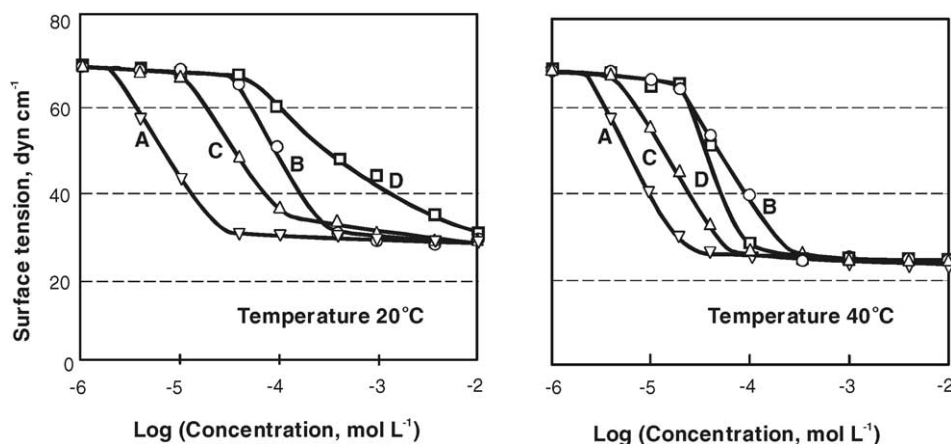


Fig. 1. Surface tension of solutions of **A–D** compounds as a function of concentration.

Table 4

CAC, γ_{CAC} , C_{20} , pC_{20} , CAC/C_{20} , a , and P values of oligomeric surfactants **A–D**, at 20 and 40 °C

Compound	A C ₅₇ H ₁₁₂ Na ₄ O ₂₄ S ₄	B C ₆₈ H ₁₂₈ Na ₄ O ₂₈ S ₄	C C ₆₈ H ₁₂₈ Na ₄ O ₂₈ S ₄	D C ₅₈ H ₁₁₀ Na ₄ O ₂₈ S ₄
At 20 °C				
CAC (mol/L)	4.68×10^{-5}	1.78×10^{-4}	1.05×10^{-4}	–
γ_{CAC} (N/m)	0.030	0.028	0.032	–
C_{20} (mol/L)	7.41×10^{-6}	3.16×10^{-5}	2.88×10^{-5}	–
pC_{20}	5.13	4.50	4.54	–
CAC/C_{20}	6.32	5.63	3.65	–
a (Å ²) ^a	95–118	83–104	102–128	–
P^a	0.71–0.85	0.81–1.07	0.65–0.82	–
At 40 °C				
CAC (mol/L)	3.98×10^{-5}	2.45×10^{-4}	5.62×10^{-5}	1.26×10^{-4}
γ_{CAC} (N/m)	0.025	0.025	0.028	0.025
C_{20} (mol/L)	6.31×10^{-6}	5.62×10^{-5}	1.48×10^{-5}	4.36×10^{-5}
pC_{20}	5.20	4.25	4.82	4.36
CAC/C_{20}	6.30	4.36	3.59	2.82
a (Å ²) ^a	101–125	124–156	99–124	76–95
P^a	0.66–0.83	0.53–0.67	0.67–0.84	0.88–1.09

^a Lowest and highest values correspond to $n = 4$ and $n = 5$, respectively.

for **A–C** surfactants. However, all four surfactants are surface active at 40 °C. A similar behavior with the temperature has been reported for anionic gemini surfactants having aromatic rings as rigid spacing groups [9]. Aggregation takes place at concentrations in the 10^{-4} to 10^{-5} mol/L range, which is a distinctive feature of dimeric and oligomeric surfactants. The CAC values of these tetrameric compounds depend on the architecture of the spacers. Increasing the number of dioxane rings of the surfactant spacer increases the CAC value, as the oxyethylene spacing units of the poly(ethylene oxide)-based gemini surfactants [6]. Indeed, surfactant **A** has smaller CAC values than those of surfactants **B–D**. The dioxane rings appear to act as hydrophilic units, which contribute to increasing CAC values. Furthermore, a comparison between homologues compounds, as surfactants **B** and **C**, reveals that the higher the flexibility of the spacer the higher the CAC, as expected. This behavior is more evident at 40 °C.

The values of the surface tension at the CAC are not meaningfully different as far as we can compare them for **A–D** surfactants. The γ_{CAC} values are all below 0.032 N/m at 20 °C, and about of 0.025 N/m at 40 °C. These values are similar to those of C₁₀ double-chain and triple-chain surfactants with two sulfonate groups (0.027–0.036 N/m), which in turn are much smaller than those for the corresponding single-chain surfactant (0.039 N/m) [10].

The C_{20} values reveal a good tendency of these surfactants to be adsorbed at the surface and to reduce the surface tension, which improves at increasing temperature except for surfactant **B**. This opposing behavior is not really understood. The pC_{20} value of the surfactant **A** (5.13 at 20 °C) is larger than those of the corresponding to the **B–D** surfactants, which are quite similar (about of 4.50 at 20 °C). This reveals that the pC_{20} values decrease with an increase in the number of dioxane rings, in accordance with the fact that the shortest spacing group provides the maximum efficiency [11].

Concerning the tendency to form aggregates relative to the capability to be adsorbed at the air/water interface, the CAC/C_{20} values indicate a higher relative preference of these compounds to form aggregates than do gemini surfactants. This might be due to the four hydrophobic groups are more suitable oriented to accommodate themselves in the internal part of the aggregates than the two hydrophobic group of the gemini surfactants. The aggregation is favored, relative to the adsorption, as the number of dioxane rings in the spacer group increases, as revealed by the CAC/C_{20} values for the surfactants **A** and **B**. Furthermore, the higher the rigidity of the spacer the higher the relative capability to aggregate, as shown the CAC/C_{20} values for the homologues surfactants **B** and **C**, which in turn are higher than the corresponding value for the surfactant **D** having the most rigid spacing group.

Concerning the capability of aggregate formation, we present a preliminary study based on the concept of molecular packing parameter P [12]. In spite of the limitations of the P approach [13], this provides us with a simple framework to rationalize the effect of the structural difference of surfactant headgroups. The packing parameter was calculated by the $P = (v/a)l$ formula, where the volume v occupied by the hydrophobic moiety of the amphiphile molecule and the critical length l in the full extended conformation were estimated using Tanford's equations [14]. In particular, we used four volumes occupied by a C₁₀ alkyl chain to stand v in the original formula, since surfactants **A–D** are with quadruple hydrophobic tails. The optimal cross-section surface area a occupied by the surfactant headgroup at the water–aggregate interface was estimated from the surface excess Γ . This estimation is quite uncertain due to the value of the fraction of bound counterions n for oligomeric surfactants need to be known. Some studies reported values of a based on $n = 2$ or $n = 3$ for ionic dimeric surfactants depending on their ionization state. The same problem arises for these four anionic headgroups for which $n = 4$ or $n = 5$ should be used. Due to

this uncertainty, the values of a reported in Table 4 are based on both n values (i.e., $n=4$ and $n=5$) and they should be taken as approximate ones. The a values (ranging from 83 to 128 Å², at 20 °C) are less than four times the value for the single-chain surfactant C₁₀H₂₁SO₃Na (about 43 Å²), indicating that these tetrameric surfactants are somewhat more closely packed at the air–solution interface than the single-chain reference compound. For surfactants **A** and **C**, the range of the estimated area per molecule does not change upon increasing the temperature from 20 to 40 °C. Nevertheless, the size of the headgroup of surfactant **B** is significantly increased. This would be attributable to the greater flexibility of the spacing group of **B** compared to those of **A** and **C**. The packing parameter model predicts that vesicles and/or bilayers should be formed for these surfactants **A–D**. In all cases, the presence of the oxygen atoms in the spacers confers an additional hydration ability that should assist in bringing the anionic headgroups closer, despite opposed electrostatic effects. Further experimental studies would be necessary to corroborate the aggregation properties of these compounds.

4. Conclusions

We have synthesized a novel series of anionic tetrameric surfactants using tetraglycidyl ethers as key intermediates for connecting four amphiphilic moieties. The surfactants were prepared by a three-step procedure from cheap tetraols, in good yields. The surface-active properties were reported and the effect of their structural differences on behavior of these oligomeric surfactants was discussed. The CAC, γ_{CAC} and CAC/C₂₀ values distinguish the surfactant **A** as the most powerful of all compounds synthesized in this work. Although a good ability of these surfactants to lower surface tension was found, the high relative propensity to form aggregates is their

distinctive feature. This ability of aggregation is favored, relative to the adsorption, as the number of dioxane rings in the spacer group increases and the spacer group is less flexible.

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