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# Cation Effect on the Binary and Ternary Phase Behaviors of Double-Tailed Methanesulfonate Amphiphiles

Jesús F. Ontiveros,<sup>1</sup> Bing Hong,<sup>1</sup> Kenji Aramaki,<sup>2</sup> Christel Pierlot,<sup>1</sup> Jean-Marie Aubry,<sup>1</sup>

Véronique Nardello-Rataj\*<sup>1</sup>

<sup>1</sup> Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, Cité Scientifique F-59655 Villeneuve d'Ascq, France

<sup>2</sup> Graduate School of Environment and Information Sciences, Yokohama National University, Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, Japan.

\* Corresponding Author: E-mail: [veronique.rataj-nardello@univ-lille.fr](mailto:veronique.rataj-nardello@univ-lille.fr) Tel: +33 (0)3 20 33 63 69

## Abstract

A series of symmetrical dialkyl methanesulfonate amphiphiles  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  ( $n = 6, 7, 8$ ) with different counter-cations ( $\text{M}^{m+} = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sc}^{3+}$ ) were synthesized in five steps. Their solubility and critical micelle concentration (CMC) in water were determined highlighting a huge effect of the chain length and the nature of the cation. The hydrophilic-lipophilic balance of the surfactants were assessed with the PIT-slope method based on the deviation from the Phase Inversion Temperature (PIT) of the reference  $\text{C}_{10}\text{E}_4/n\text{-octane}/0.01\text{M NaCl}_{(\text{aq})}$  emulsion system through addition of increasing amounts of the dialkyl methanesulfonates. The hydrophilicity of the surfactants was thus ranked in terms of  $d\text{PIT}/dx_{\text{sulfonate}}$ . A "cation" scan with the  $[\text{DiC}_6\text{CHSO}_3]_m\text{M}/\text{benzene}/\text{water}$  systems at  $f_w = 0.5$  was finally performed confirming the hydrophilicity ranking obtained with the PIT-slope method. It revealed that the  $[\text{DiC}_6\text{CHSO}_3]_2\text{Mg}$  behaves as a "Balanced Surfactant" able to form spontaneously a three-phase microemulsion system (Winsor III) just in the presence of water and oil, in the same way as the catalytic surfactant dimethyldioctylammonium molybdate, which has the same PIT-slope.

## Keywords

Dialkyl methanesulfonate, Critical micelle concentration, PIT-slope, Microemulsion, Cation scan.

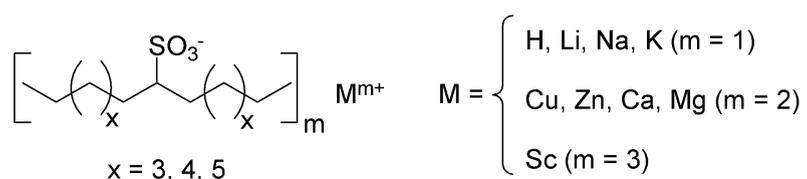
## Introduction

Anionic surfactants represent an important class of surfactants due to their extensive use in cleaning products. Among them, alkyl carboxylates, alkyl(benzene) sulfonates and alkyl sulfates are the most widely used (Tadros, 2006). Compared to alkyl sulfates, alkyl sulfonate surfactants with the same hydrophobic tail show different properties, notably higher CMCs (Dahanayake, Cohen & Rosen, 1986; Sadeghi & Shahabi, 2011), a lower foaming ability (Azira, Tazerouti & Canselier, 2008), weaker interactions with cationic surfactants (Chen, Xiao & Ma, 2004), and a lower sensitivity towards hydrolysis (Cross, 1998). In addition, sulfonates have replaced sulfates in some personal care product formulations such as shampoos because they would be less skin irritant. All these differences can be ascribed to the charge distribution at the headgroup, *i.e.* "the sulfonate ion net charge in surfactant molecules is much lower than that of the sulfate" (Huibers, 1999). However, the properties of surfactants are not only related to the nature of the headgroup but also to the structure of the hydrophobic tail (Myers, 2005). For example, the Krafft point of branched surfactants is much lower than that of the linear homologues (Ma, Boyd & Drummond, 2006). Besides, the molecule shape modification due to the branched hydrophobic tail also changes the phase behavior of the surfactant in lyotropic phases, emulsions and microemulsions (Ma *et al.*, 2006; Bawab, Bozeya & Odeh, 2014).

Among the sulfonate-based surfactants, the alkylbenzene sulfonates and the dialkyl sulfosuccinates such as the well-known sodium dioctyl sulfosuccinate (AOT) have been largely studied and industrially used. Commercial alkylsulfonates are always complex mixtures of isomers, which results from the preparation and purification process. For example, the Hostapur<sup>®</sup> SAS manufactured by Clariant and obtained by photosulfoxidation of *n*-paraffin are a mixture of secondary alkylsulfonates with the ionic head at different positions (Pfoertner & Oppenländer, 2012). The current methods for the preparation of secondary

alkylsulfonates include the chlorination of sulfides and the subsequent hydrolysis of the obtained sulfonyl chloride (Volfson & Melnikov, 1950), the direct oxidation of sulfide by nitric acid (Granet & Piekarski, 1986), the **thioesterification followed** by oxidation (Schechter *et al.*, 1985), or even the direct photosulfoxidation of **alkanes** (Ogata, Izawa & Tsuda, 1965; Ramloch & Täuber, 1979). However, these methods **require** a tedious purification step and always **result** in complex mixtures of isomers. As a consequence, the physicochemical properties of monodisperse branched alkylsulfonates are rarely reported in the literature (Dusart, 1985; Granet, Khadirian & Piekarski, 1990; Fraaije *et al.*, 2013).

Herein, we report on the synthesis and characterization of a series of well-defined symmetrical double-tailed methanesulfonic acid and methanesulfonates with alkyl chains bearing a total of 13, 15 and 17 carbon atoms as depicted in **Figure 1**. They were synthesized in five steps, including the Grignard reaction, Appel reaction, the conversion of bromide to thiol and oxidation (Smaldone & Moore, 2007). Different monovalent alkali cations, divalent and trivalent metallic ions, were used as counter-ions and their influence on their surfactant properties are discussed. **Figure 1** summarizes the different investigated compounds.



**Figure 1.** Structure of the symmetric dialkyl methanesulfonic acid and sulfonates  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  ( $n = 6, 7$  and  $8$ ) investigated in this work.

Water-solubility and critical micelle concentration (CMC) **have been** determined for the 24 compounds and their relative amphiphilicity was compared using the PIT-slope method (Ontiveros *et al.*, 2014, 2015), recently reported as a simple and convenient method affording a reliable classification of surfactants in relation to their hydrophilic/lipophilic balance.

Finally, a "cation" scan was performed with the  $[\text{DiC}_6\text{CHSO}_3]_m\text{M}$  series showing that depending on the cation, Winsor I, II or III microemulsions systems (abbreviated as WI, WII and WIII respectively) could be obtained.

## Materials and Methods

**Materials.** 1-Bromohexane (98%), 1-bromoheptane (98%), 1-bromooctane (98%), ethyl formate (97%), Mg,  $\text{CBr}_4$  (99%),  $\text{PPh}_3$  (98.5%), thiourea (99%) and peracetic acid (36-40 wt.%) were purchased from Sigma-Aldrich (Switzerland). Benzene (99%) and propyl acetate (99%) were obtained from Panreac (Germany) and Acros-Organics (Belgium) respectively. All chemicals were used as received. For the PIT-slope method, the pure tetraethylene glycol monodecyl ether ( $\text{C}_{10}\text{E}_4$ ) was synthesized according to the previously reported method (Gibson, 1980), *n*-octane (99%) was obtained from Sigma-Aldrich (Switzerland) and sodium chloride ( $\geq 99.5\%$ ) was supplied by Acros Organics (Belgium). The dialkyl methanesulfonic acid and sulfonate synthesis is covered in the results, discussion and Supporting Information sections. Their high purity ( $> 99.8\%$ ) was confirmed by NMR and elemental analysis. The purity of  $\text{C}_{10}\text{E}_4$  was confirmed not only by GC and NMR but also by comparing its cloud point with the reference value (Schlarmann, Stubenrauch & Strey, 2003). The water used in all the experiments was purified by Millipore (18.2 M $\Omega$ /cm; Simplicity 185).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance AV 300 spectrometer.

**Water-solubility measurements.** A series of samples of different concentrations was prepared and stirred at 25 °C overnight. The concentration at which the precipitation occurred was noted as the solubility.

**Surface tension measurements.** Surface tension was measured with the tensiometer K11 (Krüss) using a Wilhelmy plate. All the solutions were prepared with Ultrapure water

(Millipore water,  $\sigma = 72.0 \text{ mN}\cdot\text{m}^{-1}$  at  $25 \text{ }^\circ\text{C}$ ). The surface tension was measured as reported in previous works (Hong *et al.*, 2013)

**PIT-slope method.** A surfactant/oil/water (SOW) system containing the same mass of water and *n*-octane ( $m_w = m_o = 4.250 \text{ g}$ ), and 3.0 wt.% of tetraethylene glycol monodecyl ether ( $\text{C}_{10}\text{E}_4$ ) was prepared. The phase inversion experiments were carried out according to a protocol described elsewhere (Ontiveros *et al.*, 2014) and were repeated in the presence of increasing amounts of the alkylsulfonates (noted as the second surfactant  $\text{S}_2$ ), while readjusting the  $\text{C}_{10}\text{E}_4$  concentration to 3.0 wt.%. The molar fraction of the added surfactant  $\text{S}_2$  is calculated according equation 1:

$$x_2 = \frac{m_{s_2}/MW_2}{m_{s_1}/MW_1 + m_{s_2}/MW_2} \quad (1)$$

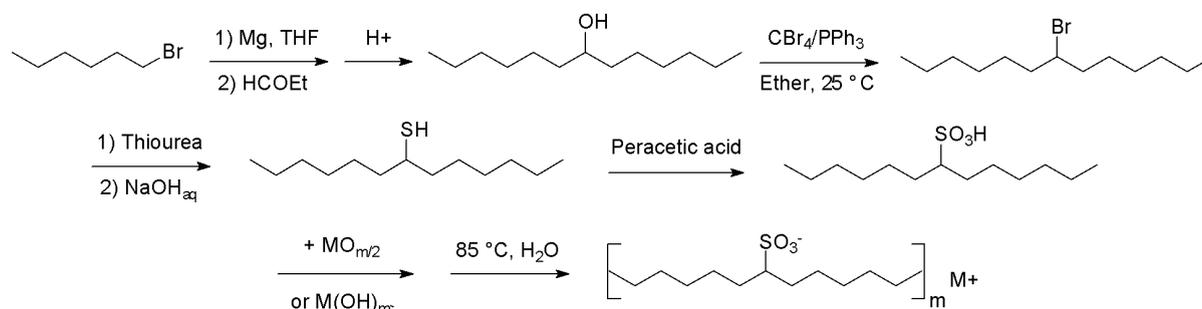
The phase inversion temperature (PIT) was calculated by the parallel tangent method (Ontiveros *et al.*, 2014, 2015).

**Winsor type microemulsions.** Samples were prepared in 2 mL vials by weighing oil (O), surfactant (S) and water (W). In all samples, the water-to-oil weight ratio was equal to 1. (water weight fraction  $f_w = 0.5$ ). Surfactant concentration was 2.7 wt.%. The vials, gently mixed, were then placed in a thermostatic bath HUBER Ministat 125 at  $25 \pm 0.1 \text{ }^\circ\text{C}$  until equilibrium was reached. The phase behavior was then determined by visual inspection and the systems were classified according to the Winsor nomenclature: Winsor I (WI), Winsor II (WII) and Winsor III (WIII) (Winsor, 1954).

## Results and Discussion

Dialkylmethane sulfonic acid and sulfonates  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  ( $n = 6, 7$  and  $8$ ) were synthesized from 1-bromoalkane ( $\text{C}_n\text{Br}$ ) following the steps summarized in **Figure 2**. Compared to the previously reported procedures (Volfson & Melnikov, 1950; Ogata *et al.*, 1965; Schechter *et al.*, 1985; Granet & Piekarski, 1986), the reactions were easier to perform

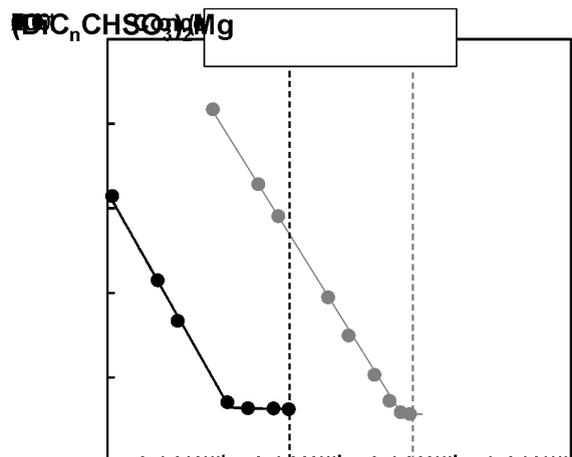
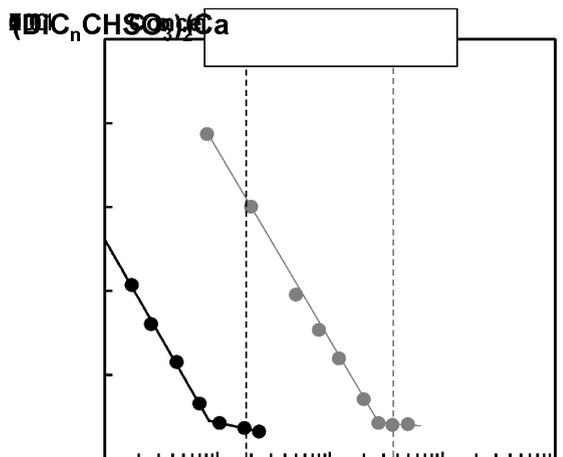
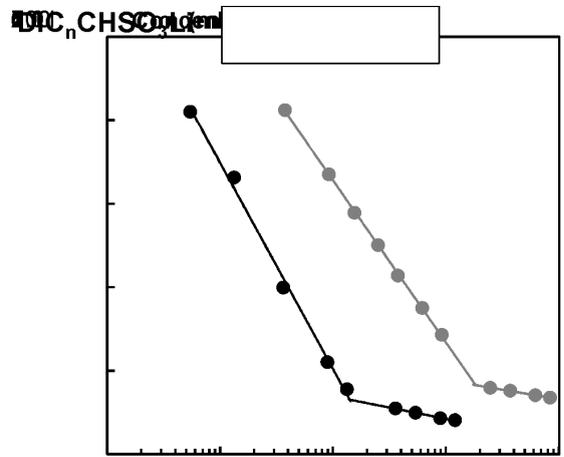
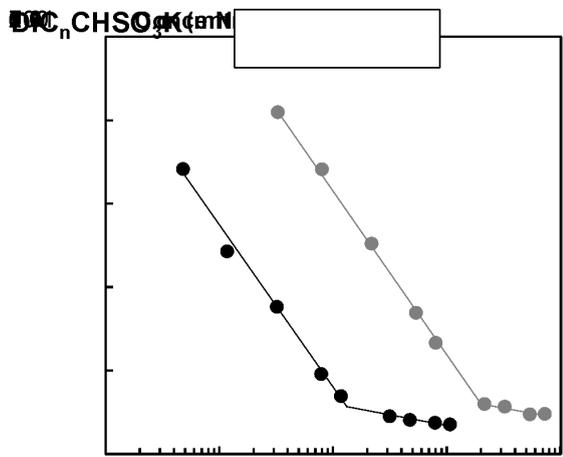
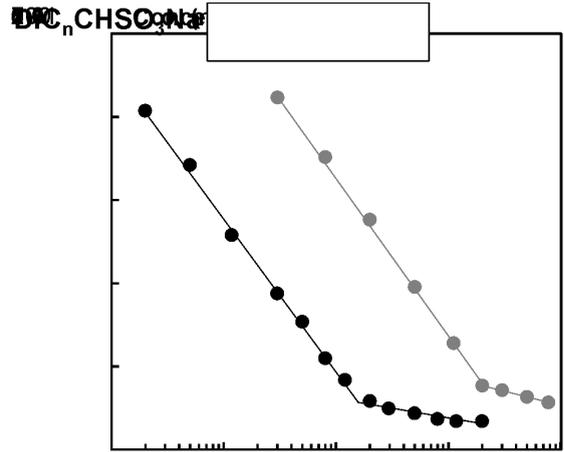
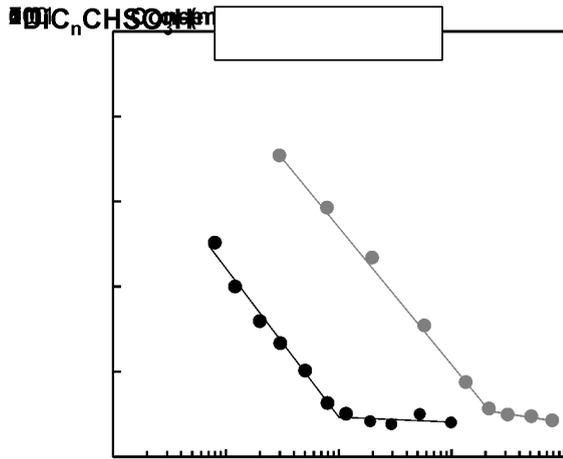
without tedious purification procedure. The metal sulfonates were prepared directly by acid-base reaction between the metal oxide or metal hydroxide and the sulfonic acid. Details are given in the **Supporting Information**.

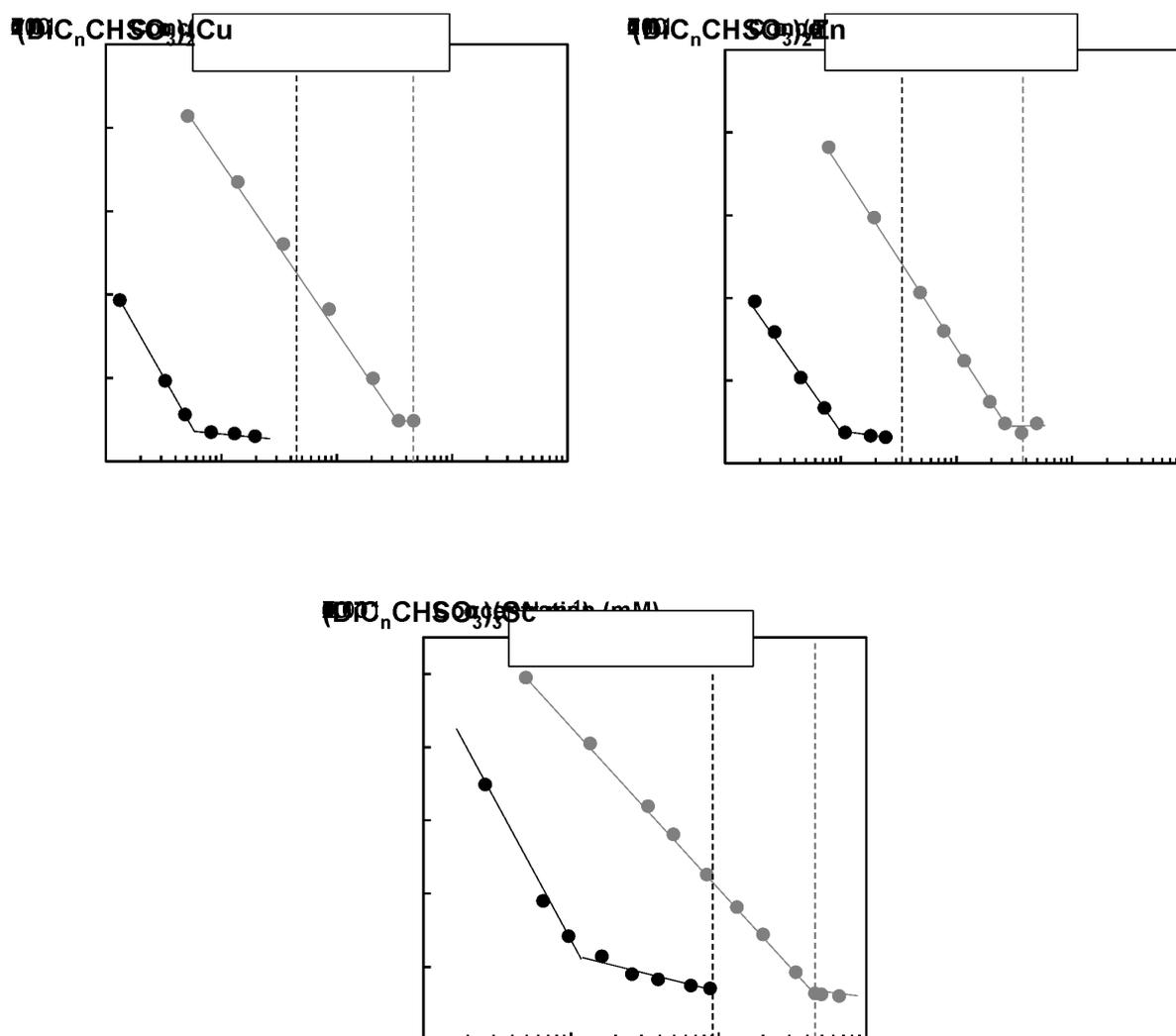


**Figure 2.** Synthesis of the symmetrical dihexyl substituted methanesulfonate  $[\text{DiC}_6\text{CHSO}_3]_m\text{M}$  ( $m = 1$  for  $\text{M} = \text{H}, \text{Li}, \text{Na}, \text{K}$ ;  $m = 2$  for  $\text{M} = \text{Cu}, \text{Zn}, \text{Ca}, \text{Mg}$ ;  $m = 3$  for  $\text{M} = \text{Sc}$ ). The procedure is identical for the  $\text{C}_7$  and  $\text{C}_8$  derivatives.

### 1. Aqueous phase behavior of $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$ in dilute solution

$[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  exhibit a relatively low water-solubility except for the monovalent cations which have a  $T_{\text{Krafft}}$  lower than  $5\text{ }^\circ\text{C}$ . It is also noteworthy that the position of the ionic group in the alkyl chain plays a significant role since the  $T_{\text{Krafft}}$  for the linear  $\text{C}_{13}\text{SO}_3\text{Na}$  is  $35.5\text{ }^\circ\text{C}$  (Weil *et al.*, 1963) thus indicating that the solubility of  $[\text{DiC}_6\text{CHSO}_3]_m\text{M}$  is enhanced compared to that of linear sulfonates. Regarding the di- and trivalent cations,  $T_{\text{Krafft}}$  could not be determined at 1 wt.% since the surfactants are not soluble at this concentration. The surface tension *versus* concentration profiles are shown in **Figure 3** for the  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  with  $n = 6$  or 8. For sake of clarity, data for  $[\text{DiC}_7\text{CHSO}_3]_m\text{M}$  are given in the **Supporting Information**.





**Figure 3.** Surface tensions ( $\sigma$ ) at 25 °C plotted against surfactant concentration for  $[DiC_6CHSO_3]_mM$  (●) and  $[DiC_8CHSO_3]_mM$  (●) ( $m = 1$ ,  $M = H, Li, Na, K$ ;  $m = 2$ ,  $M = Cu, Zn, Ca, Mg$ ;  $m = 3$ ). The vertical gray and black dashed lines respectively indicate the limit of solubility of the C<sub>6</sub> and C<sub>8</sub> derivatives.

Miyamoto (Miyamoto, 1960) has shown that the surface tension-concentration profile of calcium dodecyl sulfate does not change for concentrations below the CMC even at temperatures lower than  $T_{Krafft}$  as long as the surfactant is soluble.

The CMC and the surface tension at CMC ( $\sigma_{\text{CMC}}$ ) were determined from the breakpoint of the surface tension *versus* surfactant concentration profiles. The values of maximum surface excess ( $\Gamma$ ) and the area per molecule at the interface ( $a_1^s$ ) were also calculated using the Gibbs equation, expressed as follows for a monovalent ionic surfactant  $A^-B^+$ :

$$\Gamma = - \frac{1}{4.606RT} \left( \frac{d\gamma}{d \log C} \right)_T \quad (2)$$

where  $\sigma$  is the surface tension (mN/m), T is the absolute temperature (K), R= 8.314 J/mol·K.

The area per molecule at the interface ( $a_1^s$ ) is expressed in square angstroms using eq. 3:

$$a_1^s = \frac{10^{16}}{N\Gamma} \quad (3)$$

where N is the Avogadro's constant and  $\Gamma$  is in mol/cm<sup>2</sup>. **Table 1** summarizes the water-solubility at 25 °C, the CMC and the surface tension at CMC for all the  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$ . The maximum surface excess and the area per molecule at the water-air interface have been calculated only for monovalent surfactants for which the hypothesis of complete dissociation can be assumed.

**Table 1.** Water-solubility, critical micelle concentration (CMC) and surface tension at CMC ( $\sigma_{\text{CMC}}$ ) at 25 °C for  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  with m = 1, M = H, Li, Na, K; m = 2, M = Cu, Zn, Ca, Mg; m= 3, M = Sc) and for n = 6, 7, 8.

Cation	Solubility (mM)	CMC (mM)	$\sigma_{\text{CMC}}$ (mN.m <sup>-1</sup> )	$\Gamma_{\text{max}} \cdot 10^{10}$ (mol/cm <sup>2</sup> )	$a_1^s$ (Å <sup>2</sup> )
<b><math>[\text{DiC}_6\text{CHSO}_3]_m</math> (m = 1, 2, 3)</b>					
H <sup>+</sup>	> 100	23	25.5	2.8	58

<b>Li<sup>+</sup></b>	> 100	18	28.3	3.4	49
<b>Na<sup>+</sup></b>	> 100	21	27.6	3.4	50
<b>K<sup>+</sup></b>	> 100	18	26.2	3.5	47
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<b>Mg<sup>2+</sup></b>	4.1	3.1 <sup>a</sup>	25.9	-	-
<b>Ca<sup>2+</sup></b>	3.6	2.7	24.2	-	-
<b>Cu<sup>2+</sup></b>	4.6	3.8	24.7	-	-
<b>Zn<sup>2+</sup></b>	3.7	2.7	24.4	-	-
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<b>Sc<sup>3+</sup></b>	0.45	0.44 <sup>a</sup>	26.3	-	-
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<b>[DiC<sub>7</sub>CHSO<sub>3</sub>]<sub>m</sub> (m = 1, 2, 3)</b>					
<hr/>					
<b>H<sup>+</sup></b>	8.9	3.0	24.4	2.8	59
<b>Li<sup>+</sup></b>	28.9	4.4	26.5	2.6	63
<b>Na<sup>+</sup></b>	20.0	5.2	25.7	2.5	65
<b>K<sup>+</sup></b>	21.8	6.8	25.0	2.8	58
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<b>Mg<sup>2+</sup></b>	1.2	0.54	24.8	-	-
<b>Ca<sup>2+</sup></b>	0.88	0.44	23.9	-	-
<b>Cu<sup>2+</sup></b>	1.1	0.68	23.9	-	-
<b>Zn<sup>2+</sup></b>	1.0	0.41	24.6	-	-
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<b>Sc<sup>3+</sup></b>	0.16	0.081	27.9	-	-
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<b>[DiC<sub>8</sub>CHSO<sub>3</sub>]<sub>m</sub> (m = 1, 2, 3)</b>					
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<b>H<sup>+</sup></b>	5.2	1.2	24.1	2.8	58
<b>Li<sup>+</sup></b>	12.1	1.4	26.5	4.3	38
<b>Na<sup>+</sup></b>	5.0	1.6	25.7	3.2	51
<b>K<sup>+</sup></b>	7.9	1.5	25.0	3.4	49
<hr/>					
<b>Mg<sup>2+</sup></b>	0.36	0.11	26.4	-	-
<b>Ca<sup>2+</sup></b>	0.17	0.081	24.6	-	-
<b>Cu<sup>2+</sup></b>	0.44	0.089	23.3	-	-
<b>Zn<sup>2+</sup></b>	0.24	0.10	23.7	-	-
<hr/>					
<b>Sc<sup>3+</sup></b>	0.09	0.012	30.1	-	-

<sup>a</sup> For these compounds, an "apparent" CMC must be considered as the breaking point of the tension surface curve occurs at the limit of the surfactant solubility.

First of all, we can notice that all compounds show a good surface activity and lower the surface tension down to 23-26 mN.m<sup>-1</sup>, except for the scandium derivatives for which  $\sigma_{\text{CMC}}$  varies between 26.3 and 30.1 mN.m<sup>-1</sup>. It is noteworthy that sulfonates with di- and trivalent cations exhibit a relatively low water-solubility limit as indicated by the dashed lines on the graphs of **Figure 3**. In addition, for some compounds like **[DiC<sub>6</sub>CHSO<sub>3</sub>]<sub>3</sub>Sc**, this solubility limit seems to coincide with the surface tension breaking point making the CMC determination less straightforward. However, given the relatively important surface tension reduction observed with these compounds (up to 26 mN.m<sup>-1</sup> for **[DiC<sub>6</sub>CHSO<sub>3</sub>]<sub>3</sub>Sc**), we can consider that the reported CMCs in **Table 1** are quite reliable. The CMCs decrease from the mono- to the di- and to the trivalent cations with relatively important differences ranging from a factor 6 to 15. Unlike already reported values for the sulfate surfactants, the CMC of the alkali dialkylmethane sulfonates does not decrease from Li to K (Rosen, 2004; Slavchov, Karakashev & Ivanov, 2014). On the other hand, for a same cation, the CMC logarithmically decreases as the number of carbon atoms N increases following the empirical Klevens equation (Klebens, 1953):

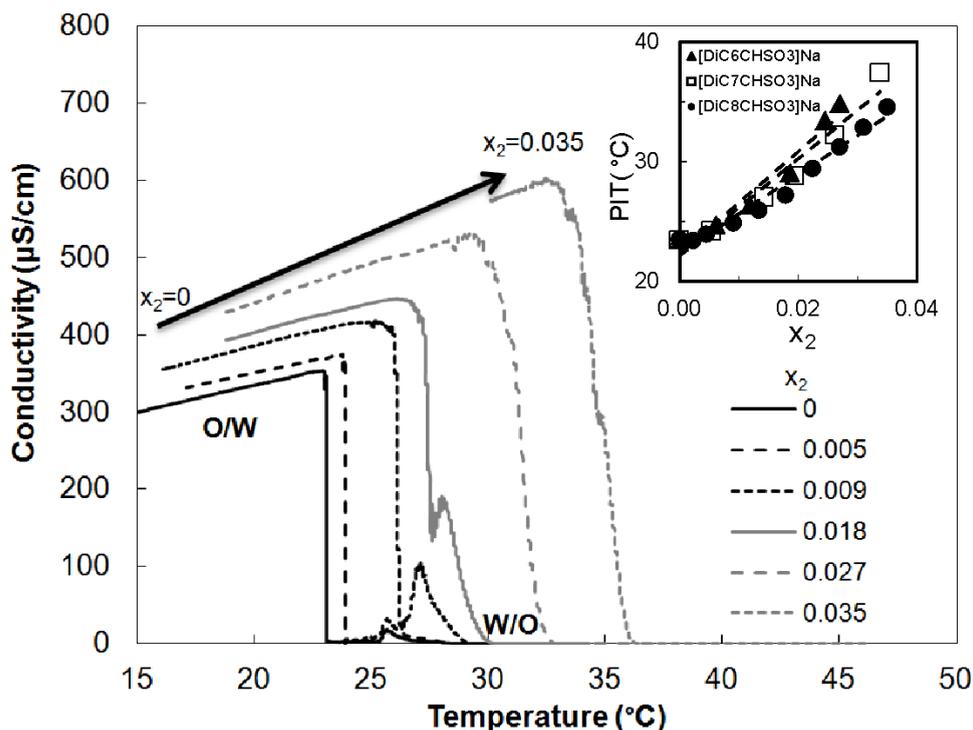
$$\text{Log CMC} = A - B \times N \quad (4)$$

Considering N as the total number of carbons of the alkyl chain, *i.e.* N = 13, 15 and 17, the average B coefficient is, as reported for surfactants, equal to 0.29 for monovalent cations, 0.38 for divalent cations and 0.39 for the trivalent Sr<sup>3+</sup>. There is a slight increase of B with the valence cation reflecting the stronger binding of the divalent and trivalent cations onto the surface of the micelles. Finally, as reported, the CMC of the linear C<sub>13</sub>SO<sub>3</sub>Na and C<sub>13</sub>SO<sub>3</sub>H at 25 °C are 3.5 and 2.5 mM (Weil *et al.*, 1963), respectively. In comparison, **DiC<sub>6</sub>CHSO<sub>3</sub>Na** and **DiC<sub>6</sub>CHSO<sub>3</sub>H** have a CMC 6 times higher suggesting that their "apparent" alkyl chain length is lower than 13 carbon atoms and that they are more hydrophilic. The same trend is observed for n = 7 and n = 8. These results corroborate the observations of Dusart *et al.*

(Dusart, 1985) and Ma *et al.* (Ma *et al.*, 2006) about the variation of interfacial properties with increasing branching for ionic surfactants: when the ionic head group is in the center of the molecule, the CMC increases.

## 2. Determination of the hydrophilic/lipophilic Balance by the PIT-slope method

The different dialkyl methanesulfonate surfactants were characterized using the PIT-slope method. This recently developed method provides a relative scale of surfactant classification allowing the assessment of their hydrophilic/lipophilic behavior using a temperature scan. Indeed, it is based on the variation of the phase inversion temperature PIT of a well-defined ternary system ( $C_{10}E_4/n$ -octane/water) induced by the addition of second surfactant  $S_2$ . The water-to-oil ratio ( $f_w$ ) and the amount of  $C_{10}E_4$  are fixed to 0.5 and 3 wt.% respectively. Depending on its water/oil interfacial activity, the addition of  $S_2$  results in a more or less important increase or decrease of the emulsion PIT leading to a linear variation of the PIT versus the amount of  $S_2$ . The slope of the linear regression is  $dPIT/dx_2$  (Ontiveros *et al.*, 2015) if the concentration is expressed as a molar fraction or  $dPIT/dC$  (Ontiveros *et al.*, 2014) if mass percentages are considered. **Figure 4** shows the conductivity *versus* temperature profiles when **DiC<sub>8</sub>CHSO<sub>3</sub>Na** is added to the reference system.



**Figure 4.** Temperature-dependence of the conductivity of the emulsion formed with 3 wt.%  $\text{C}_{10}\text{E}_4/n\text{-Octane}/10^{-2}\text{M NaCl} + \text{DiC}_8\text{CHSO}_3\text{Na}$  at  $f_w = 0.5$ , on the second cooling cycle. On the top-right side: evolution of the Phase Inversion Temperature (PIT) as a function of the  $\text{DiC}_n\text{CHSO}_3\text{Na}$  molar fraction. (●)  $n = 8$ , (◻)  $n = 7$ , (▲)  $n = 6$ .

All conductivity-temperature profiles exhibit the expected shape of a phase inversion process. The high conductivity at low temperature indicates that the continuous phase of the emulsion is water (O/W) until a temperature range in which the conductivity drastically falls, indicating that emulsions invert into a water-in-oil emulsion (W/O). The figure inserted in the top-right side shows the evolution of the PIT value as a function of  $\text{DiC}_8\text{CHSO}_3\text{Na}$ ,  $\text{DiC}_7\text{CHSO}_3\text{Na}$  and  $\text{DiC}_6\text{CHSO}_3\text{Na}$  molar fraction in the mixture  $\text{C}_{10}\text{E}_4/\text{DiC}_1\text{CHSO}_3\text{Na}$ ; the dotted line represents the best linear fit for the data ( $0.95 < R^2 < 0.97$ ). The values of the slopes, namely  $d\text{PIT}/dx_2$  (molar basis) and  $d\text{PIT}/dC$  (weight percentage basis), for the  $\text{DiC}_n\text{CHSO}_3\text{Na}$  with  $n = 6, 7$  and  $8$  and for  $\text{DiC}_6\text{CHSO}_3\text{M}$  with different cations  $M$  are reported in Table 2. It is

noteworthy that compounds with divalent cations dissociate into two double alkyl anionic chains and the value of  $dPIT/dx_2$  can be apparently "greater" than values reported for monovalent cations because the quantity of anionic surfactant at the interface is higher but they do not necessarily present a higher interfacial activity. In order to take into account the dissociation of the surfactant, the values of  $dPIT/dx_2$  reported in **Table 2** are divided by the number of anions after complete surfactant dissociation. The error in  $dPIT/dx_2$  is less than 10%.

**Table 2.**  $dPIT/dx_2$  ( $^{\circ}C$ ) and  $dPIT/dC$  ( $^{\circ}C/wt.\%$ ) for double-tailed methanesulfonic salts.

Surfactant	$dPIT/dx_2$ ( $^{\circ}C$ )	$dPIT/dC$ ( $^{\circ}C/wt.\%$ )
$[DiC_8CHSO_3]Na$	325	99
$[DiC_7CHSO_3]Na$	405	120
$[DiC_6CHSO_3]Na$	422	158
$[DiC_6CHSO_3]K$	457	142
$[DiC_6CHSO_3]Li$	415	171
$[DiC_6CHSO_3]H$	316	125
$[DiC_6CHSO_3]_2Mg$	240 (480) <sup>a</sup>	97
$[DiC_6CHSO_3]_2Ca$	194 (388) <sup>a</sup>	77
$[DiC_6CHSO_3]_2Cu$	106 (211) <sup>a</sup>	37

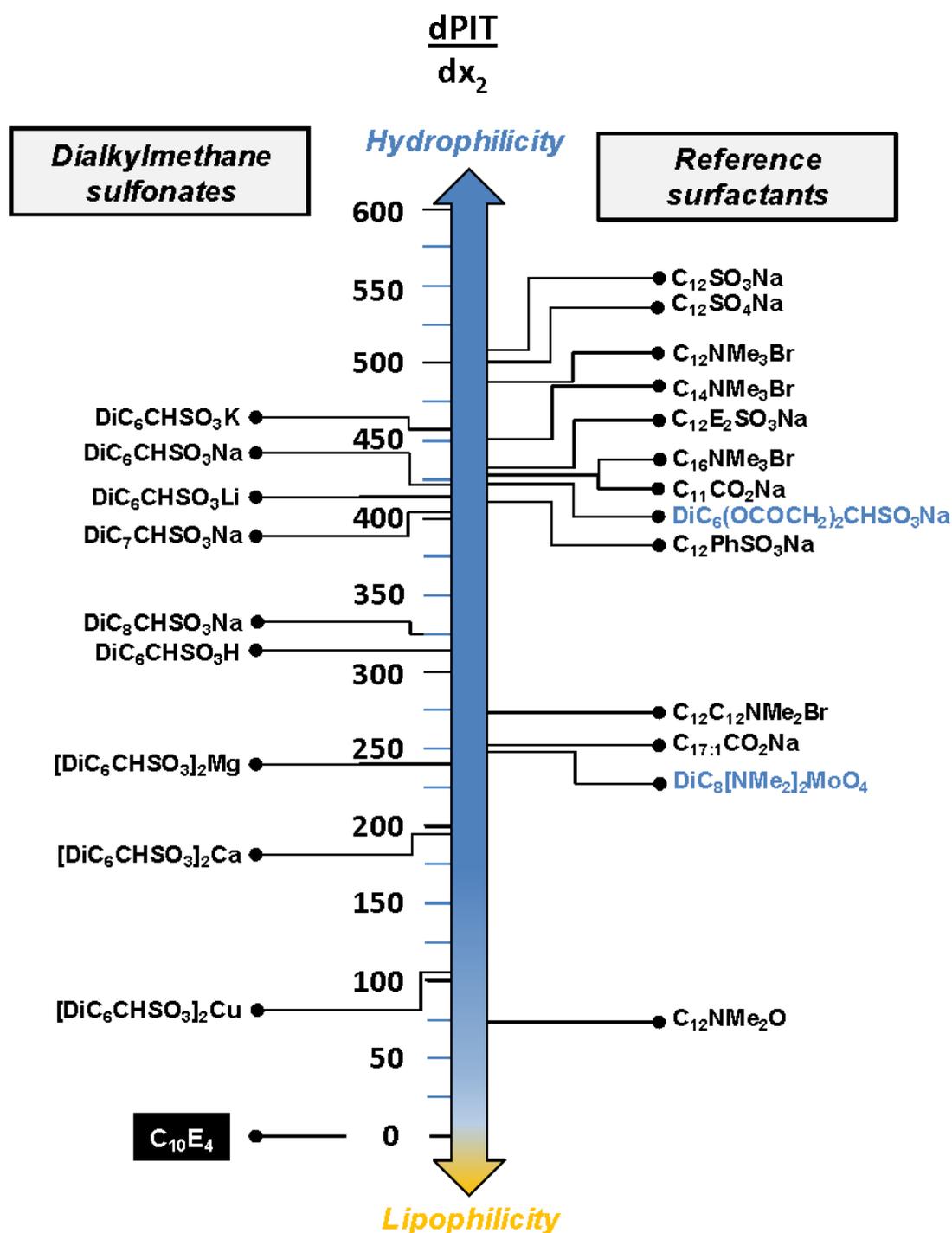
<sup>a</sup> Values in parentheses correspond to the PIT-slope without taking into account the dissociation of the surfactant anion.

By comparing the  $dPIT/dx_2$  in the  $DiC_nCHSO_3Na$  series, we can see that it linearly decreases when alkyl chain length increases, following the tendency of the packing parameter which decreases indicating an increase of the hydrophobicity as expected. On the other hand, by comparing the  $dPIT/dx_2$  of the  $DiC_6CHSO_3M$  series, the PIT-slope method clearly highlights the difference between monovalent alkali cations ( $Li^+$ ,  $Na^+$ ,  $K^+$ ) and divalent cations ( $Cu^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ). It is noteworthy that the equivalent sulfonic acid (e.g.  $DiC_6CHSO_3H$ ) is

clearly less hydrophilic than the monovalent alkali cations. Accordingly, the hydrophilicity decreasing order can be established for dialkyl sulfonates as follows:  $K^+ > Na^+ \sim Li^+ > H^+ > Mg^{2+} > Ca^{2+} > Cu^{2+}$ . Referring to another anionic polar group like carboxylate, it is well known that potassium oleate is slightly more hydrophilic than sodium oleate (Davies, 1957). Thus, even if carboxylate and sulfonate anionic groups have different matching water affinities (kosmotropic and chaotropic) (Vlachy *et al.*, 2008; Kunz, 2010), our results show that the potassium counter-ion is more hydrophilic than sodium and there is no *inversion* in the Hofmeister series, at least when the dihexylmethyl sulfonate anion is compared to the oleate group.

The maximum molar fraction of monovalent surfactant leading to an emulsion inversion with monovalent alkali surfactants is 0.03. Higher molar fractions produce O/W emulsions insensitive to temperature changes, as reported for several anionic-nonionic mixtures (Salager *et al.*, 1979; Kunieda *et al.*, 1985; Binks, Fletcher & Taylor, 1997; Anton *et al.*, 2008). In order to compare the different surfactants with divalent cations on the same basis as monovalents, the  $dPIT/dx_2$  was evaluated at  $x_2 < 0.03$ . As expected, the divalent cations notably reduce the hydrophilicity of the double-tailed alkyl methanesulfonates, and their addition to the reference emulsion system *does* not produce O/W emulsions insensitive to temperature, at least in the studied range of concentrations. **Figure 5** gives a classification of the different dialkyl methanesulfonates according to their hydrophilic lipophilic balance determined with the PIT-slope method. For comparison, typical cationic and anionic surfactants have also been positioned on the right and the PIT-slope of two other double tailed surfactants, i.e. the dihexyl sodium sulfosuccinate ( $DiC_6(OCOCH_2)_2SO_3Na$ ) and the dioctyl dimethylammonium molybdate ( $[DiC_8NMe_2]_2MoO_4$ ), have also been determined. *The*  $dPIT/dx_2$  are *equal to 423* and 246 °C respectively.  $[DiC_8NMe_2]_2MoO_4$  has been reported as a

"balanced surfactant" as it is able to form spontaneously a Winsor III system just in the presence of water and oil without addition of salt or alcohol (V. Nardello-Rataj *et al.*, 2008).



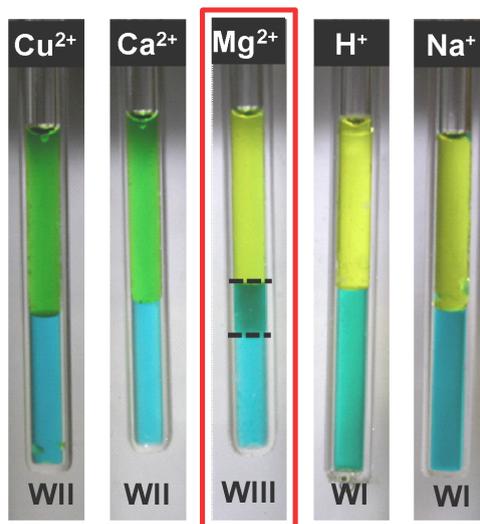
**Figure 5.** Double-tailed methanesulfonic salts classification using the PIT-slope method.

All dihexyl methane sulfonate of alkali metals have a  $dPIT/dx_2$  inferior to that of dodecyl sodium sulfonate but comparable to that of other typical dodecyl anionic surfactants such as

dodecyl sodium diether sulfonate or sodium laurate. The positioning of the sulfonate polar headgroup significantly modifies the hydrophilicity of the surfactant. In this sense, Doe *et al.* (Doe, Wade & Schechter, 1977), using hexadecyl benzene sulfonates, showed that hydrophilicity is higher when the polar headgroup is located at the end of the alkyl chain, **in accordance with the dPIT/dx<sub>2</sub> scale of the alkyl sulfonates**. When the polar head is in the middle of the chain, the surfactant is less hydrophilic because of the decrease of the effective chain length and the increase in the volume of the alkyl chain of the surfactant, thus **leading to a higher** packing parameter of the system.

The dPIT/dx<sub>2</sub> of **DiC<sub>6</sub>CHSO<sub>3</sub>Na** (422 °C) matches with that of dihexyl sodium sulfosuccinate. All anionic surfactants in this region such as dihexyl sodium sulfosuccinate (Baran *et al.*, 1994), sodium laurate (Bravo *et al.*, 2006) or dodecyl benzene sulfonate (Salager *et al.*, 2001) are able to produce a **three-phase system (Winsor III)** with alkanes using **either a** salinity scan (dihexyl sodium sulfosuccinate, dodecyl benzene sulfonate) or a pH scan (sodium laurate/lauric acid). From these results, the dihexyl methane **sulfonates** of alkali cations **are also** expected to **give** WIII systems with alkanes. This is in good agreement with the work of Granet (Granet *et al.*, 1990) who studied the interfacial tension of SOW systems containing double-tailed sulfonates at 45 °C and reported ultralow tensions ( $\approx 10^{-3}$  mN/m) for the **DiC<sub>7</sub>CHSO<sub>3</sub>Na**/heptane/water system at 1.75 wt.% NaCl and for the **DiC<sub>8</sub>CHSO<sub>3</sub>Na**/heptane/water system at 0.175 wt.%. It is also **noteworthy that** **[DiC<sub>8</sub>NMe<sub>2</sub>]<sub>2</sub>MoO<sub>4</sub>** and **[DiC<sub>6</sub>CHSO<sub>3</sub>]<sub>2</sub>Mg** have similar dPIT/dx<sub>2</sub> values. **[DiC<sub>8</sub>NMe<sub>2</sub>]<sub>2</sub>MoO<sub>4</sub>** is known as a balanced catalytic surfactant (Nardello-Rataj *et al.*, 2008) that forms a three-phase microemulsion system with benzene at 25 °C, without **addition of** salt or alcohol, an uncommon property for ionic surfactants **that reflects** a packing parameter close to 1. The relation between dPIT/dx<sub>2</sub> and the oil which allows to obtain a WIII behavior is well described for nonionic surfactants (Ontiveros *et al.*, 2018) but not for ionic ones. To verify the robustness of the PIT-slope

method, which predicts that  $[\text{DiC}_6\text{CHSO}_3]_2\text{Mg}$  should also lead to a WIII system, a counter-ion scan has been performed with the  $[\text{DiC}_6\text{CHSO}_3]_2\text{M}$  in the presence of benzene (Figure 6).



**Figure 6.** Phase behavior of 2.7 wt.%  $[\text{DiC}_6\text{CHSO}_3]_2\text{M}$ /benzene/water system at  $f_w = 0.5$ . Blue and yellow dyes were added to the aqueous and oily phases respectively in order to enhance the visual contrast.

Interestingly, a WIII system could also be obtained with the magnesium dihexylmethane sulfonate  $[\text{DiC}_6\text{CHSO}_3]_2\text{Mg}$  which behaves as the  $[\text{DiC}_8\text{NMe}_2]_2\text{MoO}_4$  under the same conditions. More hydrophilic surfactants (sulfonic acid, sodium, lithium and potassium salts) form Winsor I systems, in which the affinity of the surfactant for the aqueous phase is higher than for the oily phase. For the  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  counter-ions, the surfactant affinity for the oily phase is higher. Systems in the vicinity of the Winsor III behavior (i.e.  $\text{H}^+$  and  $\text{Ca}^{2+}$ ) show an enhanced solubility, i.e. for  $\text{DiC}_6\text{CHSO}_3\text{H}$ , the aqueous phase appears slightly green, indicating the solubilisation of some oil by the surfactant. For  $[\text{DiC}_6\text{CHSO}_3]_2\text{Ca}$ , the green color of the oily phase and its higher volume compared to the oily phase with sodium surfactant indicates a WII behavior.

These findings support the PIT-slope results reported in Table 2 and the previous discussion about the influence of the counter-ion in the hydrophilic-lipophilic balance of the surfactant. For divalent cations, the two double-tailed alkyl chains notably increase the hydrophobicity of the surfactant compared to alkaline cations or to the sulfonic acid which have only one double-tailed structure. However, the differences in the phase behavior between divalent ( $\text{Mg}^{2+}$  vs  $\text{Cu}^{2+}$  or  $\text{Ca}^{2+}$ ) or monovalent cations ( $\text{H}^+$  vs  $\text{Na}^+$ ,  $\text{Li}^+$  or  $\text{K}^+$ ) cannot be explained only in terms of hydrophobic interactions or hydration radius of cations. Indeed, Eastoe *et al.* (Eastoe, Chatfield & Heenan, 1994) have studied the effect of hydration radius in the phase behavior of several bis (2-ethylhexyl) sulfosuccinate surfactants (AOT) as  $[\text{Na}^+][\text{AOT}^-]$  and  $[\text{R}_4\text{N}^+][\text{AOT}^-]$  in the surfactant/heptane/ $\text{NaCl}(\text{aq})$  system and "only small changes in the interfacial tension –salinity profiles with ion radius were observed". The effect of the specific counter-ion must be more deeply examined. Based on the scale proposed by Vlachy *et al.* (Vlachy *et al.*, 2009) who have classified different anionic surfactant headgroups according to their ability to form close ion pairs with cations, the  $\text{K}^+$  ion would have stronger interactions with the sulfonate than other alkali and divalent cations which are strongly hydrated. This concept is based on the theory of matching water affinities developed by Collins (Collins, 2004). Nihonyanagi *et al.* (Nihonyanagi, Yamaguchi & Tahara, 2014) have studied the counter-ion effect of chloride salts on water at interface in a micellar sodium dodecylsulfate solution using heterodyne-detected vibrational sum-frequency generation spectroscopy. They concluded that the interfacial water molecules are less bonded than the bulk water molecules and the cations ( $\text{Mg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Cs}^+$ ,  $\text{TMA}^+$ ) do not form close ion pairs with the sulfate. Therefore, the hydrogen-bond strength of the water molecular at the interface is altered by the cations, following the Hofmeister series:  $\text{TMA}^+ \ll \text{Li}^+ \sim \text{Cs}^+ < \text{Mg}^{2+}$ . As established by Kunz (Kunz, 2010), the application of the Collins's theory is only a first approximation to analyze the phenomena. Most of these results come from aqueous systems. The specific effects of ions in

the stabilization of water/oil interfaces are just beginning to be understood at the molecular level, *i.e.* the charge of the ionic polar head of the surfactant changes not only the water disposition at the interface but also the oil disposition (Scheu *et al.*, 2014). Vera *et al.* (Vera *et al.*, 2020) have examined the effect of different salts on the interfacial tension, interfacial rheology parameters and optimal salinity of the sodium dodecyl benzene sulfonate/heptane/water system with and without sec-butanol as cosurfactant. The work of Vera shows that the salinity needed to get a WIII behavior follows the order  $\text{Ca}^{+2} < \text{Mg}^{+2} < \text{NH}_4^+ < \text{Na}^+$  and that SOW equilibrated systems with salting-in ions like  $\text{NH}_4^+$  presents lower interfacial rigidity and ultralow interfacial tension than other cations at optimum formulation. The work of Vera (Vera *et al.*, 2020) and our results highlight that the cation effects are involved not only in the aqueous behavior of anionic surfactants but also in the phase behavior of SOW systems. To our knowledge, this is the first "cations scan" reported in the literature leading to transitions between the Winsor multiphase microemulsions: WI ( $\text{Na}^+$  and  $\text{H}^+$ )  $\square$  WIII ( $\text{Mg}^{+2}$ )  $\square$  WII ( $\text{Ca}^{+2}$  and  $\text{Cu}^{+2}$ ). Such systems open up relevant perspectives for catalysis in nanodispersed systems.

## Conclusion

A series of 24 pure amphiphilic sulfonates  $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$  ( $n = 6$  to  $8$ ) with symmetric dialkyl chains were successfully synthesized and purified. The CMCs of these ionic surfactants with different counterions ( $[\text{DiC}_n\text{CHSO}_3]_m\text{M}$ ;  $\text{M} = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sc}^{3+}$ ) have been determined and discussed. Indeed, both the chain lengths and counter-ions show important effects on the water-solubility and aggregation behavior. For example, the CMCs decreases about 5 times when only one more  $\text{CH}_2$  group is added to the alkyl chain and on the other hand, the one valence increase of the counter-ions results in about ten times decrease of the CMCs.

Double-tailed methanesulfonate surfactants have also been characterized by the PIT-slope method ( $dPIT/dx_2$ ), a comparative data that allows to quantify their hydrophilic character through a temperature scan.  $DiC_6CHSO_3K$  is the most hydrophilic surfactant of the series while  $[DiC_6CHSO_3]_2Cu$  is the most hydrophobic one, highlighting the importance of the counter-cation over the alkyl chain length. Finally,  $[DiC_6CHSO_3N]_2Mg$  was found to be a "balanced surfactant", which can form a three-phase microemulsion system just in the presence of water and oil, as already reported for the catalytic surfactant dioctyldimethylammonium molybdate.

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### Supplementary material

Synthesis of double-tailed methanesulfonate amphiphiles. Surface Tension data for  $[DiC_7CHSO_3]_mM$

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