# LANGM Callech Library

Interface-Rich Materials and Assemblies

Subscriber access provided by Caltech Library

### Synthesis, Properties and Aggregation Behavior of Tetrasiloxane-based Anionic Surfactants

Yue Huang, Lina Meng, Mengdong Guo, Peijian Zhao, Hongyan Zhang, Shuwen Chen, Jie Zhang, and Shengyu Feng

Langmuir, Just Accepted Manuscript • DOI: 10.1021/acs.langmuir.8b00825 • Publication Date (Web): 22 Mar 2018 Downloaded from http://pubs.acs.org on March 23, 2018

#### Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.



165x53mm (150 x 150 DPI)

## Synthesis, Properties and Aggregation Behavior of Tetrasiloxane-based Anionic Surfactants

Yue Huang, Lina Meng, Mengdong Guo, Peijian Zhao, Hongyan Zhang, Shuwen Chen, Jie Zhang\*, and Shengyu Feng\*

Key Laboratory of Special Functional Aggregated Materials & Key Laboratory of Colloid and Interface Chemistry (Shandong University), Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

**ABSTRACT**: Three silicone surfactants, 3-tris(trimethylsiloxy)silylpropyl sulfonate with different alkaline counterions (lithium, sodium and potassium), were synthesized for the first time. Their chemical structures were confirmed by FT-IR spectra, <sup>1</sup>H NMR and ESI-MS, and their behaviors in aqueous solutions were investigated by surface tensiometry, electrical conductivity, dynamic light scattering, and different transmission electron microscopy techniques. These anionic silicone surfactants exhibited remarkable surface activity, and could reduce the surface tension of water to as low as 19.8 mN/m at the critical aggregate concentration (CAC). The adsorption and aggregation behavior of these surfactants were assessed by determining the adsorption efficiency, minimum average area per surfactant molecule, and thermodynamic parameters. The cryo-TEM results verified these molecules could form vesicles in water above CAC. Moreover the lowest surface tension, the smallest CAC value,

#### Langmuir

and the biggest aggregate size have been reached with potassium counterion. Thus different behavior of these surfactants in water can be explained by different size of hydrated ions.

Keywords: Anionic silicone surfactants, counterions, aggregation in water, vesicles

#### Introduction

Silicone surfactants have performed important roles ranging from facilitating delivery of drugs and agriculture ingredients to foam stabilization<sup>1-7</sup>. Like common hydrocarbon surfactants, they have both hydrophobic and hydrophilic groups. The permethylated siloxane groups, which act as hydrophobic groups, grafted with one or more hydrophilic group ensure the good surface activity of silicone surfactants in both aqueous and nonaqueous solutions<sup>8-10</sup>. Their extraordinary qualities attribute to some unique characteristics: (i) the flexible silicone bonds that make it possible for the molecules to pack more efficiently at different interfaces; (ii) low cohesive energy that contributes to greater volume and cross-sectional area of the siloxane unit; (iii) low glass transition temperature even for high molecular weight surfactants. Due to the distinctive chemical and physical properties, especially their low toxicity, wide operating temperature, and high surface activities, silicone surfactants have been widely used and investigated in recent decades<sup>1, 11</sup>. Particularly, trisiloxane surfactants are able to decrease the surface tension of water to approximately 20 Nm/m<sup>12, 13</sup>.

Cationic silicone surfactants have been commonly utilized as fabric softening agents<sup>14</sup>, and also can be used as antibacterial agents due to the presence of abundant positive charges<sup>15, 16, 17</sup>.

However, the positive charges also limit their wide applications. Silicone surfactants with different chemical structures show different aggregation behavior. Tan et al. investigated a series of cationic silicone surfactants with the same hydrophilic groups but different hydrophobic silicone groups. Their results indicated that the surfactant aggregation behavior highly related on the length and spatial structure of the hydrophobic group<sup>18</sup>.

Cationic silicone surfactants cannot be used as dyeing materials in the industry of yarn spinning and textile manufacture for their positive charge<sup>19, 20</sup>. Alternatively, nonionic silicone surfactants have been commercialized for textile, cosmetics, agriculture, printing, dyeing, and other applications<sup>21-24</sup>.

Comparatively, anionic silicone surfactants have yet to be investigated. Anionic hydrocarbon surfactants have been used in a wide range of applications due to their special properties, thus raising our research interest in anionic silicone surfactants. Recently, Xing et al. reported a synthetic method for an anionic gemini silicone surfactant and tested its surface activity<sup>25</sup>. Their obtained anionic silicone surfactant had remarkable surface activity in aqueous solution. Ervithayasuporn et al. synthesized silicon-based organic-inorganic hybrid silsesquioxane containing the maximum number of sulfonic acid groups through oxidation reaction under mild conditions with a high yield<sup>26</sup>.

In this study, we synthesized three novel sulfonate anionic silicone surfactants (Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na, and Si<sub>4</sub>ASO<sub>3</sub>Li,) via thio-ester oxidation reaction. They all had the same chemical structure on the tetrasiloxane chain (as the hydrophobic segment), and the sulfonate (as the hydrophilic group), but different counterions were chosen. Our work present a convenient, straightforward synthetic route to obtain sulfonate anionic silicone surfactants (Figure 1). We investigated their structures and solution behaviors in detail. The tetrasiloxane-based structures

are expected to orient themselves in an "umbrella-shaped" distribution of the hydrophobic groups on the aqueous surface<sup>18, 27</sup>. Their surface activity was stronger ( $\gamma_{CAC} \approx 20 \text{ mN/m}$ ) and more efficient (CAC  $\approx 4.5 \text{ m mol/L}$ ) than a conventional anionic surfactant, sodium laurysulfonate (SLS) ( $\gamma_{CMC} \approx 33 \text{ mN/m}$  and CMC  $\approx 12.4 \text{ m mol/L}$ )<sup>28</sup>. DLS and TEM results indicated that their aggregation behavior was influenced by the counterions, which provide a way to obtain surfactant aggregations with controlled size and narrow distribution.



Figure 1. Synthesis route of Si<sub>4</sub>ASO<sub>3</sub>M (M= K, Na and Li).

#### Experimental

#### Materials

Trimethylchlorosilane,  $\gamma$ -chloropropyltrichlorosilane, potassium thioacetate, sodium thioacetate and lithium thioacetatewere purchased from Energy Chemical (shanghai). Isopropanol, ethyl alcohol, *N*,*N*-dimethylethanolamine and dichloromethane were obtained from Sinopharm Chemical Reagent Beijing Co.,Ltd. All the reagents were used as received. Triply distilled water was used to prepare all the solutions.

#### Methods

 <sup>1</sup>H NMR spectra were recorded by using a Bruker AV 300 spectrometer in chloroform $d(CDCl_3)$ . FT-IR spectra were recorded by using a Nicolet FT-IR spectrometer, and samples were dispersed in anhydrous KBr pellets for testing. ESI-MS data were recorded using an Agilent Technologies 6510 Q-TF LC/MS and with methanol as solvent.

Surface tension measurements were carried out on a model BZY-1 tensiometer (Shanghai Hengping Instrument Co., Ltd, accuracy  $\pm$  0.1 mN/m) by Du Nouy ring method at 298.15 K. All measurements were repeated until the values were reproducible.

Electrical conductivity measurements of the anionic sulfonate silicone surfactant solutions were carried out using a S230 SevenCompact<sup>TM</sup> conductivity analyzer (Mettler Toledo Instrument Co., Ltd., accuracy  $\pm 0.5\%$ ) with a thermostatic bath (DC-0506, Shanghai Hengping Instrument Co., Ltd.).

The dynamic light scattering (DLS) measurements were performed using a Dynapro Titan system (Wyatt Technology, Santa, Barbara, CA) at a scattering angle of 90°.

The morphologies of anionic silicone surfactants aggregations in aqueous solution were examined with a JEM-1011 TEM (JEOL, Japan) at 100 kV. The samples were prepared by dropping anionic silicone surfactant solution on a carbon coated grid. Phosphotungstic acid solution (2 wt%) was used to stain the samples, and then the grids were dried at room temperature.

Freeze-fracture transmission electron microscope (FF-TEM) (Leica, BAF060) was used to investigate the microstructures and transition of self-assemblies formed by these amphiphilic molecules in solutions. A little sample solution (normally 1  $\mu$ L) was enclosed into a sandwich of a copper support disk of 3 mm in diameter, thickness of 100  $\mu$ m. The sandwich was held

#### Langmuir

together by stainless steel tweezers. Then the copper sandwich was frozen by plunged into liquid propane which had been cooled by liquid nitrogen. In order to maintain the structures of the solutions and obtain the veritable microstructures of the solutions, a mechanical plunging device was built for rapid transfer of the sandwich with sample solution into liquid propane. The plunging rate and the depth under the liquid propane/air interface were controlled by the mechanical device.

Cryogenic transmission electron microscopy (cryo-TEM) was a vital way to investigate the vesicles' microstructures. The TEM-grid loaded with our sample solution was dropped into liquid nitrogen instantaneous to maintain the microstructure of our products, and then the copper was visualized by JEOL 1400 under frozen temperature.

#### *Preparation of γ-chloropropyltri(trimethylsiloxy)silane (Si<sub>4</sub>ACl)*

Chlorotrimethylsilane (0.12 mol, 13.03 g) and  $\gamma$ -chloropropyltrichlorosilane (0.02 mol, 4.23 g) were placed in a three-necked flask equipped with a Vigreux column and a dropping funnel, and isopropanol (0.18 mol, 10.80 g) was added. Then, water (0.18 mol, 3.24 g) was added drop wise into the resulting solution. After stirring at room temperature for 3 h, the organic layer was separated from the hydrolysate, and washed with water till neutral reaction. The product was distilled in vacuum, and the yield was 95%. The <sup>1</sup>H NMR (CDCl<sub>3</sub>) of Si<sub>4</sub>ACl exhibits the following:  $\delta$  (ppm) = 0.11~0.14 ppm (SiCH<sub>3</sub>, 27 H), 0.54~0.63 ppm (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, 2H), 1.77~1.87 ppm (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, 2H), and 3.50~3.55 ppm (CH<sub>2</sub>CH<sub>2</sub>Cl, 2H).

#### *Preparation of S-3-tris(trimethylsiloxy)silypropylethanethiolate (Si<sub>4</sub>ASAc)*

A mixture of  $\gamma$ -chloropropyltri(trimethylsiloxy)silane (0.0134 mol, 5.0 g) and potassium thioacetate (0.023 mol, 2.68 g) was added into a flask. Then, DMF (10 ml) was added to the

mixture, which was stirred at room temperature for 16 h. Water (30 ml) was added into the solution, and the organic layer was separated and washed twice. Then it was distilled in vacuum to provide S-3-tris(trimethylsiloxy)silypropylethanethiolate (Si<sub>4</sub>ASAc) with the yield of 85%. The structure of Si<sub>4</sub>ASAc was confirmed by <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) = 0.05~0.14 ppm (Si*CH*<sub>3</sub>, 27 H), 0.49~0.55 ppm (Si*CH*<sub>2</sub>CH2, 2H), 1.54~1.64 ppm (CH<sub>2</sub>CH<sub>2</sub>, 2H), 2.315 ppm (*CH*<sub>3</sub>CO, 3H), 2.85~2.89 ppm (CH<sub>2</sub>CH<sub>2</sub>S, 2H).

#### *Preparation of potassium 3-tris(trimethylsiloxy)silylpropyl sulfonate (Si<sub>4</sub>ASO<sub>3</sub>K)*

Si<sub>4</sub>ASAc (0.01 mol, 4.128 g) was dissolved in ethanol (20 ml). Potassium carbonate (0.005 mol, 0.691 g) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (0.03 mol, 3.4 g) was added and the mixture was stirred in a neutral environment at ambient temperature for 20 h. The ethanol was removed by vacuum distillation to give colorless oil. The oil was dissolved in 10 ml water and the solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 ml). The aqueous solution was dried by vacuum distillation to give a white solid, and the yield was 70%. Si<sub>4</sub>ASO<sub>3</sub>K. <sup>1</sup>H NMR (CDCl3):  $\delta$  (ppm) = 0.05~0.15 ppm (Si*CH*<sub>3</sub>, 27 H), 0.48~0.53 ppm (Si*CH*<sub>2</sub>CH2, 2H), 1.73~1.84 ppm (CH<sub>2</sub>*CH*<sub>2</sub>CH<sub>2</sub>, 2H), 2.85~2.90 ppm (CH<sub>2</sub>*CH*<sub>2</sub>S, 2H); FT-IR (KBr, cm<sup>-1</sup>): 2,960, 2,901, 1,579, 1,414, 1,256, 1,198, 1,054, 844, 756, and 669. The stretching vibrational frequencies of  $-SO_3^-$  were observed in region of  $v_{max} \sim 1,198-1,054$ ; ESI-MS (+ESI): 457.0888, calculated m/z (Si<sub>4</sub>ASO<sub>3</sub>K+H<sup>+</sup>): 457.07.

Synthesis of sodium 3-tris(trimethylsiloxy)silylpropyl sulfonate (Si<sub>4</sub>ASO<sub>3</sub>Na) and lithium 3tris(trimethylsiloxy)silylpropyl sulfonate (Si<sub>4</sub>ASO<sub>3</sub>Li).

#### Langmuir

Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li were synthesized and characterized using the same method as Si<sub>4</sub>ASO<sub>3</sub>K using lithium carbonate and sodium carbonate in place of potassium carbonate.

Si<sub>4</sub>ASO<sub>3</sub>Na: <sup>1</sup>H NMR (CDCl3):  $\delta$  (ppm) = 0.07~0.10 ppm (Si*CH*<sub>3</sub>, 27 H), 0.48~0.53 ppm (Si*CH*<sub>2</sub>CH2, 2H), 1.73~1.84 ppm (CH<sub>2</sub>*CH*<sub>2</sub>CH<sub>2</sub>, 2H), 2.85~2.90 ppm (CH<sub>2</sub>*CH*<sub>2</sub>S, 2H); FT-IR (KBr, cm<sup>-1</sup>): 2,961, 2,901, 1,579, 1,438, 1,257, 1,210, 1,056, 844, 756, 712 and 689. The stretching vibrational frequencies of  $-SO_3^-$  were observed in region of  $v_{max} \sim 1,210-1,056$ ; ESI-MS (+ESI): 441.1143, calculated m/z (Si<sub>4</sub>ASO<sub>3</sub>Na+H<sup>+</sup>): 441.1.

Si<sub>4</sub>ASO<sub>3</sub>Li: <sup>1</sup>H NMR (CDCl3):  $\delta$  (ppm) = 0.08~0.10 ppm (Si*CH*<sub>3</sub>, 27 H), 0.48~0.52 ppm (Si*CH*<sub>2</sub>CH2, 2H), 1.74~1.84 ppm (CH<sub>2</sub>*CH*<sub>2</sub>CH<sub>2</sub>, 2H), 2.83~2.90 ppm (CH<sub>2</sub>*CH*<sub>2</sub>S, 2H); FT-IR (KBr, cm<sup>-1</sup>): 2,960, 2,900, 1,588, 1,449, 1,257, 1,205, 1,062, 847, 756, 702 and 606. The stretching vibrational frequencies of  $-SO_3^-$  were observed in region of  $v_{max} \sim 1,205-1,062$ ; ESI-MS (+ESI): 425.1266, calculated m/z (Si<sub>4</sub>ASO<sub>3</sub>Li+H<sup>+</sup>): 425.12.

#### **Results and discussion**

#### Surface tension results

The surface tensions of these anionic silicone surfactants in the aqueous solutions were measured to evaluate the surface activity. Figure 2 shows plots of the surface tension ( $\gamma$ ) versus concentration (C) for the aqueous solutions of Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li at 25 °C.

As shown in Figure 2, the surface tension decreased initially when the surfactant concentration increased, suggesting the surfactants were adsorbed at the air/solution interface. The plateaus which appear in the ( $\gamma$ -lg C) plots indicated that aggregates were formed. The critical aggregation concentration (CAC) is regarded as the concentration at the break point of

the two linear points of the  $\gamma$ -lg C plot. The estimation of these linear was based on Li's papers<sup>29, 30, 31</sup>. In particular, we had examined how the  $\gamma$ -lg C curve behaves just below the CMC because this is the part that has the most influence on the value of  $\Gamma_{CMC}$  obtained by ST-Gibbs. No minimum appeared in the  $\gamma$ -lg C plot, indicating a high purity of these three surfactants.

The surface tension at CAC ( $\gamma_{CAC}$ ) and surface pressure at CAC ( $\pi_{CAC}$ ) can also be used to evaluate the surface activities of surfactants. The  $\pi_{CAC}$  is defined by Eq. (1)<sup>32</sup>

$$\pi_{CAC} = \gamma_0 - \gamma_{CAC} \tag{1}$$

where  $\gamma_0$  is the surface tension of pure water and  $\gamma_{CAC}$  is the surface tension at CAC. The values of  $\gamma_{CAC}$  and  $\pi_{CAC}$  were obtained and listed in Table 1. The  $\gamma_{CAC}$  of Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li were calculated to be 19.8, 20.1 and 20.8, respectively. The values are lower than those of conventional anionic surfactants, such as sodium laurysulfonate (SLS,  $\gamma_{CMC} = 33.0$ mN/m) and sodium dodecyl benzene sulfonate (SDBS,  $\gamma_{CMC} = 35.0$ )<sup>28, 33</sup>. And the  $\pi_{CAC}$  values of these anionic silicone surfactants are larger than those of hydrocarbon anionic surfactants. Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li showed a significant capability to reduce the water surface tension. This result was attributed to the flexible Si-O-Si bonds which enables the methyl groups to orient in low energy configurations. Then the surfactant easily arranged itself on the surface of the solution<sup>34, 35, 36</sup>. These silicone surfactants revealed smaller critical aggregation concentration (CAC), (CAC  $\approx$  5.0 mM) than classical sulfonate anionic surfactants, such as sodium undecane-1-sulfonate (SUS, CMC = 42.7 mM) and sodium laurylsulfonate (SLS, CMC = 12.4 mM)<sup>28</sup>. Obviously, the sulfonate anionic silicone surfactants exhibited remarkable surface activity and their lower CAC values compared with classical sulfonate surfactants, which indicate a good potential for future applications.



**Figure 2.** Surface tension vs concentration for  $Si_4ASO_3K$ ,  $Si_4ASO_3Na$  and  $Si_4ASO_3Li$  in aqueous solutions at 25 °C.

The maximum excess surface concentration ( $\Gamma$ max) and the area occupied by a single amphiphile molecule at the air/liquid interface (Amin) were calculated according to Eq. (2)<sup>37</sup>

$$\Gamma_{\max} = -\frac{1}{nRT} \left( \frac{d\mathbf{Y}}{d \ln C} \right) \tag{2}$$

where  $\gamma$  is the surface tension, R is the gas constant, T is the absolute temperature, C is the surfactant concentration, (d $\gamma$ /d lnC) is the slope of the linear fit of the data below the CAC in the surface tension plots. The value of n is theoretically dependent on the surfactant type and structure, and it can also be affected by the extra electrolytes and impurities in the water solution. Here, n = 2 was taken based on the anionic surfactant structure<sup>38</sup>. With the  $\Gamma_{max}$  obtained, the value of A<sub>min</sub> is estimated using Eq. (3)<sup>32</sup>

$$A_{\min} = \frac{10^{16}}{N_A \Gamma_{\max}}$$
(3)

where  $N_A$  is Avogadro's number. The values of  $\Gamma_{max}$  and  $A_{min}$  are listed in Table 1.

A greater  $\Gamma_{max}$  value or smaller  $A_{min}$  value means a denser arrangement of surfactants at the air/liquid interface. As shown in Table 1, the  $A_{min}$  values were 169 Å<sup>2</sup> for Si<sub>4</sub>ASO<sub>3</sub>K, 177 Å<sup>2</sup> for Si<sub>4</sub>ASO<sub>3</sub>Na and 189 Å<sup>2</sup> for Si<sub>4</sub>ASO<sub>3</sub>Li, and they were larger than those of conventional hydrocarbon anionic surfactants, i.e., SLS,  $A_{min} = 56.7 \text{ Å}^{2.28}$ . These surface activity parameters of our products compared with SLS had been shown in Table 1. The larger  $A_{min}$  values than SLS which with linear hydrophobic groups might be the result of the "umbrella" shaped trimethylsilyloxyl groups arranging themselves with a greater distance between surfactant molecules, and thus resulting in the siloxanyl groups orienting parallel to the water surface<sup>27, 39</sup>. The  $A_{min}$  values of the anionic surfactants followed the order:  $Si_4ASO_3K < Si_4ASO_3Na < Si_$ Si<sub>4</sub>ASO<sub>3</sub>Li. The sample Gouy-Chapman-Stern theory was used as the adsorption model. According to the model described by Warszynski i.e., the negative surfactant head groups were adsorbed in the stern layer while the hydrated counterions were small enough to penetrate into the stern layer, suggesting that the most surfactant charges in the stern layer could be compensated by the smallest hydrated potassium ions<sup>40</sup>. This phenomenon indicated that in the presence of the smaller counterions the adsorption layer performed densely packing. This theoretical model well fitted to our results shown in Figure  $2^{41}$ . The results showed the curve of Si<sub>4</sub>ASO<sub>3</sub>Na was similar with Si<sub>4</sub>ASO<sub>3</sub>Li, far apart from Si<sub>4</sub>ASO<sub>3</sub>K, which could be explained by hydration radius of the counterions (Table 2). The Amin value at water interface of Si<sub>4</sub>ASO<sub>3</sub>Li was larger than that of Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>K, due to the largest size of hydrated counterions bound to the surfactant molecule as shown in Table 2.

**Table 1.** Critical aggregate concentration (CAC) and adsorption parameters of  $Si_4ASO_3K$ ,  $Si_4ASO_3Na$ ,  $Si_4ASO_3Li$  and SLS in aqueous solutions at 298.15 K.

	CAC <sup>a</sup>	CAC <sup>b</sup>	γсас	$\pi_{\mathrm{CAC}}$	$\Gamma_{\max}$	A <sub>min</sub>
	(m mol/L)	(m mol/L)	(mN/m)	(mN/m)	$(\mu mol/m^2)$	(Å <sup>2</sup> )
Si <sub>4</sub> ASO <sub>3</sub> K	4.5±0.2	3.0±0.2	19.8±0.2	52.2±0.2	0.98±0.10	169±16
Si <sub>4</sub> ASO <sub>3</sub> Na	10.8±0.3	3.1±0.2	20.1±0.2	51.9±0.2	$0.94{\pm}0.05$	177±13
Si <sub>4</sub> ASO <sub>3</sub> Li	11.5±0.3	3.4±0.3	20.8±0.2	51.2±0.2	$0.88 \pm 0.1$	189±19
SLS	12.4		33.0	39.0	2.93	56.7

(a: Determined from surface tension b: Determined from electrical conductivity)

**Table 2.** Values for the nonhydrated and hydrated counterion radius <sup>41</sup>.

	nonhydrated ion radius (nm)	hydrated ion radius (nm)
Li <sup>+</sup>	0.068	0.38
$Na^+$	0.095	0.36
$K^+$	0.133	0.33

#### Conductometry results

The CAC of Si<sub>4</sub>ASO<sub>3</sub>Li was first determined by electrical conductivity measurements at 25 °C which plots the conductivities of surfactant solutions as a function of the concentrations, as shown in Fig. 3. The CAC value was determined by the intersection of the two straight lines in the  $\kappa$ -C plot. Figure 3 shows that as the temperature changed, the conductivity value changed slightly, indicating that the electrical characteristics were minimally influenced by temperature. The counterion binding degree ( $\beta$ ) is known to be influenced by the hydrophilicity of the counterions. The increasing hydrophilicity of the K, Na and Li counterions can decrease their

affinity for the surfactant molecules<sup>42, 43, 44</sup>. Therefore, our alkali salt products with different counterions showed the similar conductivity results. As previously reported, the  $\beta$  values of cationic silicone surfactants were always larger than those of our products, for most of which are alkalescent salts, and the hydrophobicity of the counterions with surfactant head groups would increase their binding with each other<sup>18, 27, 45, 46</sup>.



Figure 3. Conductivity as a function of concentration for Si<sub>4</sub>ASO<sub>3</sub>Li at different temperatures.

As shown in Table 1, the CAC values of the three surfactants that determined by electrical conductivity were similar, but it can be still seen that with the counterion hydrophilicity decreased, the CAC values decreased correspondingly. Compared to the lithium ion ( $Li^+$ ), the potassium ion ( $K^+$ ), with the smallest hydrated ion radius, could penetrate into the stern layer, and reduce the charge repulsion of the head groups more efficiently. This behavior reduced the thickness of diffuse part of the double layer. Thereby making Si<sub>4</sub>ASO<sub>3</sub>K form aggregates more easily.

The degree of counterion binding ( $\beta$ ) can be obtained from the conductivity measurement with Eq. (4)<sup>47</sup>

#### Langmuir

58 59

60

$$\beta = 1 - \frac{\alpha_1}{\alpha_2} \tag{4}$$

where  $\alpha_1$  and  $\alpha_2$  are the slopes of the straight lines above and below the CAC in the conductivity plots, respectively. The electrical conductivity versus surfactant concentration for Si<sub>4</sub>ASO<sub>3</sub>Li at different temperatures is shown in Figure 3, and the values of  $\beta$  at each temperature for Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li were obtained as summarized in Table 3.

As shown in Table 3, the  $\beta$  values of the three anionic surfactants were low, indicating that the self-repulsion was stronger than the attraction between the head groups and the counterions<sup>48,</sup> <sup>49, 50</sup>. And the  $\beta$  values of Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li decreased with the increase of temperature, which can be attributed to the increased motion of the surfactant molecules as temperature increases.

**Table 3**. Degree of counterion binding ( $\beta$ ) and thermodynamic parameters of aggregate formation for Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li in aqueous solutions at different temperatures.

surfactants	T (K)	β	$\Delta G_m^{\ \Theta}$	$\Delta H_m^{\ \Theta}$	$-T\Delta S_m^{e}$	$\Delta S_m^{\ e}$
			(KJ/mol)	(KJ/mol)	(KJ/mol)	(J/mol K)
Si <sub>4</sub> ASO <sub>3</sub> K	288.15	0.1856±0.05	-28.10±0.360	-9.16±0.770	-18.94±0.410	65.73±1.422
	293.15	0.1853±0.05	$-28.48 \pm 0.362$	-9.48±0.792	-19.0±0.40	64.81±1.363
	298.15	0.1847±0.05	-28.85±0.365	-9.80±0.833	-19.05±0.483	63.89±1.620
	303.15	0.1830±0.05	-29.19±0.368	-10.12±0.859	-19.07±0.491	62.91±1.616
	308.15	0.1797±0.05	-29.50±0.375	$-10.42 \pm 0.883$	$-19.08 \pm 0.508$	61.92±1.649
Si <sub>4</sub> ASO <sub>3</sub> Na	288.15	0.1682±0.05	-27.89±0.388	-13.96±1.194	-13.93±0.814	48.34±2.825
	293.15	0.1591±0.05	-27.95±0.406	-14.33±1.237	-13.62±0.831	46.46±2.835
	298.15	$0.1499 \pm 0.05$	$-28.00\pm0.427$	-14.71±1.279	-13.29±0.852	44.57±2.858

	303.15	$0.1493 \pm 0.05$	-28.36±0.430	-15.20±1.223	-13.16±0.793	43.41±2.616
	308.15	0.1369±0.05	-28.43±0.462	-15.53±1.367	-12.90±0.905	41.86±2.937
Si <sub>4</sub> ASO <sub>3</sub> Li	288.15	0.2665±0.05	-30.02±0.271	-12.06±0.952	-17.96±0.681	62.33±2.363
	293.15	0.2355±0.05	-29.58±0.297	-12.18±0.986	-17.40±0.689	59.36±2.350
	298.15	0.2274±0.05	-29.57±0.306	-12.51±1.019	-17.06±0.713	57.22±2.391
	303.15	0.2164±0.05	-29.56±0.319	-12.81±1.053	-16.75±0.734	55.25±2.421
	308.15	$0.1902 \pm 0.05$	-29.33±0.352	-12.95±1.118	-16.38±0.766	53.16±2.486

Thermodynamic analysis of aggregation

The thermodynamic parameters, such as the standard Gibbs energy  $(\Delta G_m^{e})$ , the standard entropy  $(\Delta S_m^{e})$ , and the standard enthalpy  $(\Delta H_m^{e})$ , were estimated to understand the aggregation of the novel sulfonate anionic silicone surfactants. The  $\Delta G_m^{e}$  can be calculated according to Eq.  $(5)^{51}$ 

$$\Delta G_m^{\theta} = (1+\beta)RT \ln \chi_{cmc} \tag{5}$$

where  $\chi_{cmc}$  is the mole fraction of silicone surfactant at the CAC, T is the absolute temperature, and R is the gas constant. Then, the enthalpy of aggregate formation can be calculated using the Gibbs-Helmboltz equation, Eq. (6)<sup>51</sup>

$$\Delta \mathbf{H}_{m}^{\theta} = \left[\frac{\partial \left(\Delta G_{m}^{\theta} / T\right)}{\partial \left(1 / T\right)}\right]$$
(6)

and the entropy of formation is obtained by Eq.  $(7)^{51}$ 

$$\Delta S_{\rm m}^{\theta} = \frac{\Delta H_{\rm m}^{\theta} - \Delta G_{\rm m}^{\theta}}{T} \tag{7}$$

#### Langmuir

The values of  $\Delta G_m^{\ e}$ ,  $\Delta H_m^{\ e}$ , and  $\Delta H_m^{\ e}$  were obtained and are presented in Table 3. Over the whole investigated range, all of the  $\Delta G_m^{\ e}$  values are negative, indicating that the aggregation of the surfactants is spontaneous.

#### Effect of counterion on the aggregation properties

It is known that compared to temperature, the counterion has a vital effect on the surface activity parameters of these anionic surfactants, such as CAC and  $A_{min}$ . So we investigated the counterion effect on the aggregation behavior of the surfactants. It can be seen in Figure 2 that the number of Si<sub>4</sub>ASO<sub>3</sub>Li at the interface is less than Si<sub>4</sub>ASO<sub>3</sub>K and Si<sub>4</sub>ASO<sub>3</sub>Na due to the larger hydrated lithium ion. Freeze-fracture transmission electron microscope (FF-TEM) is the first choice to identify the surfactants microstructures in solution. Figure 4 (a, b) presents the FF-TEM result of Si<sub>4</sub>ASO<sub>3</sub>Li in aqueous solution at the concentration of 0.01M and 25 °C. It is obvious that our products performed as vesicles. FF-TEM images illustrated that the vesicles size was uniform and lower than 200 nm. The result indicated a spherical vesicles microstructure for our tetrasiloxane-based surfactants. Therefore, the vesicles can provide their potential application in delivery system etc. In order to clarify the structure of vesicles, cryo-TEM was further used to obtain their instantaneous microstructure in aqueous solution (Figure 4 c-f). The cryo-TEM results indicated that these tetrasiloxane surfactants could form multilaminar vesicles (Figure 4 c, d), and multi-ventricular vesicles (Figure 4 e, f). It is deductive that a model of multilaminar layer vesicles structure could be imitated and shown in Figure 5.



**Figure 4.** a,b) FF-TEM images of Si<sub>4</sub>ASO<sub>3</sub>Li in aqueous solution above CAC (10.0 mM); c-f) cryo-TEM images of Si<sub>4</sub>ASO<sub>3</sub>K in aqueous above CAC ((c,d) 6.0mM and (e,f) 10.0mM).



Figure 5. Model of multilaminar layer membrane structure of vesicles.

The counterions' difference could also influence the aggregate behavior. Morphology and size distribution of our series of surfactants were investigated by TEM and DLS. Figure 6 shows the TEM images of Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li in aqueous solution at the same temperature (298.15 K) and the same concentration of 6.0 mM. Spherical aggregates were

observed with diameters ranging from 180 nm to 400 nm. The aggregate sizes followed the order of  $Si_4ASO_3K>Si_4ASO_3Na>Si_4ASO_3Li$ . And as all the TEM results were carried out under the same condition (the same concentration and same testing temperature), the different morphologies of the three anionic surfactants could only be affected by the type of counterions. As for the order of size, it is hypothesized that hydrated K ions with smallest radius could penetrate the double layer more easily and reduce the head group repulsion more efficiently, and then result in more monomer packing of surfactants (See figure 7)<sup>41, 52-55</sup>.



**Figure 6.** TEM images of Si<sub>4</sub>ASO<sub>3</sub>K (a, b); Si<sub>4</sub>ASO<sub>3</sub>Na (c, d); Si<sub>4</sub>ASO<sub>3</sub>Li (e, f) in aqueous solution (6.0 mM).







Figure 7. The effect of different hydrated counterions on surfactant packing.

DLS measurement was carried out to investigate the hydrodynamic diameters of aggregates, which formed by the surfactant series above the CAC. Figure 8 shows the size distribution of Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li in aqueous solution at 298.15K and 6.0 mM (above CAC). All the product DLS curves showed that the aggregates exhibited a monomodal function and the size distribution ranged from 200 nm to 400 nm, similar with the TEM results. Taking Si<sub>4</sub>ASO<sub>3</sub>Li as a sample, DLS result showed average hydrated radium of 99 nm, very close to the FF-TEM result (~200nm). The vesicles size could also be measured through TEM images (~180nm). Thus, it is concluded that the vesicles formed by the tetrasiloxane-based surfactants had uniform and steady size above CAC. The hydrodynamic diameters of surfactants showed the same trend when the counterion changed, following the order of Si<sub>4</sub>ASO<sub>3</sub>K > Si<sub>4</sub>ASO<sub>3</sub>Na > Si<sub>4</sub>ASO<sub>3</sub>Li. The smaller sized hydrated counterions could penetrate into the stern layer and reduce the charge repulsion of the head groups more efficiently, thereby allowing the aggregates to pack more tightly<sup>55, 56</sup>. Therefore our study provides a convenient way to adjust the vesicles size by changing the counterions of the anionic sulfonate surfactants.





**Figure 8.** Size distributions of Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na andSi<sub>4</sub>ASO<sub>3</sub>Li at 6.0 mM concentration in aqueous solution.

#### Conclusion

Three sulfonate anionic silicone surfactants, Si<sub>4</sub>ASO<sub>3</sub>K, Si<sub>4</sub>ASO<sub>3</sub>Na and Si<sub>4</sub>ASO<sub>3</sub>Li were successfully synthesized for the first time. This work provides a simple and mild route to obtain these unique anionic sulfonate silicone surfactants. The product aggregation behavior in aqueous solution was investigated systematically. The results showed that the silicone surfactant demonstrated superior surface activity compared with common hydrocarbon surfactants because of the special properties of the siloxane. These compounds not only showed a lower surface tension that is equal to the cationic silicone surfactants, but also had lower CAC values than the cationic silicone surfactants and classical hydrocarbon anionic surfactants<sup>27, 28, 45</sup>. The counterion

affected the surface activity and the aggregation behavior obviously. The CAC values and the  $A_{min}$  following the order:  $Si_4ASO_3K < Si_4ASO_3Na < Si_4ASO_3Li$ . Cryo-TEM images showed that this sulfonate surfactant in aqueous solution could form spherical vesicles spontaneously, and the size of the vesicles ranging from 200 nm to 400 nm could be adjusted by changing the counterions. DLS and TEM results indicated that our products had stable and mono-distributed aggregation sizes both in and out of aqueous solution.

The anionic silicone surfactants with these characteristics possess the ability to replace the conventional hydrocarbon anionic surfactants used in emulsifiers, cosmetics and oil extraction<sup>57-60</sup>. Moreover, due to the nontoxicity and the negative charge, they are good candidates to overcome the limitations of cationic silicone surfactants in biomaterials, as drug carriers and in textile dyeing. This investigation contributes to understanding the aggregation of novel anionic silicone surfactants and provides a convenient way to adjust the vesicles size. It will be helpful in designing novel and efficient silicone surfactants with controlled and narrow vesicles size distributions, which may expand the potential applications of silicone surfactants in biotechnology, controlled release and electrochemistry.

#### Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21774070) and Special Fund for Shandong Independent Innovation and Achievements transformation (No.2014ZZCX01101).

#### References

1. Algorzata, Z. Silicone Surfactants as Potential Lubricating Substances and Bases. *Tribology Ttransactions* **2016**, *38*, 106-113.

2. Smid-Korbar, J. Efficiency and Usability of Silicone Surfactants in Emulsions. *Int. J. Cosmet. Sci.* **1990**, *12*, 135-139.

 Pawel, G. P.; Gabriel, R. Hyperbranched Poly(Ether-Siloxane) Amphiphiles of Surprisingly High Solubility in Supercritical Carbon Dioxide. *J. Supercrit. Flud.* 2014, 95, 222-227.

4. Zhaosheng, H.; Chengyou, K. Polysiloxanes with Quaternary Ammonium and Polyether Groups for Silyl-Terminated Polypropylene Oxide Waterborne Emulsions. *J. Surfactants Deterg.* **2016**, *19*, 739-745.

5. Randal, M. H. Silicone Surfactants-New Developments. *Curr.Opin. Colloid Interface Sci.* **2002**, *7*, 255-261.

6. Zhang, X.D.; Macoskoa.; Davisa. Role of Silicone Surfactant in Flexible Polyurethane Foam. *J. Colloid Interface Sci.* **1999**, *215*, 270-279.

7. David, C. S.; Brian, H. R.; Julian, E.; Richard, K. H. Lamellar Aggregates in the L2 Phase of a Nonionic Silicone Surfactant (L77-Oh). *Langmuir* **1994**, *10*, 2213-2218.

8. Hidemi, T.; Hironobu, K.; Asao, H. Phase Behavior of Polyoxyethylene Trisiloxane Surfactant in Water and Water-Oil. *Langmuir* **1998**, *14*, 5113-5120.

 Naofumi, E.; Yoshifumi, W.; Hideharu M. Amphiphilic Block-Random Copolymer Surfactants with Tunable Hydrophilic/Hydrophobic Balance for Preparation of Non-Aqueous Dispersions by an Emulsion Solvent Evaporation Method. *React. Funct. Polym.* 2017, *110*, 10-20.

 Uddin, M. H.; Rodriguez, C.; Watanabe, K. Phase Behavior and Formation of Reverse Cubic Phase Based Emulsion in Water/Poly(Oxyethylene) Poly(Dimethylsiloxane)
 Surfactants/Silicone Oil Systems. *Langmuir* 2001, *17*, 5169-5175. 11. Lu, T.; Yingjie, Y.; Xiaoyu, L.; Jinglin, S.; Xia, X. Supramolecular Hydrogels
Facilitated by A-Cyclodextrin and Silicone Surfactants and Their Use for Drug Release. *Colloids Surf. A.* 2017, *522*, 470-476.

12. X, Li.; Davis, H.T. Phase Behavior and Microstructure of Water/Trisiloxane E12 Polyoxyethylene Surfactant/Silicone Oil Systems. *Langmuir* **1999**, *15*,2267-2277.

13. Bonnington, L. S.; Henderson, W.; Zabkiewicz, J. A. Characterization of Synthetic and Commercial Trisiloxane Surfactant Materials. *Appl. Organomet. Chem.* **2004**, *18*,28-38.

14. Wuhuan, H. Synthesis and Characterization of Silicone Based Esterquat for Fabric Softening Application. *Fine Chem.* **2012**, *29*, 1167-1171.

15. Steven, A. S.; Michael, J. O. Zwitterionic Organofunctional Siloxanes as Aqueous Surfactants: Synthesis and Characterization of Betaine Functional Siloxanes and Their Comparison to Sulfobetaine Functional Siloxanes. *Langmuir* **1991**, *7*, 868-871.

16. He, M.; Scriven, L. E.; Davis, H. T. Aggregation Behavior and Microstructure of Cationic Trisiloxane Surfactants in Aqueous Solutions. *J. Phys. Chem.* **1994**, *98*, 6147-6158.

17. Xiao, C.; Congde, Q.; Shijie, W.; Yunqiao, D.; Chuanming, H.; Junying, Li. Synthesis, Surface Properties, and Antibacterial Activity of Polysiloxane Quaternary Ammonium Salts Containing Epoxy Group. *Colloid Polym. Sci.* **2015**, *293*, 1971-1981.

 Jinglin, T.; Depeng, M.; Shengyu, F.; Changqiao, Z. Effect of Hydrophobic Chains on the Aggregation Behavior of Cationic Silicone Surfactants in Aqueous Solution. *ColloidPolym. Sci.* 2013, 291, 1487-1494.

19. Dipak, D. P.; Archana, S. B.; Usha, S. Application of Silicone Surfactant Along with Hydrocarbon Surfactants to Textile Washing for the Removal of Different Complex Stains. *J. Surfactants Deterg.* **2016**, *20*, 287-295.

20. Suchada, T.; Pratik, K.; Ampornphan, S.; Edga, r A. O.; Nantaya Y. Silicon-Compound Coating for Preparation of Water Repellent Cotton Fabric by Admicellar Polymerization *Colloids Surf. A.* **2011**, 384, 381-387.

#### Langmuir

21. Youjie, S.; Xiujuan, W.; Shouxiang, L.; Changhai, L. Experimental Study on Foam Properties of Mixed Systems of Silicone and Hydrocarbon Surfactants. <i>J. Surfactants Deterg.</i> <b>2016</b> , <i>19</i> , 823-831.
22. Michael, R. Sunscreen Formulations Comprising Gemini Surfactants and Silicone Based Surfactants Official gazette of the United States Patent and Trademark Office. <i>Patents</i> <b>2017</b> .
23. Liujun, P.; Ping, W.; Juanjuan, L.; Jiping, W. Effect of Nonionic Surfactant on the Micro-Emulsifying Water in Silicone Media. <i>J. Surfactants Deterg.</i> <b>2016</b> , <i>20</i> , 247-254.
24. Masaki, I. Agricultural Chemical-Spreading Agent Composition Official gazette of the United States Patent and Trademark Office. <i>Patents</i> <b>2016</b> .
25. FengLan, X. Synthesis of Anionic Gemini Silicone Surfactant. <i>Textile Auxiliaries</i> <b>2016</b> , 05,12-14.
26. Rungthip, K.; Thapakorn, J.; Vuthichai, E. Polyhedral Oligomeric Silsesquioxane (Poss) Containing Sulfonic Acid Groups as a Metal-Free Catalyst to Prepare Polycaprolactone. <i>Polymer</i> <b>2017</b> , <i>108</i> , 173-178.
27. Liying, F.; Jinglin, T.; Yan, Z.; Ge, Y.; Jiangtao, Y.; Shengyu F. Synthesis, Aggregation Behavior of Novel Cationic Silicone Surfactants in Aqueous Solution and Their Application in Metal Extraction. <i>J. Mol. Liq.</i> <b>2017</b> , <i>231</i> , 134-141.
28. Anna, W. C.; Manila1, D.; Milton, J. R. Surface and Thermodynamic Properties of Some Oxyethylenated Sulfates and Sulfonates. <i>J. Phys. Chem.</i> <b>1986</b> , <i>90</i> , 2413-2418.
29. Peixun L.; Application of the Gibbs Equation to the Adsorption of Nonionic Surfactants and Polymers at the Air–Water Interface: Comparison with Surface Excesses Determined Directly using Neutron Reflectivity. <i>Langmuir</i> <b>2013</b> , <i>29</i> , 9324-9334.
<ul> <li>30. Peixun L.; Limitations in the Application of the Gibbs Equation to Anionic Surfactants at the Air/Water Surface: Sodium Dodecylsulfate and Sodium</li> <li>Dodecylmonooxyethylenesulfate Above and Below the CMC. <i>Langmuir</i> 2013, <i>29</i>, 9335-9351.</li> </ul>

31. Peixun L.; Limitations in the Use of Surface Tension and the Gibbs Equation To Determine Surface Excesses of Cationic Surfactants. *Langmuir* **2014**, *30*, 6739-6747.

32. M. J. Jaycock Chemistry of Interfaces. John Wiley and sons 1981.

33. Pan, H.; Guo, X.;Song, T.;Li, X.; Li, S. The Influence of Additive on the Cmc of Sodium Dodecyl Benzene Sulfonate Solution. *Appl. Chem. Ind.* **2011**, *40*, 634-636.

34. Nazish, F.; Manorama, P.; Din, K. Mixed Micellization of Novel Cationic Ester-Bonded Gemini Surfactants: Investigations by Conductometric and Tensiometric Measurements. *J. Mol. Liq.* **2016**, *219*, 959-966.

35. Saurabh, S. S.; Vinod K. A.; Prem S. G. Micellar Structure of Silicone Surfactants in Water from Surface Activity, Sans and Viscosity Studies. *J. Phys. Chem. B* **2002**, *106*, 2606-2617.

36. Sonnek, G.; Schmaucks, G.; Wuestneck, R.; Herbst, M.; Ramm, M. Effect of Siloxanyl Groups on the Interfacial Behavior of Quaternary Ammonium Compounds. *Langmuir* **1992**, *8*, 1-28.

37. Jitendra, M.; Dharmesh, V.; Prashant, B. Aggregation Behavior of Quaternary Salt Based Cationic Surfactants. *Thermochimica*. *Acta* **2005**, *428*, 147-155.

38. Zhang, S.; Yan, H.; Zhao, M.; Zheng, L. Aggregation Behavior of Gemini Pyrrolidine-Based Ionic Liquids 1,1'-(Butane-1,4-Diyl)Bis(1-Alkylpyrrolidinium) Bromide (C(N)Py-4-C(N)PyBr2) in Aqueous Solution. *J. Colloid Interface Sci.* **2012**, *372*, 52-57.

39.Yanyan, Z.; Guoyong, W.; Wanxu, W.; Zhiping, D.; Jieqiong, Q. Polyglycerol Modified Polysiloxane Surfactants: Their Adsorption and Aggregation Behavior in Aqueous Solution. *J. Ind. Eng. Chem.* **2017**, *47*, 121-127.

40. Warszynski, P.; Czichocki, G. Effect of Counterions on the Adsorption of IonicSurfactants at Fluid-Fluid Interfaces. *Langmuir* **2002**, *18*, 2506-2514.

#### Langmuir

41. Oh, S. G.; Shah. D. O. Effect of Counterions on the Interfacial Tension and Emulsion Droplet Size in the Oil/Water/Dodecyl Sulfate System. *J. Phys. Chem.* **1993**, *97*, 284-286.

42. AnTao, G.; Hang, X.; JinXin, X. Effects of Counterion Structure on the Surface Activities of Anionic Fluorinated Surfactants Whose Counterions Are Organic Ammonium Ions. *Colloids Surf. A* 2014, *459*, 31-38.

43. Sanjay, K. Y.; Sanjeev, K. Counterion-Specific Clouding in Aqueous Anionic Surfactant: A Case of Hofmeister-Like Series. *Colloid and Polymer Sci.* **2017**, *295*, 869-876.

44. Lifei, Z.; Yanyan, D.; Xiaohong, Z.; Xia, G. Micellization of Lactosylammonium Surfactants with Different Counter Ions and Their Interaction with DNA. *J. Chem. Eng. Data* **2016**, *61*, 2969-2978.

45. Jinglin, T.; Peijian, Z.; Depeng, M.; Shengyu, F.; Changqiao, Z. Effect of Hydrophobic Chains on the Aggregation Behavior of Cationic Silicone Surfactants in Aqueous Solution. *Colloid Polym. Sci.* **2013**, *291*, 1487-1494.

46. Wagay, T. A. Aggregation and Surface Behavior of Aqueous Solutions of Cis-Bis(1,3-Diaminopropane)Bis(Dodecylamine)Cobalt(Iii) Nitrate. A Double-Chained Metallosurfactant. *RSC Advances* 2016, *6*, 66900-66910.

47. Hang, X.; Peng, Y.; Kong-Shuang, Z.; JinXin, X. Effect of Headgroup Size on the Thermodynamic Properties of Micellization of Dodecyltrialkylammonium Bromides. *J. Chem. Eng. Data* **2011**, *56*, 865-873.

48. Filipe, S. L.; Iolanda, M. C.; Hernan, C. Sodium Triflate Decreases Interaggregate Repulsion and Induces Phase Separation in Cationic. *Langmuir* **2015**, *31*, 2609-2614.

49. Panfeng, L.; Jingcheng, H. Influence of Counterions on Micellization of Tetramethylammonium Perfluorononanoic Carboxylate in 1-Butyl-3-Methylimidazolium Ionic Liquid. *J. Phys. Chem. B* **2012**, *116*, 7669-7675

50. Hisham, J. Y. E. Conductometry and Thermodynamics Study of Metal Dioctylsulfosuccinate in Aqueous Solution. *J. Dispersion Sci. Technol.* **2010**, *31*, 557-562.

51. Olutaş, E. B.; Acımış M. Thermodynamic Parameters of Some Partially Fluorinated and Hydrogenated Amphiphilic Enantiomers and Their Racemates in Aqueous Solution. *J. Chem. Thermodyn.* **2012**, *47*, 144-153.

52. Thakkar, K.; Bharatiya, B.; Bahadur, P. Cationic Surfactants Modulate Aqueous Micellization and Wetting on Ptfe by Triton X-100: Effect of Alkyl Chainlength, Headgroup and Counterion. *J. Mol. Liq.***2017**, *241*, 136-143.

53. Bhat. M.; Gaikar. V. G. Characterization of Interaction between Butyl Benzene Sulfonates and Cetyl Trimethylammonium Bromide in Mixed Aggregate Systems. *Langmuir* **1999**, *16*, 1580-1592.

54. Nazima, S. Investigations on the Binding Behavior of Competitive Ions to a Cationic by H-1-Nmr Studies Indian. J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.
2016, 55, 1443-1448.

55. Li-Sheng, H.; Ni, Y.; GuangYu, X.; YunFeng, J.; YanQing, N. Specific Ion Effects on the Micellization of Aqueous Mixed Cationic/Anionic Surfactant Systems with Various Counterions. *Colloids Surf. A* **2016**,*504*, 161-173.

56. Meijide, F.; Coello, A.; Nunez E. R. Aggregation Behavior of Sodium Cholate in Aqueous Solution. *J. Phys. Chem.* **1993**, *97*, 10186-10191.

57. Delphine, D. D.; Isabelle, P.; Christine, D.; Ljepsa, K. Elastic Properties of Crude Oil/Water Interface in Presence of Polymeric Emulsion Breakers. *Colloids Surf. A* **2005**, *270*, 257-262.

58. Nazir, H.; Zhang, W.; Liu Y.; Chen, X.; Ma, G. Silicone Oil Emulsions: Strategies to Improve Their Stability and Applications in Hair Care Products. *Int. J. Cosmet. Sci.* **2014**, *36*, 124-133.

59. Moon, J. R. Trend on Development of Polymeric Organosilicone Surfactants. *J. Korean Oil Chem. Soc.* **2015**, *32*, 546-567.

60. Lisa, B.; Michael, W.; Claudia, V. Novel Concentrated Water-in-Oil Emulsions Based

on	on a Non-Ionic Silicone Surfactant: Appealing Application Properties and Tuneable				
Vi	scoelasticity. Eur. J. Pharm. Biop	pharm. 2017,120, 34-42.			
Fc	<text></text>	Multilaminar Layer	double layer		
	ACS F	'aragon Plus Environment	28		