P-ISSN : 2442-9910
E-ISSN : 2548-642X
SPEKTRA: Jurnal Kajian Pendidikan Sains 5(2) (2019)
DOI: 10.32699/spektra.v5vi2i.106

TETRAPROPYLAMMONIUM SURFACTANTS AS MICELLAR MODIFIERS FOR ENHANCED OIL RECOVERY APPLICATION

Tretya Ardyani[1], Azmi Mohamed[2]*, Suriani Abu Bakar[2]
[1]Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia
[2]Department of Chemistry, Nanotechnology Research Centre, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia
*Corresponding author: tretyaardyani@gmail.com
Phone No: +60195550320

Dikirimkan: 31/07/2019. Diterima: 10/09/2019 Dipublikasikan: 12/10/2019

Abstrak

The article addresses an interesting yet unexplored issue in the development of surfactants for microemulsion stabilisation: the role of surfactant headgroup modification to tune the surfactant performances in CO_2,water, and cyclohexane. The aqueous properties, and phase behaviour of novel tetrapropylammonum (TPA) surfactants is described. For comparison purposes, the related sodium surfactant (Na-AOT, Na-AOT4, and Na-TC14) are also used to form microemulsions. Observation on the surfactant aqueous properties revealed that the swapping into TPA does not significantly increases the effectiveness of the surfactant in lowering the surface air-water (a/w) tension. The introduction of bulky TPA counterions to normal sulfosuccinate surfactant generally leads to a transition from spherical micellar to extended sheet-like micellar aggregates in water. All in all, the results point minor effect on the headgroup structure modification towards the compatibility of surfactant with CO_2.

Key Words Surfactant, Micelle, CO_2

PRELIMINARY

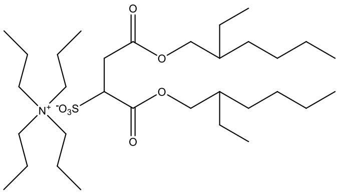
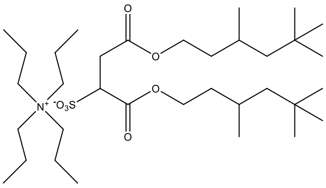
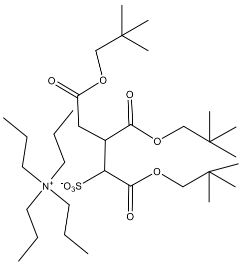
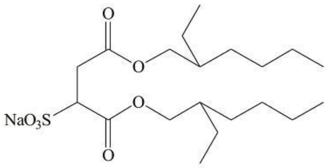
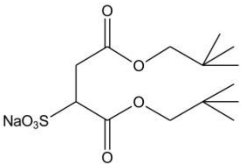
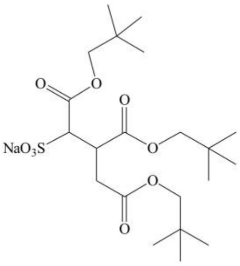
In colloidal chemistry, it is a common lore that ionic surfactants will aggregate forming micelles in solution to accommodate their dual nature. Typically, the headgroup resided at the surface where the bound counterions and solvent media are contained in the interfacial region. Moreover, the micellar properties also highly linked with the charge and type of the counterion in the surfactant molecule. In the last few years, the direction of surfactant synthesis has been focused into surfactants having hydrophobic counterions. One of the most widely studied counterion types in anionic surfactant systems are quaternaryalkylammonium cations [1-5]. Studies on the effect of exchanging the standard Na^+ cation for quaternary alkyl ammoniums on Aerosol-OT (AOT) surfactants have been previously reported [6-7].

The work reported here is based on varying the identity of the quaternaryalkylammonium (TAA) counterions on the sulfosuccinate surfactant structure and water-in-oil (w/o) microemulsions. Na-AOT is well known for its ability to stabilise w/o microemulsions to form spherical reversed micelles in organic solvents [8]. Interestingly, the introduction of tetrapropylammonium (TPA) counter ions has an important effect on surfactant aggregation in organic solvents by inducing a sphere-to-rod like micellar transition at low volume fractions. The results represent the first example of the effect of hydrophobic counterions on sulfosuccinate surfactants in stabilising w/o microemulsions in organic solvent media [7].

Due to lack of CO_2 solubility, works encompassing the effect of varying surfactant counterion towards the formation of stable water-in-CO2 (w/c) microemulsions remain scarce. Literatures suggested CO_2-philicity could be achieved by fluorination [9-11], introduction of a third alkyl chain [12-13], and addition of terminal methyl groups on surfactant chains [14]. Thus, it is crucial to investigate how the counterions affect the CO_2-philicity of surfactants. Recently, the self assembly of counterion exchange surfactants that promote sphere-to-rod like micelles has been tested in CO_2 [15-16]. One commercial example of CO_2 application is in enhanced oil recovery. However, due to the low viscosity of CO_2, its full potential is yet to be met. Interestingly, result shows that relative viscosity enhancement of CO_2 up to 90% was observed by exchanging Na^+ to Ni^{2+} or Co^{2+} cations of the fluorinated surfactant di-HCF4 [15]. This is the first example of counterion exchanged surfactants used as a micellar modifier in CO_2. However, due to environmental disadvantages associated with fluorine and transition metal salt compounds, there is an obvious need to change direction away from fluorine and metal free hydrocarbon surfactants for CO_2.

In order to improve understanding of structure performance relationships with CO_2-philicty, surface tension measurements were carried out. In addition, to overcome the weak properties of CO_2, the introduction of low levels of added cosolvent was necessary to increase solvent quality. The use of co-solvents has recently been used to enhance the solubility of micellar systems [17-18].

Table 1. Tetrapropylammonium (TPA) surfactants used in this work.

Name	Surfactant Structure
TPA-AOT	
TPA-AOT4	
TPA-TC14	
Na-AOT	
Na-AOT4	
Na-TC14	

METHOD

Tetrapropylammonium (TPA) based surfactants TPA-AOT, TPA-AOT4 and TPA-TC14 were synthesised according to methods described in literature [6-7]. The chemical structure of synthesised surfactants described in this study is given in Table 1. Water with resistivity of 18.2 MΩ cm was obtained from an Elga water system; deuterium oxide (D_2O) and deuterated cyclohexane (C_6D_{12}) were from Goss Scientific. CO_2 CP grade was supplied by BOC.

All chemical were used without further purification.

Surface tension measurements

Solution of 50% nitric acid was used for glassware cleaning which was then followed by repeated rinsing with distilled water. The glassware was then dried in compressed air. The platinum (Pt) plate was flame-cleaned in between measurements. Tensiometric measurements were performed at 25°C on either a Krüss K11 or K100 instrument following the Wilhelmy plate method.

Small-Angle Neutron Scattering (SANS)

Scattering analysis was measured at ambient pressure on the time-of-flight LOQ instrument at ISIS, UK. The neutron wavelength of $\lambda = 2.2 – 10$ Å was employed to give Q range between 0.007 – 0.23 $Å^{-1}$. The absolute intensities of I(Q) (cm^{-1}) were determined from the scattering of deuterated standard to within 5%. For the TPA – surfactant studies, deuterated water (D_2O) and cyclohexane (C_6D_{12}) were used as a solvent with hydrogenated surfactants providing the necessary contrast. The samples were placed in Hellma quartz cells with a 2 mm path-length and held on automatic sample changer equipped with thermostat at 25°C. For high pressure experiments in liquid CO_2 the SANS2d instrument was combined with a high pressure cell. The path length was 10 mm, the neutron beam width was 10 mm, pressure = 380 bar and T = 25°C. The data were normalised for solvent background, empty cell, pressure induced changes in cell volume, and transmission following previous measurement [9, 19]. For liquid CO_2, ρ_{co2} ~ 2.50 x mass density x 10^{10} cm^{-2} [20]. At the experimental pressure of 380 bar the CO_2 density ~ 1.0 gcm^{-3} so that ρ_{CO2} ~ 2.50 x10^{10} cm^{-2}. The contrast was provided using hydrogen containing surfactants. For SANS experiments using mixtures of d-cyclohexane and CO_2 the SLD of the mixed solvent ($\rho_{CO2/C6D12}$) was calculated as a first order summation weighted by the different volume fractions.

RESULTS AND DISCUSSIONS

Aggregation Structure in Water – A Small Angle Neutron Scattering Study

SANS provides key evidence for the presence of surfactant microstructures: it is well suited to micellar dimensions and is a non-destructive technique. The particle form factor P(Q) of the scattering profiles give information on the shapes of aggregate formed in the system. Figure 1 shows log-log SANS profiles and model fits for TPA-AOT, TPA-AOT4 and TPA-TC14 micelles at 0.08 mol dm^{-3} in D_2O and 25°C.

For Na-TC14 the scattering shown in Figure 1, is consistent with charged ellipsoidal micelles with a polar radius R_1, aspect ratio X and modelled by Hayter-Penfold electrostatic interparticle factor S(Q) [21]. The fitted micellar dimensions for Na-TC14 R_1 = 11 Å and X = 2.3 are consistent with those in the literature [17]. Moving to other chemical structures, most scattering profiles show obvious Q^{-2} regimes with undulations at lower Q regions indicative of lamellar or long range sheet-like structures. These profiles were fitted using a multilamellar stack model with the local extent of planarity R, a mean thickness of M bilayers L and superimposed Gaussian distribution of L and D described as σ_L and σ_D respectively. The parameters obtained from fitting the SANS data are given in Table 2.

The bilayer thickness L is in concordant with the total molecular sizes of both cation and anion [22]. The introduction of the bulky counterion, increases the interlamellar distance of ~ 370 Å for Na–surfactants to ~ 700Å for the TPA-surfactants. The results indicate that the bulky counterion and its position strongly impact the shape of the aggregates.

Table 2. Parameters obtained from fitting the SANS data [Surfactant] = 0.08 mol dm^{-3} T = 25°C.

Surfactant	L ±0.5	σ_L ± 0.05	R*±10	M ± 0.5	D ±10	σ_D ± 0.05
TPA-AOT4	26	0.4	985	14.3	702	0.1
Na-AOT4	16	0.3	768	3.2	692	0.2
TPA-AOT	26	0.4	502	15.3	533	0.2
Na-AOT	13	0.2	230	4.9	369	0.2
TPA-TC14	25	0.4	964	15.6	720	0.2

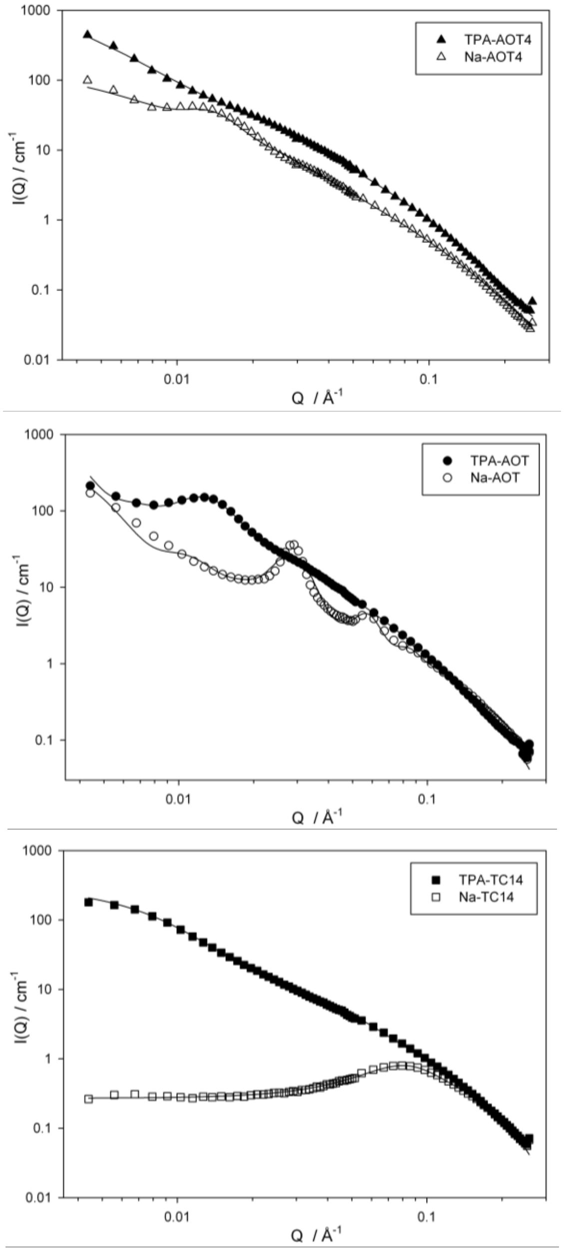
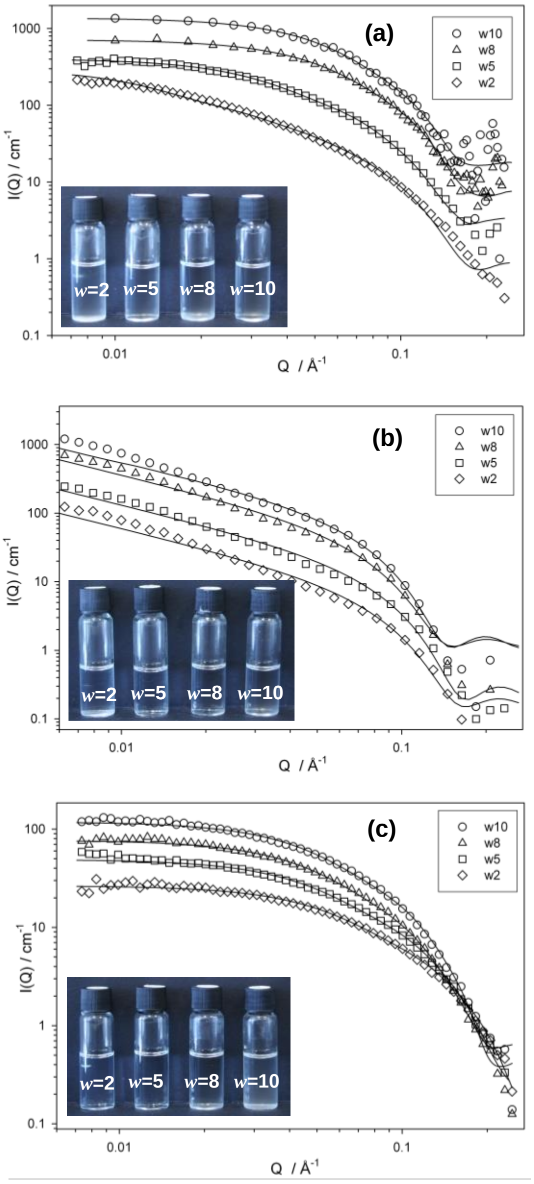


Figure 1. SANS profiles for TPA – Surfactant in D_2O. [Surfactant] = 0.08 mol dm^{-3}

Aggregation structure in cyclohexane

Studying self-assembly in high pressure environments is experimentally challenging therefore ambient pressure solvents which have a similar range of dielectric constants to CO_2, (e.g. cyclohexane) can provide useful information about the behaviour of these surfactants. SANS measurements are helpful for indicating the shape and size of surfactant self-assembled structure. At low Q values (< 0.10 Å^{-1}) the scattering profile may scale as I (Q) ~ Q^{-D}, whereby the exponent power law decay, D, is indicative of fractal dimension. Non-interacting spheres, rods and discs have power law decays (gradient of log-log plot) of 0, -1 and -2 respectively. For water-in-oil (w/o) microemulsion systems stabilised by Na-AOT4 and Na-TC14 (Figure 2 d) the absence of any decay in the low Q region confer the formation of small spherical droplets [17]. However, with the introduction of bulky TPA organic counter-ions, the scattering profiles for surfactants are distinctly different to those of the Na^+ analogue, with a gradient of approximately -1, consistent with rod-like micelles. Figure 2 (a – c) shows the log-log SANS profiles for the TPA-

TC14, TPA-AOT and TPA-AOT4 surfactants at a concentration of 0.075 mol dm^{-3} over a range of *w* values. The data were quantitatively fitted using a form factor for non-interacting rods. Table 3 lists the fitted parameters for rod radius, R and length, L. The results show an agreement and are consistent with the introduction of water, inducing transition from spherical to rod-like micelle [6,7]. The behaviour of the TPA sulfosuccinate surfactants is remarkably similar to that of divalent transition metal (Ni^{2+} and Co^{2+}) sulfosuccinate surfactants [23,24], presenting themselves as promising candidates for viscosity enhancement of CO_2.



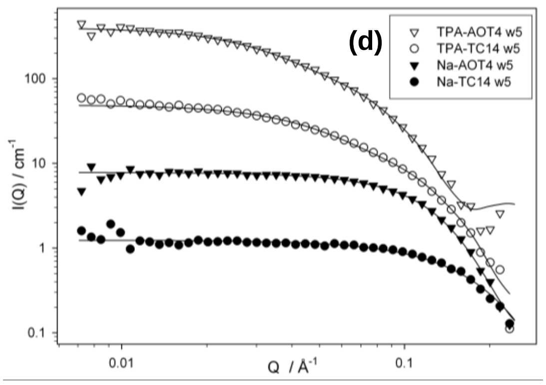


Figure 2. SANS profiles for (TPA – Surfactant) / H_2O/ C_6D_{12} systems, at different (water / surfactant) ratios, *w*, [Surfactant] = 0.075 mol dm^{-3} (a) TC14 (b) AOT (c) AOT4 (d) data for Na^+ analogues added for comparison.

Aggregation structures in CO_2

As shown in Table 4 exchanging the counterion from Na^+ to TPA significantly affects the phase stability. The P_{trans} for TPA-TC14 increased, with a translucent appearance still evident at 380 bar. Meanwhile a lump of TPA-AOT4 surfactant in a background of CO_2 was observed. The formation of a lump on the pressure cell window was attributed to the low solubility of TPA-AOT4.

High Pressure Small-Angle Neutron Scattering (HP-SANS) experiments were performed in order to study the surfactant aggregates in CO_2. Experiments were performed at 380 bar. Figure 3 shows that the SANS profiles of Na-TC14 and TPA-TC14 are broadly the same, suggesting the formation of dry spherical reversed micelles of the surfactant. The scattering data were fitted following a Schultz distribution of polydisperse spheres and the fitted radii are given in Table 4. The results also show that the spherical radius increases with the introduction of TPA counterions.

Table 3. Fitted parameters to SANS data in C_6D_{12}.

Surfactant	***w* ratio**	**Volume Fraction, Φ**	**Guinier Plot**	**Model Fit**	
			Radius R/ Å ± 2Å	**Radius, R/ Å ± 2Å**	**Length, L Å ± 5Å**
Na-TC14	5	0.032	13	15	-
TPA-TC14	2	0.035	13	13	87
	5	0.038	16	15	101
	8	0.042	18	18	102
	10	0.045	19	18	104
TPA-AOT	2	0.032	22	23	263
	5	0.036	23	23	278
	8	0.039	24	24	271
	10	0.042	24	25	280
Na-AOT4	5	0.031	19	21	-
TPA-AOT4	2	0.034	20	21	371
	5	0.037	21	22	145
	8	0.041	21	21	92
	10	0.044	22	22	91

Table 4. Fitted parameters for SANS data in liquid CO_2 and a liquid CO_2 / C_6D_{12} mixture.

Sample	**Phase behavior (25°C)**	**Radius / Å ± 2Å**
Na-TC14 *w* = 0	P_{trans} = 160 bar	11
TPA-TC14 *w* = 0	translucent	13
TPA-TC14 *w* = 0 30 wt% C_6D_{12}	translucent	11
TPA-AOT4 *w* = 0	lump	-

An alternative approach to improving the solubility of surfactants in liquid CO_2 is by adding a cosolvent. Preliminary research has shown that loading compressed CO_2 into water-in-alkane (w/o) microemulsions results in enhanced phase stability [25]. This is a significant approach to improve solvent quality to stabilise microemulsions. More recently, mixed CO_2 – alkane solvent systems have been studied using commercial ionic surfactants. It was shown that AOT surfactant (insoluble in CO_2) aggregates in heptane – CO_2 mixtures above 30 wt% of heptane [18]. This suggests that mixed alkane - CO_2 solvents interact more favourably with the surfactant tails. For this work, d-cyclohexane (C_6D_{12}), which is fully miscible with CO_2 [16], was introduced as a cosolvent to enhance solubility of TPA-TC14. solvent mixture, shown in Figure 3. The data were then fitted to a model of Schultz polydisperse spheres and the radii were comparable to spherical droplets formed with However, prior to addition of 30 wt% of C_6D_{12}, the phase of TPA-TC14 remained translucent at 380 bar. Again HP-SANS was employed to examine the aggregate structures in this solvent mixture, as shown in Figure 3. The scattering data were fitted to a model of Schultz polydisperse spheres and the radii were comparable to spherical droplets formed with Na-TC14 in pure CO_2 [12,17]. Although pure TPA-AOT4 has poor solubility in CO_2, an attempt to introduce C_6D_{12} to enhance the solubility was not successful.

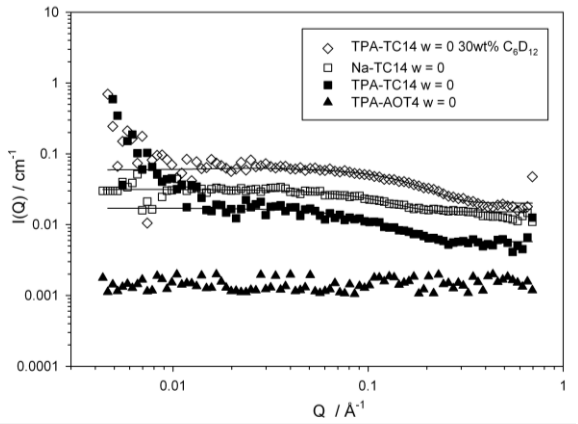


Figure 3. SANS profiles for TPA-surfactants in CO_2, [Surfactant] = 0.04 mol dm^{-3}, P = 380 bar and T = 25°C.

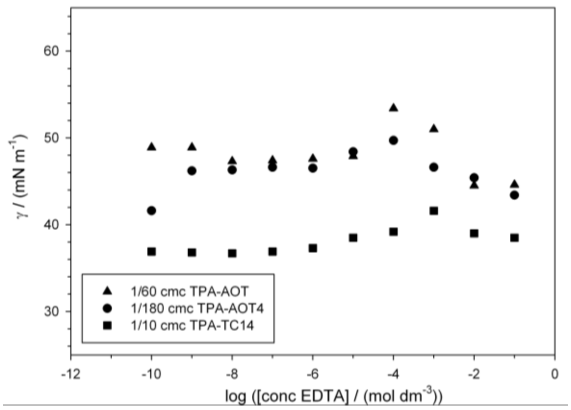


Figure 4. Effect of EDTA on surface tensions of TPA-surfactants.

Surface tension measurements

For the surfactants studied in this work, polyvalent (in particular divalent) cations are the most important cause of surface impurities. These are introduced to the surfactant during the sulfonation stage by impurities present in the raw materials. Studies have shown that M^{2+} concentrations as low as 10^{-4} mol dm^{-3} may be sufficient to affect the measured surface tension, particularly at low concentrations. This in turn effects the determination of A_{cmc} via the Gibbs isotherm. To alleviate this, these divalent ions can be sequestered by EDTA [26-27].

As the surfactant is the source of contamination, to ensure that correction is effective for the entire isotherm, a constant ratio of EDTA to surfactant is used. The amount of EDTA required to sequester any divalent cations present in the sample differs for Na-surfactants and TPA-surfactants due to variability in the purity of inorganic reagents. It is therefore important to determine the appropriate ratio to be used for each batch of surfactant prepared (Figure 4). Surface tension curves and values obtained from these data, including cmc's and limiting surface tensions, γ_{cmc}, are given in Figure 5 and Table 5. The main surfactants of interest are hydrophobic TPA compounds. The other Na-surfactant compounds were studied to provide comparison. The clean break and the absence of any dip in the surface tension around the cmc are consistent with pure surfactants. Experiments were performed using the appropriate level of EDTA of 10^{-4} mol dm^{-3} and 10^{-3} mol dm^{-3} for TPA-AOT, TPA-AOT4 and TPA-TC14.

The surface excesses which are plotted as a function of surfactant / cmc (reduced concentration) in Figure 6, can be used to compare the adsorption isotherm behaviour of surfactants. Table 5 give values for the adsorption parameter for A_{cmc} at cmc obtained from the plots in Figure 5, using the Gibbs isotherm. Comparisons of the cmc values between Na vs. TPA revealed an increase in the total hydrophobicity on counterion exchange of the surfactant. A similar trend was reported for ionic liquids [22]. Rosen and Kunjappu reported that the introduction of this hydrophobic counterion possessing three or more CH_2 groups interacts strongly with the hydrophobic component of the ionic micelles and consequently the cmc's shift to lower concentration depending on the counterion hydrophocity [28].

Limiting surface tension γ_{cmc} values are in a similar range (Table 5). It is believed that these values begin to approach the limit of reducing surface tension ability of a hydrocarbon surfactant with increase in surfactant efficiency on introducing terminal methyls on surfactant chains. The results clearly illustrate the minor influence of counterion on surfactant efficiencies. If viewed from molecular packing consideration, the TPA-surfactant occupies larger area at the interface, as one would expect, resulted from having larger head group. It should be noted that the introduction of a bulky counterion has little impact on the tail volume or the packing parameter. This may be due to alkyl chains on the counterion penetrating into the hydrophobic micellar core [22].

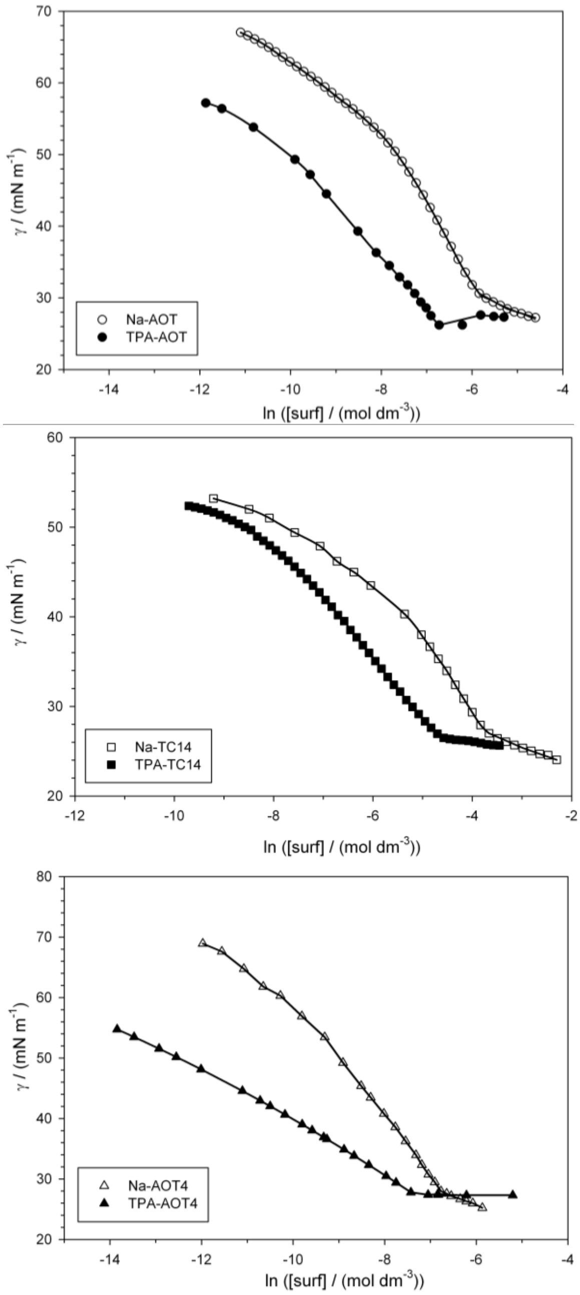


Figure 5. Air – water surface tension γ_{cmc} vs. ln (concentration) for TPA vs. Na-surfactants at 25°C. Quadratic lines are fitted to pre-cmc data, with linear fits to post-cmc.

Table 5. Parameters derived from surface tension measurements.

surfactant	**cmc / (mmol dm^{-3}) ± 0.03**	**γ_{cmc} / (mN m^{-1}) ±1**	**A_{cmc} / Å^2 ± 2**	**Packing parameter P_c**
Na-AOT	2.49	31.8	75	0.49
TPA-AOT	1.20	26.2	97	0.38
Na-AOT4	1.10	28.0	70	0.54
TPA-AOT4	0.86	27.4	104	0.36
Na-TC14	21.63	27.0	80	0.74
TPA-TC14	10.26	26.5	133	0.45

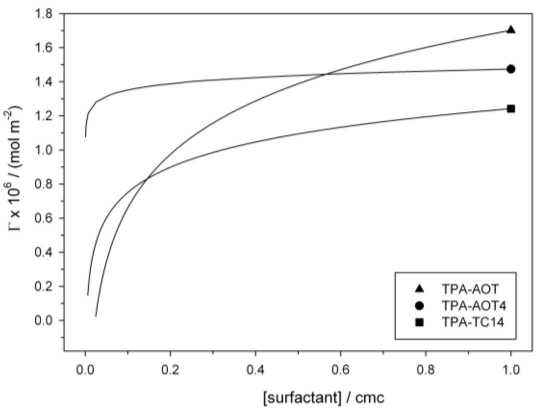


Figure. 6. Reduced adsorption isotherms for surfactants derived from data shown in Figure 5

Critical Packing Parameter

In general, molecular geometry plays an important role in the micellisation process. In these studies, changes in counterion have been shown to have quite dramatic effects on aggregation properties. For example, in water-in-oil (w/o) microemulsions, it has been shown that Na-AOT surfactants form spherical reversed micelles. Counterion exchange to tetrapropylammonium (TPA) produces lamellar sheet-like structure in water and rod-like micelles in cyclohexane. For the corresponding surfactants, cmc's and parameters derived from surface tension measurement also change remarkably. This observed change in aggregation can be accounted for in terms of counterion size, i.e. increasing electrostatic head-group repulsion and interfacial curvature [7].

Since all surfactants are generally used above their cmc's, surfactant aggregation structure may be a key to understanding the interfacial behaviour. The relationship between aggregation structure and surface tension was investigated by calculating the critical packing parameter of the surfactant [29]. The packing parameter P_c can be calculated by using

$$P_c = \frac{V}{tA_{cmc}} \qquad (1)$$

where V is the volume of hydrophobic tail, t is the surfactant chain length, and A_{cmc} is the effective headgroup area. Calculation and approximation of the surfactant chain volumes and length were performed by SPARTAN (Wavefunction Inc., Irvine, CA) molecular modelling. The molecules were created with all bonds in the *trans* configuration, with energy minimization calculations using a Merck molecular force field (MMFF). Table 5 lists the packing parameters of surfactants. The packing parameters of sodium type surfactants show a dramatic increase with increasing terminal methyls added to the surfactant chain. However, introduction of TPA counterions shows the opposite tendency, hence the inability to predict structural changes seen with Na- surfactant. This points at some limitations of the P_c model in regard to large bulky organic cations and specific anion – cation interactions at the micellar interface [22].

CONCLUSIONS

The results presented in this work demonstrate important insight into the behaviour of hydrophobic tetrapropylammonium (TPA) counterion hydrocarbon sulfosuccinate surfactants in three solvents media: CO_2, water, and cyclohexane. The introduction of TPA counterions to a sulfosuccinate surfactant generally induces a transition from spherical micellar structures to extended sheet-like micellar aggregates in water. Air/water (a/w) tensiometric studies suggest a weak dependence of surfactant effectiveness, on the presence of TPA counterions. This indicates that the interfacial properties are highly controlled by the nature of the surfactant anion. The area occupied by surfactant molecule at the cmc, A_{cmc}, significantly increases depending on how the TPA counterions partition at the micellar surface. However, the structural changes that take place upon inclusion of a TPA counterion are not possible to predict using the packing parameter model due to specific interactions between the surfactants and counterions at the micellar surface [22]. In an organic solvent, namely cyclohexane, the behaviour of custom-made TPA counterion surfactants TC14 and AOT4 are still reminiscent of the direct analogue commercial AOT surfactant in w/o microemulsions [6,7]. The addition of water can induce the transition of sphere-to-rod like micelles stabilised by the TPA-surfactants. This transition is driven by the inability of larger counterions such as TPA to approach the sulfonate headgroup as closely as a small ion like Na^+ [6,7]. However, there are still remaining challenges in extending the work from simple hydrocarbon oils to unusual solvents such as CO_2. Previously, the introduction of a third branch as well as terminal methyl groups on TC14 has been shown to enhance the solubility of hydrocarbon surfactants in CO_2 [12,17]. In addition, the quality of the CO_2 solvent is also improved by the introduction of an alkane cosolvent [16,18]. The addition of a cosolvent has a direct impact on the phase stability of hydrocarbon surfactants by lowering P_{trans}. Interestingly, the surfactant presented in this study, TPA-TC14, aggregates in CO_2. However, the solubility conditions remain extreme and a major limitation is its ability to disperse water. TPA-AOT and TPA-AOT4 do not dissolve in CO_2. It also appears that the introduction of a cosolvent has less effect on TPA-surfactant solubility in CO_2. Therefore, bulky counterions can not be considered to enhance CO_2-philicity.

ACKNOWLEDGMENT

The project was supported by JSPS [KAKENHI, Grant-in-Aid for Young Scientists (A), No. 23685034], KAKENHI, Grant-in-Aid for Scientific Research (B), No. 26289345, Fund for the Promotion of Joint International Research (Fostering Joint International Research) No. 15KK0221. The authors thank the Science and Technology Facilities Council for allocation of beam time, travel and consumables (experiment number RB1710004).

REFERENCES

[1] Brown, Paul *et al*. 2014. Anionic surfactants and surfactant ionic liquids with quaternary ammonium counterions. *Langmuir, 27*(8), p. 4563-4571.

[2] Cummings, Stephen *et a*l. 2012. Design principles for supercritical CO_2 viscosifiers. *Soft Matter, 8*(26), p. 7044-7055.

[3] Cummings, Stephen *et a*l. 2012. Amphiphiles for supercritical CO_2. *Biochimie, 94*(1), p. 94-100.

[4] Zhang, Shanshan *et al*. 2014. Micellization parameters of six Gemini quaternary ammonium surfactants from measurements of conductivity and surface tension. *Journal of Chemical and Engineering Data, 59*(9), p. 2891-2900.

[5] Ferrer-Tasies, Lidia *et al*. 2013. Quatsomes: vesicles formed by self-assembly of sterols and quaternary ammonium surfactants. Langmuir, 29(22), p. 6519-6528

[6] Eastoe, Julian *et al*. 1994. Effect of counterion radius on surfactant properties in Winsor II microemulsion systems. *Langmui, 10,* p. 1650-1653.

[7] Eastoe, Julian *et al*. 1993. Water-in-oil microemulsions formed by ammonium and tetrapropylammonium salts of Aerosol OT. *Langmuir, 9*(11), p. 2820-2824.

[8] Nave, Sandrine *et al.* 2000. What is so special about Aerosol-OT? 2. Microemulsion systems. *Langmuir, 16*(23), p. 8741-8748.

[9] Sagisaka, Masanobu *et al*. 2012. Effective and efficient surfactant for CO_2 having only short fluorocarbon chains. *Langmuir, 28*(30), p.10988-10996.

[10] Sagisaka, Masanobu *et al*. 2013. Nanostructures in water-in-CO_2 microemulsions stabilized by double-chain fluorocarbon solubilizers. *Langmuir, 29*(25), p. 7618-7628.

[11] Mohamed, Azmi *et al*. 2015. Economical and efficient hybrid surfactant with low fluorine content for the stabilisation of water-in-CO_2 microemulsions. *The Journal of Supercritical Fluids, 98,* p.127-136.

[12] Hollamby, Martin *et al.* 2009. Tri-chain hydrocarbon surfactants as designed micellar modifiers for supercritical CO_2. *Angewandte Chemie International Edition.* 2009, *121,* p. 4993-4995.

[13] Sagisaka, Masanobu *et al*. 2013. Highly methyl-branched hydrocarbon surfactant as a CO_2-philic solubilizer for water/supercritical CO_2 microemulsion. *Journal of Oleo Science, 62*(7), p. 481-488.

[14] Sagisaka, Masanobu *et al*. 2014. Hyper-branched hydrocarbon surfactants give fluorocarbon-like low surface energies. *Langmuir, 30*(21), p. 6057-6063.

[15] Trickett, Kieran *et al.* 2009. Rod-like micelles thicken CO_2. *Langmuir 26(1),* p. 83-88.

[16] Trickett, Kieran *et al*. 2009. Hydrocarbon metallosurfactants for CO2. *Langmuir* 26(7), p. 4732-4737.

[17] Mohamed, Azmi *et al*. 2010. Universal surfactant for water, oils, and CO_2. *Langmuir 26(17),* p. 13861-13866.

[18] Hollamby, Martin *et al*. 2009.Surfactant aggregation in CO_2/heptane solvent mixtures. *Langmuir* 2009, *25(22),* p. 12909-12913.

[19] Hatzopoulos, Marios *et al*. 2014. Effects of small ionic amphiphilic additives on reverse microemulsion morphology. *Journal of Colloid and Interface Science*, 421, p. 56-63.

[20] James, Craig, Eastoe, Julian. (2013). Ion specific effects with CO2-philic surfactants. *Current Opinion in Colloid & Interface Science*, 18(1), p. 40-46.

[21] Hayter, J. B.; Penfold, J. 1983. Determination of micelle structure and charge by neutron small-angle scattering. *Colloid and Polymer Science*, *261*, p. 1022-1030.

[22] Brown, Paul *et al*. 2011. Anionic surfactants and surfactant ionic liquids with quaternary ammonium counterions. *Langmuir*, *27,* p. 4563-4571.

[23] Cummings, Stephen *et a*l. 2010. CO_2: a wild solvent, tamed. P*hysical Chemistry Chemical Physics, 13(4),* p. 1276-1289.

[24] Eastoe, Julian *et al*. 1992. Variation of surfactant counterion and its effect on the structure and properties of Aerosol-OT-based water-in-oil microemulsions. *Journal of the Chemical Society, Faraday Transactions*, *88*, p. 461-471.

[25] Shen, Dong *et al*. 2005. Compressed CO_2 in AOT reverse micellar solution: effect on stability, percolation, and size. *Journal of Physical Chemistry B, 109*, p. 5796-5801.

[26] Kumar, Naveen; Tyagi, Rashmi. 2105. Synthesis and surface studies of anionic gemini surfactant in the different counter-ions. *International Journal of Industrial Chemistry, 691)*, p.59-66.

[27] Alexander, Shirin *et al*. 2014. Low surface energy surfactants with branched hydrocarbon architectures. *Langmuir*, 30(12), p. 3413–3421.

[28] Rosen, M.J. ; Kunjappu, J.T. 2012. *Surfactants and Interfacial Phenomena*. New Jersey: John Wiley & Sons

[29] Israelachvili, J. N.; Mitchell, D. J. 1975. A model for the packing of lipids in bilayer membranes *Biochimica et Biophysica Acta - Biomembranes. 389(1)*, p.13-19.