



Transport potential of super-hydrophobic organic contaminants in anionic-nonionic surfactant mixture micelles



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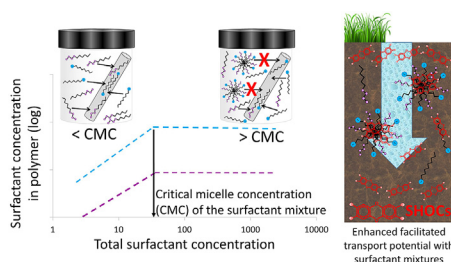
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HIGHLIGHTS

- Validation of polymer-water sorption isotherm approach for surfactant mixtures.
- Micelle composition an important determinant of extent of partitioning of SHOCs.
- K_{MI} data enable quantification of apparent aqueous solubility enhancement for SHOCs.
- Log K_{MI} -log K_{OW} relationship depends on type of SHOC and micelle composition.
- New insight into enhancement of SHOC transport potential by surfactant mixtures.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactant mixtures are commonly used in agricultural and soil remediation applications, necessitating an understanding of their micellization behavior and associated impact on the fate of co-existing chemicals in the subsurface. A polymer-water sorption isotherm approach was shown to present an alternative to traditional methods for quantifying, understanding and predicting surfactant mixture properties. Micelle compositions were measured for anionic-nonionic surfactant mixtures. This is important since micelle composition can alter the apparent aqueous solubility of super-hydrophobic organic contaminants (SHOCs) resulting in surfactant facilitated transport (SFT). A key parameter in predicting SFT for SHOCs is their micelle-water partition constant (K_{MI}). These were determined for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated biphenyls (PCBs) with representative anionic-nonionic surfactant mixtures using a polymer depletion method. These previously unreported constants were intermediate between those for pure anionic and nonionic surfactant solutions, with magnitude depending on micelle composition. Separate linear relationships were found between log K_{MI} and log K_{OW} for PCDDs and PCBs. This work provides new methods and preliminary results relating to binary surfactant mixtures (e.g. critical micelle concentration and micelle composition) and SHOCs (K_{MI}).

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that are important in the evaluation of the fate and transport of SHOCs in the subsurface environment and provide insight into the environmental mobility of these important contaminants.

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1. Introduction

Surfactants are an economically important and diverse group of chemicals ubiquitously present in the environment due to discharge and emissions from a wide range of industrial applications and a steadily growing worldwide production (“TechNavio. Global Surfactants Market, 2017–2021”, 2017). Amphiphilic surfactant monomers comprising hydrophilic (ionic or polar) and hydrophobic groups aggregate into three-dimensional structures known as micelles above the critical micelle concentration (CMC) (Rubingh, 1979). In aqueous systems these aggregates are configured with the hydrophilic groups oriented towards the outer surface, shielding a hydrophobic core that provides an attractive partition medium for hydrophobic contaminants (Jafvert et al., 1994). In this manner, an organic contaminant's apparent aqueous solubility can be increased in the presence of surfactant micelles and facilitated transport of organic contaminants in the subsurface environment can occur (Pennell et al., 2003; Paria, 2008; Grant et al., 2011). The more hydrophobic (and typically least mobile) contaminants have greater apparent aqueous solubility factor increases due to solubilisation by surfactant micelles, and therefore have the highest surfactant-facilitated transport (SFT) potential (Schacht et al., 2016). This contaminant group includes persistent, bioaccumulative and toxic super-hydrophobic organic contaminants (SHOCs; $\log K_{OW} > 6$) such as congeners of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated biphenyls (PCBs).

Surfactant mixtures are often employed to optimize performance in various applications, such as during pesticide application or in soil washing processes (Mahajan and Nandni, 2012), and if released into the environment, micelles comprised of different monomers can form. Unless the component surfactants are very similar in structure, such mixed micelles can exhibit different physico-chemical properties, such as critical micelle concentration (CMC) values, compared to those of single surfactants (Rubingh, 1979; Scamehorn, 1986; Holland and Rubingh, 1992). In addition, their CMC values do not necessarily reflect ideal mixing and thus cannot be described by a simple linear relationship based on their mole fractions (Bergström and Eriksson, 2000). In addition, higher cloud points have been reported for micelles formed in nonionic-anionic surfactant mixtures (Zhou and Zhu, 2004). Well-established techniques (e.g. surface tensiometry, fluorescence spectroscopy, NMR and electrical conductivity) can be used to quantify the CMC values of surfactant mixtures (Lu et al., 2012). However, more traditional methods such as tensiometry and conductivity cannot characterize the contribution and behavior of the individual surfactants of the mixture to micelles over a range of total surfactant concentration.

SHOC partitioning to surfactant micelles is governed by the physico-chemical properties of the surfactant (e.g. CMC, micelle size and composition), as well as those of the SHOC (e.g. hydrophobicity, size) (Jafvert et al., 1994). Decreased CMCs of anionic-nonionic surfactant mixtures in comparison to those of single surfactants increases their solubilisation capacity for organic contaminants. This is advantageous for remediation of contaminated soils where surfactant mixtures are commonly used (Mulligan et al., 2001; Zhu and Feng, 2003; Yuan et al., 2007). To date, a

limited number of studies have investigated enhanced apparent solubility in surfactant mixtures compared to individual surfactants but these focus on moderately hydrophobic polyaromatic hydrocarbons (PAHs), hexachlorobenzene and some pesticides (Yuan et al., 2007; Sales et al., 2011; Galán-Jiménez et al., 2015). SHOCs have received little attention despite being hazardous to the environment and human health and showing an increased SFT potential compared to less hydrophobic contaminants (Schacht et al., 2016).

Of particular concern is that experimental approaches to determine relevant physico-chemical properties of surfactant mixtures are limited. Hence, the potential impact of anionic-nonionic surfactant mixtures on contaminant partitioning due to changes in the micelle composition over ambient component surfactant concentration ranges has not been investigated. Further, previously performed partitioning experiments involving mixed micelles have only been undertaken at contaminants' maximum solubility in surfactant solutions possibly explaining experimental artifacts such as mixture effects, e.g. co-solubilisation for PAH mixtures (Liang et al., 2016). Partition constants of SHOCs to mixed surfactant micelles (K_{MI}) have not been quantified. Consequently, predicting their SFT potential and evaluating the associated risks of off-site transport and subsurface storage has not been possible.

Here, we employ a polymer-based technique previously primarily validated for single surfactant systems (Droge et al., 2007) to determine surfactant monomer-micelle equilibria and the CMC of binary anionic-nonionic surfactant mixtures with different bulk proportions. The essential feature of the technique is that only surfactant monomers sorb to the polyacrylate (PA) or polydimethylsiloxane (PDMS) coating of a SPME fiber, and not surfactant micelles. Below the CMC, monomers establish sorption equilibrium between water and polymer, characterized by an isotherm. Above the CMC, micelles formed are not sorbed, producing a discontinuity in the isotherm that can be used to distinguish the CMC. Quantifying the monomer concentrations of each co-surfactant in a mixture above the CMC informs on the mixed micelle phase composition. 4-(2-Dodecyl)benzene sulfonic acid (C_{12} -2-LAS) and tetraethylene glycol monododecyl ether ($C_{12}EO_4$) were employed as the anionic and nonionic surfactants respectively due to their common occurrence in such mixtures and use in previous investigations which facilitates comparisons where appropriate (Rico-Rico et al., 2009; Tripathi and Brown, 2008). SHOC partition constants to single and mixed surfactant micelles of known composition were then quantified employing a polymer depletion method (Schacht et al., 2016) and quantitative relationships between K_{OW} and mixed micelle-water partition constants (K_{MI}) developed.

2. Material and methods

2.1. Materials

The individual PCB standard solutions (Table 1) were first combined and subsequently diluted in toluene as was the PCDD standard mixture (Table 1), affording a solution containing 1 mg mL^{-1} and 0.7 mg mL^{-1} of each PCB and PCDD congener, respectively.

Glass fibers of 200 μm diameter coated with a 50 μm thickness

Table 1
Chemicals and their abbreviation, vendor specific information and concentrations used in this study.

Chemicals	Vendor/Product code	Concentrations
2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD OCDD	AccuStandard (New Haven, USA)/M-8280 A	5 mg mL ⁻¹ in toluene
1,2,3,4,6,7,8-HpCDF 3,3',4,5-Tetrachlorobiphenyl (PCB 78) 2,2',4,5',6-Pentachlorobiphenyl (PCB 103) 2,2',4,6,6'-Pentachlorobiphenyl (PCB 104) 2,2',3,3',6,6'-Hexachlorobiphenyl (PCB 136) 2,2',3,4,4',5,6'-Heptachlorobiphenyl (PCB 182) 2,2',3,3',5,5',6,6'-Octachlorobiphenyl (PCB 202) 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB 206) Decachlorobiphenyl (PCB 209) 2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	Cambridge Isotope Laboratories (Andover, USA)/EF-973 AccuStandard (New Haven, USA)/C-078S AccuStandard (New Haven, USA)/C-103S AccuStandard (New Haven, USA)/C-104S AccuStandard (New Haven, USA)/C-136S AccuStandard (New Haven, USA)/C-182S AccuStandard (New Haven, USA)/C-202S AccuStandard (New Haven, USA)/C-206S AccuStandard (New Haven, USA)/C-209S AccuStandard (New Haven, USA)/C-118 N	50 mg L ⁻¹ in toluene Quantification Standard 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 35 mg L ⁻¹ in isooctane 5 mg, dissolved in toluene achieving 2 mg L ⁻¹ Quantification Standard
4-(2-dodecyl)benzene sulfonic acid (C ₁₂ -2-LAS) tetraethylene glycol monododecyl ether (C ₁₂ EO ₄) Sodium azide Ammonium acetate Ultrapure water	synthesized as the sodium salt by Zhu et al. (1998) Sigma Aldrich (Sydney, Australia) Sigma-Aldrich (Sydney, Australia) Sigma-Aldrich (Sydney, Australia) (Merck Millipore, Kilsyth, Australia)	Solid, ≥97% purity Liquid, ≥98% purity

of PDMS (Fiberguide Industries Inc, Stirling, USA) were cut to 1.0, 2.0 or 4.0 cm lengths (affording volumes of 0.39, 0.78 or 1.56 μL PDMS, respectively), washed in MilliQ water and dried. Fibers were subsequently extracted in hexane for 24 h on an orbital shaker to remove PDMS oligomers, weighed using a Mettler microbalance, and stored in methanol. The percentage relative standard deviation (%RSD) between fiber masses of a given length within each experiment was <2%.

Glass fibers of 111 μm diameter coated with a 9 μm thickness of PA (Polymicro Industries, Phoenix, AZ) were cut to 4.0 cm lengths (affording 0.13 μL PA), conditioned at 120 °C for 16 h under a nitrogen flow following the method reported by Rico-Rico et al. (2009) and subsequently stored in MilliQ water until further use.

2.2. CMC determination of individual anionic and nonionic surfactants and their binary mixtures using polymer-water sorption isotherms

Both C₁₂EO₄ and C₁₂-2-LAS monomers partition (in measurable quantities) to PA; however, only C₁₂EO₄ and not C₁₂-2-LAS partitions to PDMS (Supporting Information (SI) – Section S1, Table S1). The equilibrium distributions of C₁₂EO₄ and C₁₂-2-LAS between PA fibers and water, and of C₁₂EO₄ between PDMS fibers and water, were measured both as solutions of individual surfactants and their binary mixtures over a range of surfactant concentrations (from below to above the expected CMC) (Rico-Rico et al., 2009; Haftka et al., 2016). Employing the two different polymers allowed an assessment of potential mixture effects such as competitive sorption to SPME fibers on the derivation of the CMC of C₁₂EO₄.

Stock solutions of individual surfactants (C₁₂EO₄ and C₁₂-2-LAS; 690 and 1,435 μM , respectively) were diluted to give a series of 8 concentrations (7–690 μM for C₁₂EO₄ and 7 to 1,435 μM for C₁₂-2-LAS). Mixtures of C₁₂EO₄: C₁₂-2-LAS with molar ratios of 14:86, 31:69, 49:51, 66:34 and 81:19 (at a total surfactant concentration of approximately 2,800 μM) were prepared. Their composition ranged from mixtures predominantly comprising nonionic to those containing largely anionic surfactant. These mixtures were then diluted to provide in total 13 different solutions for each of these five surfactant mixture ratios (SI – Table S2).

Due to the known dependency of the polymer-water distribution of ionic surfactant monomers on pH and ionic strength of the medium, buffered (pH 7) MilliQ water solutions containing 5 mM

potassium phosphate were prepared. Sodium azide was added to all solutions (25 mg L⁻¹) to prevent biodegradation of the surfactants.

Clean 4 cm fibers (1.56 μL PDMS or 0.13 μL PA) were introduced to 24 mL glass vials containing surfactant solutions with minimal headspace, and left for a minimum of 6 days to ensure equilibrium was attained (SI – Section S2, Figs. S1, S2, S3). At equilibrium, the fiber was removed and surfactant monomers partitioned to the polymer were extracted and quantified along with an aliquot of the aqueous solution (further details SI – Section S3). The selected water: polymer volume ratios in both test systems i.e. PA and PDMS, were adjusted (typically >15,000:1) to achieve measurable surfactant concentrations in the polymers while adhering to published aqueous phase depletion criteria to ensure reliable results (Mayer et al., 2000). Thus at equilibrium, the ratios of total surfactant (monomers plus micelles) for C₁₂EO₄: C₁₂-2-LAS mixtures in the aqueous phase were almost identical to that in the original mixtures as defined above.

2.3. CMC determination of individual surfactants and their binary mixtures using tensiometry

CMC values for individual surfactants and their binary mixtures were also measured from tensiometry using the surface tension change from the Wilhelmy plate (Pt plate) technique at the University of Queensland (Nguyen and Nguyen, 2014). To avoid contamination due to surfactant adsorption, the plate surface was cleaned with a MilliQ water-ethanol wash followed by burning under an alcohol flame before each measurement. All experiments were carried out at constant temperature (25 ± 1 °C). A motor speed of 0.1 mm/s and an immersion depth of the plate of 5 mm were maintained throughout the measurements.

2.4. SHOC partitioning to individual surfactants and their binary mixtures

A recently reported mass balance-based polymer-depletion method (Schacht et al., 2016) was employed to quantify micelle-water partition constants (K_{M}) of SHOCs for C₁₂EO₄ and C₁₂-2-LAS, both with individual surfactants and in binary mixtures. In brief, SHOCs were loaded to 1 or 2 cm donor PDMS fibers (0.39 or 0.79 μL PDMS, respectively) at predefined concentrations using a

polymer swelling loading approach (loading solution concentration was 0.7 mg L^{-1} or 1 mg L^{-1} for each PCDD or PCB respectively, ensuring loading below the contaminant's PDMS solubility) (Grant et al., 2016). Loaded donor fibers were transferred into $360 \mu\text{L}$ inserts filled to maximum volume with surfactant solution. Surfactant solutions were prepared as described in Section 2.2 but at different total concentrations (SI – Table S3). To determine K_{MI} for SHOCs at different aqueous surfactant concentrations, surfactant solutions were prepared for individual surfactants and binary mixtures with bulk solution stoichiometric molar ratios of 81:19 and 31:69 at concentrations exceeding their CMC (SI – Table S3). Five replicates for each surfactant concentration were employed (further details SI – Section S4).

As the cloud point for $\text{C}_{12}\text{-2-LAS}$ is below room temperature, the partition constant represents SHOC partitioning to the surfactant precipitate rather than micelles in $\text{C}_{12}\text{-2-LAS}$ solutions. In mixtures with C_{12}EO_4 , the cloud point of the mixture is higher than that for $\text{C}_{12}\text{-2-LAS}$ alone and no precipitate was observed.

2.5. Chemical analysis

2.5.1. Liquid chromatography-tandem mass spectrometry (LC-MS/MS)

Partitioning of surfactant monomers to PDMS and PA to determine relevant isotherms and CMC data was carried out at Utrecht University and The University of Queensland, respectively. Resultant solutions from fiber extraction and aliquots from the water phase (SI – Section S3) were analyzed by LC-MS/MS (further details SI – Section S5).

2.5.2. Gas chromatography-high resolution mass spectrometry (GC-HRMS)

SHOC extracts from PDMS were gently evaporated under a N_2 stream to near dryness, reconstituted in toluene containing quantification standards (1,2,3,4,7,8,9-HpCDF and PCB-118) and analysed by GC-HRMS (using a method based on EPA Method 1613) as described previously (Schacht et al., 2016) in order to determine K_{MI} . PCDD and PCB quantification in these extracts was performed relative to their respective quantification standards, using an 8-point calibration series (further details SI – Section S6).

3. Results and discussion

3.1. Polymer-water sorption isotherms of binary surfactant mixtures

Sorption isotherms for C_{12}EO_4 and $\text{C}_{12}\text{-2-LAS}$ monomers with the polymer PA, derived from separate solutions of individual surfactants or for the first time as co-surfactants in binary mixtures, are shown in Fig. 1A and B. Plotted on a log-log basis, the isotherms display a similar pattern for both surfactants. Generally, a linear or near linear relationship is observed with increasing surfactant concentration until a slope discontinuity occurs, beyond which the sorbed monomer concentration becomes relatively constant or decreases with further increases in the aqueous surfactant concentration. Similar isotherms have previously been reported by Droge et al. (2007) and Rico-Rico et al. (2009) for individual surfactant solutions, including those of interest in the current work.

From Fig. 1, the nonlinearity constant (N) in fitted Freundlich isotherms was >0.96 for C_{12}EO_4 as single components or as co-surfactants in binary mixtures. Therefore, C_{12}EO_4 can be considered to partition to PA, and from the mean intercepts of the isotherms before the discontinuity, the PA-water partition constant (expressed as $\log K_{\text{PA-W}}$) is 3.46. This value is consistent with a previously reported $\log K_{\text{PA-W}}$ value of 3.32 derived when

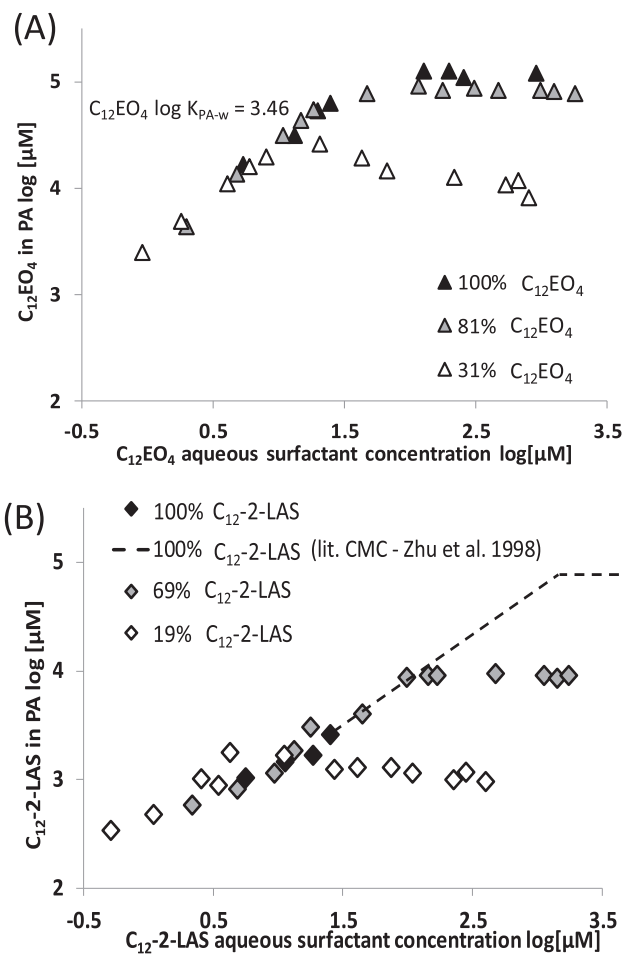


Fig. 1. Surfactant monomer sorption isotherms to PA for (A) C_{12}EO_4 and (B) $\text{C}_{12}\text{-2-LAS}$ both as individual surfactants and as co-surfactants in binary mixtures. All axes shown are on a log scale.

employing a thicker PA fiber coating compared to that in the current study (Haftka et al., 2016). In contrast, $\text{C}_{12}\text{-2-LAS}$ isotherms showed a reduced linearity (mean N in fitted Freundlich isotherms of 0.83). Fitted Freundlich isotherms for $\text{C}_{12}\text{-2-LAS}$ by itself and the mixture comprising 69% $\text{C}_{12}\text{-2-LAS}$ were very similar and afforded a Freundlich Constant (expressed as $\log K_f$) of 2.5. A slightly different slope and hence intercept for the mixture with 19% $\text{C}_{12}\text{-2-LAS}$ afforded a $\log K_f$ of 2.7 (white diamonds, Fig. 1B) possibly due to a higher experimental variability at low $\text{C}_{12}\text{-2-LAS}$ concentrations.

The partitioning of C_{12}EO_4 in binary mixtures with $\text{C}_{12}\text{-2-LAS}$ to a second type of polymer, PDMS, was investigated to ensure that the observed monomer partitioning behavior was independent of polymer type (SI – Section S7, Fig. S4).

Regardless of the employed polymer and the bulk surfactant mixture composition the sorption isotherms for both surfactants in the binary mixtures follow a similar relationship to the respective isotherms for the individual surfactants (i.e. isotherms below the slope discontinuity overlay each other as shown in Fig. 1A and SI – Fig. S4). These results are consistent with available relevant data and suggest no competitive sorption interaction between surfactants occurs permitting further investigation of surfactant mixture properties influencing SHOC partitioning behavior such as the mixture CMC.

3.2. Critical micelle concentrations of binary surfactant mixtures derived from polymer-water sorption isotherms

CMC values of individual surfactants have been determined from polymer-water sorption isotherms at the discontinuity of the isotherm due to micelles not partitioning to the polymer (Droge et al., 2007). The CMCs of the individual surfactant solutions are derived from the intersection of regression lines for sorbed concentrations above and below the discontinuity. Thus, the CMC for $C_{12}EO_4$ derived with $9\ \mu\text{m}$ PA-coated fibers is $48\ \mu\text{M}$. This is consistent with the CMC value quantified with $35\ \mu\text{m}$ PA-coated fibers employing a similar experimental setup (Haftka et al., 2016). The C_{12} -2-LAS CMC of $1260\ \mu\text{M}$ as displayed in Fig. 1B was taken from Zhu et al. (1998) due to the cloud point being reached before the CMC at the temperature ($25 \pm 1\ ^\circ\text{C}$) defined for the experiments.

For the surfactant mixtures, the situation is more complex since a discontinuity in the sorption isotherms is observed for both co-surfactants but at different individual co-surfactant concentrations due to the differing proportions of each in the mixture. Therefore, the CMC of the mixture (CMC_{Mix}) was defined as the minimum total surfactant concentration where the co-surfactants begin to exhibit a deviation from the initial linear or near linear sorption isotherms. For binary mixtures of surfactants, the discontinuities represent the contributions of each surfactant to CMC_{Mix} . To illustrate the effect of bulk solution composition on CMC values and micelle composition (Section 3.3) we focus on a predominantly nonionic (81:19 $C_{12}EO_4$: C_{12} -2-LAS) and a largely anionic (31:69 $C_{12}EO_4$: C_{12} -2-LAS) surfactant mixture. Discontinuities were observed for the former mixture at a total surfactant concentration of $41\ \mu\text{M}$ (Fig. 2A) that also represents the CMC_{Mix} . The individual surfactant concentrations contributing to CMC_{Mix} are in proportion to the bulk solution stoichiometric mole fractions (i.e. $33\ \mu\text{M}$ for $C_{12}EO_4$ and $8\ \mu\text{M}$ for C_{12} -2-LAS). Alternatively, these individual concentrations may be derived from the sorbed concentrations in Fig. 2 and sorption isotherms determined above in Fig. 1. Similarly, for the latter mixture comprising predominantly anionic surfactant, CMC_{Mix} is $42\ \mu\text{M}$ with contributions of $13\ \mu\text{M}$ for $C_{12}EO_4$ and $29\ \mu\text{M}$ for C_{12} -2-LAS.

The sorption data derived CMC_{Mix} values were validated with CMCs derived from the surface tension change measurements using the traditional Wilhelmy plate (Pt plate) (Fig. 2). The comparison for both techniques showed good agreement (Paired t -test; Two tailed P value = 0.3275; Difference not significant at $P = 0.05$).

Regardless of surfactant proportions in mixtures, measured CMC_{Mix} values are less than those predicted on the basis of ideal mixing according to Equation (1) (Rubingh, 1979; Rosen and Kunjappu, 2012).

$$\frac{1}{\text{CMC}_{\text{Mix}}} = \frac{\alpha}{\text{CMC}_{C_{12}EO_4}} + \frac{(1-\alpha)}{\text{CMC}_{C_{12}-2-LAS}} \quad (1)$$

Here, α represents the bulk solution stoichiometric mole fraction of $C_{12}EO_4$ in the surfactant mixture. With the 81:19 and 31:69 $C_{12}EO_4$: C_{12} -2-LAS mixtures for example, measured CMC_{Mix} values are $41\ \mu\text{M}$ and $42\ \mu\text{M}$ respectively and may be compared with those based on ideal mixing (Equation (1)) of $60\ \mu\text{M}$ and $140\ \mu\text{M}$.

This discrepancy indicates a negative deviation from ideal mixing behavior, previously described for other anionic-nonionic surfactant mixtures (Rubingh, 1979; Bergström and Eriksson, 2000). To account for non-ideal behavior, Rubingh (1979) developed a Regular Solution Theory approach to predicting properties of mixed surfactant solutions relevant for SHOC partitioning such as CMC. It results in relationships (Equation (2)) between CMC_{Mix} and micelle composition at total surfactant concentrations just

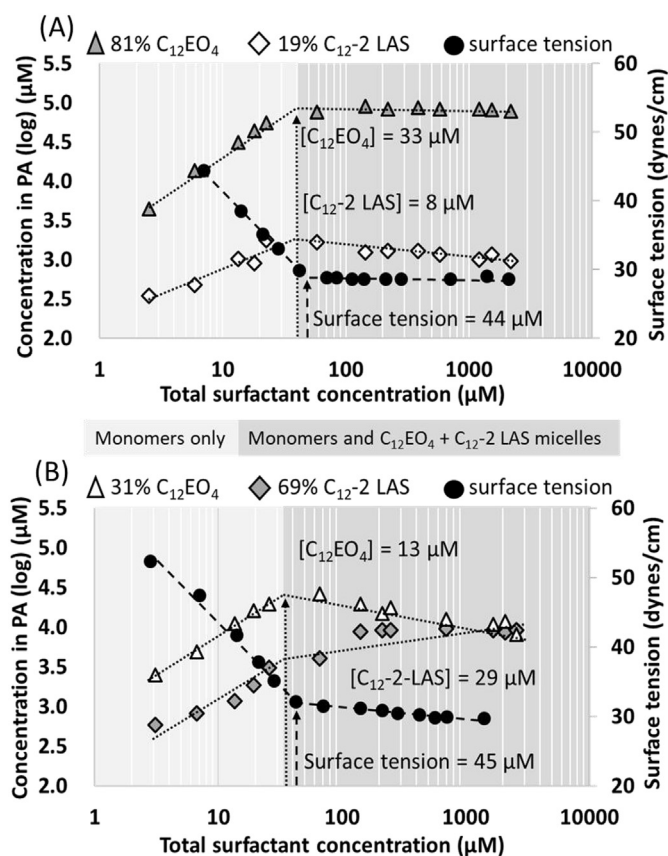


Fig. 2. CMC_{Mix} derived from sorption of $C_{12}EO_4$: C_{12} -2-LAS surfactant mixtures to PA compared to surface tension of the solution as a function of total surfactant concentration for the 81:19 (A) or the 31:69 (B) $C_{12}EO_4$: C_{12} -2-LAS mixture. Dotted lines are displayed for visualization purposes of the relationship between sorbed and aqueous monomer concentrations.

above CMC_{Mix} (further details SI – Section S8) (Treiner, 1994; Rosen and Kunjappu, 2012).

$$\frac{x^2 \cdot \ln\left(\frac{\text{CMC}_{\text{Mix}} \cdot \alpha}{\text{CMC}_{C_{12}EO_4} \cdot x}\right)}{(1-x)^2 \cdot \ln\left(\frac{\text{CMC}_{\text{Mix}} \cdot (1-\alpha)}{\text{CMC}_{C_{12}-2-LAS} \cdot (1-x)}\right)} = 1 \quad (2)$$

In these expression x represents the mole fraction of $C_{12}EO_4$ in mixed micelles at total surfactant concentrations just above CMC_{Mix} and α is defined as for Equation (1). For the 81:19 mixture (i.e. $\alpha = 0.81$), since CMC_{Mix} is $41\ \mu\text{M}$, solving Equation (2) iteratively affords $x = 0.805$ meaning the nonionic surfactant proportion in the micelle at concentrations just above CMC_{Mix} is 81% (and therefore the anionic surfactant proportion is 19%). The micelle composition at concentrations just above CMC_{Mix} is almost identical to the stoichiometric mole fraction of the bulk solution.

In contrast, for the 31:69 mixture at total surfactant concentrations just above CMC_{Mix} ($42\ \mu\text{M}$), the micelle composition is 64:36 $C_{12}EO_4$: C_{12} -2-LAS. More of the nonionic surfactant is in micelles formed just above CMC_{Mix} compared to the bulk solution stoichiometric mole fraction for this mixture. The CMC_{Mix} value is related to the Gibbs energy of micellization and includes packing, steric and electrostatic contributions (Rosen and Kunjappu, 2012). Gibbs energy is minimized and micelle formation facilitated due to the nonionic surfactant reducing coulombic repulsion between charged C_{12} -2-LAS headgroups (Grillo and Penfold, 2011; Dong et al., 2012). It has been established that for mixtures of nonionic

and ionic surfactants, the composition of the micelles first formed above CMC_{MIX} will be richer in the nonionic surfactant than the bulk solution unless there is a high proportion of the nonionic surfactant in the bulk solution itself (Treiner, 1994; Shiloach and Blankschtein, 1998; Lu et al., 2012).

Overall, these results suggest polymer-water sorption isotherms present an alternative to traditional methods for the investigation of mixed surfactant solutions and their properties. Moreover, this is the first validated application for mixtures of different surfactant types where mixed micelles are expected to form.

3.3. Variation of micellar composition with total surfactant concentration of binary surfactant mixtures

As observed in this study and others (e.g. Treiner (1994)), the mixed micelle composition may differ from the stoichiometric solution composition evidently affecting SHOC partition behavior. As micelles are in equilibrium with monomers, polymer sorption behavior and resultant measured co-surfactant monomer concentrations above CMC_{MIX} can facilitate the understanding of mixed micelle behavior over a range of total surfactant concentrations. Micelle concentrations and composition can be determined from experimental sorption data using a simple mass balance approach.

$$M_O = M_S + M_W + M_{MI} \quad (3)$$

where M_O is the total amount (moles) of a surfactant in solution, M_S and M_W are the amounts in monomeric form sorbed to polymer (PA) and in solution, respectively, and M_{MI} the amount in micellar form. The total amount of a surfactant in any dilution of a given stoichiometric composition is known (SI – Table S2), as are sorbed concentrations (Figs. 1 and 2). The sorption isotherms identified above relate sorbed monomer concentrations to monomer concentrations in solution at equilibrium. With the known volumes of both PA and solution, the amount of each surfactant of the binary mixture in the form of monomers and therefore, by difference, micelles can be determined. Applied to each component of the surfactant mixture, micelle composition can be determined (SI – Tables 4-1, S4-2, S5-1, S5-2). The relatively small polymer volume means that while there is sufficient surfactant sorbed for quantitation purposes, this amount is negligible compared to the total surfactant amount in the system and therefore only minimally affects the amounts of surfactant present in micellar and monomeric forms.

The sorption-derived micelle compositions above CMC_{MIX} derived from this mass balance approach can be compared to the Regular Solution Theory estimations from

$$x_1 = \frac{-(C - \Delta) + \sqrt{(C - \Delta)^2 + 4\alpha C\Delta}}{2\Delta} \quad (4)$$

where x_1 is the mole fraction of surfactant 1 in micelles, C the total surfactant concentration, α the bulk solution stoichiometric mole fraction as previously defined and $\Delta = \gamma_1 CMC_1 - \gamma_2 CMC_2$ which is the difference in the product of activity coefficients (γ) and CMC values of surfactants 1 and 2. The derivation of Equation (4) and expressions for the requisite activity coefficients can be found in numerous texts (e.g. Penfold et al. (1995); Lu et al. (2012)) and are summarized in SI - Section S8. While this approach has been criticized on theoretical thermodynamic grounds (Letellier et al., 2009; Letellier and Turmine, 2015) it remains a useful means of understanding and predicting surfactant mixture behavior (Lu et al., 2012; Liley et al., 2017).

Fig. 3 shows micelle composition experimentally determined

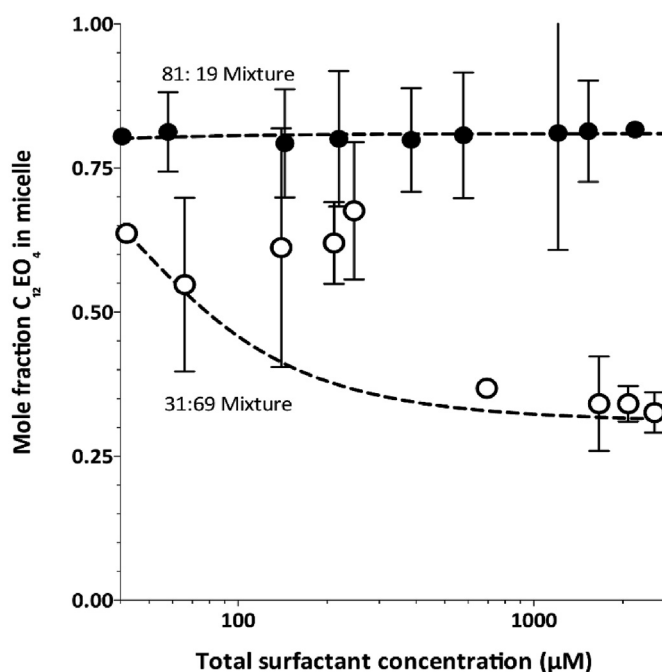


Fig. 3. $C_{12}EO_4$ mole fraction in micelles experimentally determined from polymer sorption in the 81:19 (●) and 31:69 (○) mixtures compared with compositions predicted from Equation (4) (solid lines) as a function of total surfactant concentration above CMC_{MIX} . The mole fraction of $C_{12}EO_4$ at total surfactant concentrations just above CMC_{MIX} from Equation (2) is also shown (far left data point).

from sorption data compared with those predicted from Equation (4). The agreement is excellent for the 81:19 mixture ($S_{y,x} = 0.007759$) and satisfactory for the 31:69 mixture ($S_{y,x} = 0.1483$) though three measured data points in the latter plot show a larger $C_{12}EO_4$ proportion in micelles than expected. This is due to underestimated proportions of C_{12} -2-LAS as a result of increased uncertainty associated with quantification of the relatively small amounts of this surfactant for some dilutions of this particular mixture.

The micelle composition at total surfactant concentrations just above CMC_{MIX} is governed by thermodynamic considerations with the presence of the nonionic surfactant reducing coulombic repulsion between the heads of the anionic surfactant. However, as more surfactant mixture is added, the composition it is increasingly determined by the stoichiometric ratio and ultimately approaches this ratio (Treiner, 1994; Yordanova et al., 2017). Thus, there is little change in micelle composition with total surfactant concentration for the 81:19 mixture, relatively rich in the nonionic surfactant. In contrast, micelles of the 31:69 mixture initially contain greater than 50% $C_{12}EO_4$ (SI – Tables S4–1) because of an increased proportion of the anionic surfactant in the bulk solution. With increasing total surfactant concentration though, micelle composition approaches 31:69 (Fig. 3).

The polymer sorption technique enables a detailed investigation of surfactant mixtures providing both quantitative information on monomer and micelle concentrations and compositions at total surfactant concentrations above CMC_{MIX} as well as CMC_{MIX} data for binary mixtures of anionic (C_{12} -2-LAS) and nonionic ($C_{12}EO_4$) surfactants. Few other physical techniques can achieve this, apart from NMR and small angle neutron scattering for example (Lu et al., 2012; Penfold et al., 1995). CMC_{MIX} data were validated by tensiometry and micelle composition trends are consistent with those predicted from Regular Solution Theory. Results show micelle composition depends on the bulk solution stoichiometric ratio and

the total surfactant concentration. Micelle sizes, shapes and aggregation levels have also been shown to change with micelle composition however this sorption approach cannot distinguish these. Micelle composition is nonetheless an important determinant of the extent of partitioning of SHOCs.

3.4. SHOC partitioning to surfactant mixed micelles

Commercial mixtures involving these and similar anionic and nonionic surfactants are expected to exhibit non-ideal mixing behavior as shown here. This, together with changes in the micelle composition with mixture proportions and total surfactant concentrations described above, suggests enhanced solubilization capacity and greater SFT potential for SHOCs in comparison to that of some single surfactant micelles.

SHOC (PCB and PCDD) micelle-water partition constants (K_{MI}) in solutions of the individual surfactants and for the first time in binary mixtures (81:19 and 31:69 $C_{12}EO_4$: C_{12} -2-LAS) were quantified with a polymer (PDMS) depletion technique (Schacht et al., 2016) and are summarized in Table 2. The total surfactant concentrations (>200 μ M) ensured mixture compositions were largely in the plateau regions of Fig. 2 and effectively constant. The SHOC partition constants were consequently found to have little variation with total surfactant concentration, in both the individual surfactant solutions as well as their binary mixtures. Log K_{MI} data for C_{12} -2-LAS solutions were lower than those measured in $C_{12}EO_4$ solutions for both PCDDs and PCBs. Furthermore, they showed generally a higher variability (up to 0.9 log units difference across the given concentrations) (Table 2). For the binary mixtures, log K_{MI} in the nonionic surfactant rich $C_{12}EO_4$: C_{12} -2-LAS (81: 19) mixture showed slightly higher values compared to the anionic surfactant rich $C_{12}EO_4$: C_{12} -2-LAS (31: 69) mixture reflecting the different micelle compositions identified earlier (Table 2, Fig. 4).

With an increasing $C_{12}EO_4$ proportion in the surfactant mixture and micelles, the partition constants generally increased but remained intermediate between the values determined with individual solutions of $C_{12}EO_4$ and C_{12} -2-LAS (Fig. 4). Similar observations, i.e. apparent contaminant solubility in a surfactant mixture being higher than its solubility in at least one of the component surfactants (often C_{12} -2-LAS), have been reported previously for PAHs (Yuan et al., 2007) and for pesticides (Galán-Jiménez et al., 2015). Such synergistic solubilization has also been observed in

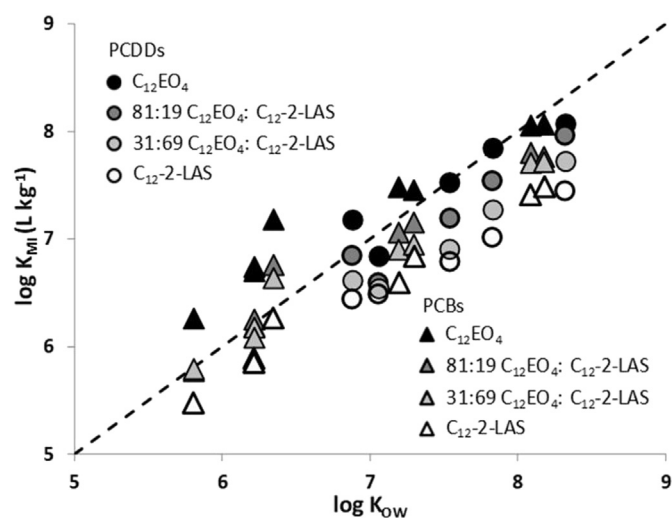


Fig. 4. Log K_{MI} for PCDDs and PCBs in single surfactant solution ($C_{12}EO_4$ or C_{12} -2-LAS) and binary mixtures as a function of contaminant log K_{OW} . The dotted line represents the 1:1 relationship line.

other anionic-nonionic surfactant systems (Zhu and Feng, 2003; Shi et al., 2015). However, the synergisms occurred only at high fractions ($\geq 90\%$) of the surfactant with the higher solubilization capacity.

SHOC micelle partitioning data enable quantification of apparent aqueous solubility enhancement. The factor increase of this can be assumed to be largely due to the product of total micelle concentration and K_{MI} (Kile and Chiou, 1989). On this basis, the increase for OCDD for a given total micelle concentration with the 81:19 and 31:69 mixtures would be 3.3 and 1.9 times respectively than that with C_{12} -2-LAS alone. This increased apparent aqueous solubility enhancement in the surfactant mixtures compared to C_{12} -2-LAS illustrates the importance of the mixture and micelle composition for predicting SFT and the evaluation for associated risks of off-site transport and subsurface storage of SHOCs.

Separate linear relationships exist between measured log K_{MI} of SHOCs and their log K_{OW} values (Fig. 4) for PCBs and PCDDs for a given surfactant or surfactant mixture composition. Slope

Table 2

Mean measured micelle-water partition constants (log K_{MI}) for PCDDs and PCBs in individual $C_{12}EO_4$ or C_{12} -2-LAS solutions and two binary $C_{12}EO_4$: C_{12} -2-LAS mixtures together with literature data for log K_{OW} and log K_{PDMSw} . %RSD was derived from unlogged K_{MI} data.

	log K_{MI} ($L\ kg^{-1}$)								log K_{OW}	log K_{PDMSw}
	$C_{12}EO_4$	% RSD	$C_{12}EO_4$: C_{12} -2-LAS 81:19	% RSD	$C_{12}EO_4$: C_{12} -2-LAS 31:69	% RSD	C_{12} -2-LAS	% RSD		
2,3,7,8-TCDD	7.18	2%	6.85	6%	6.63	7%	6.45	12%	6.88 ^a	6.00 ^c
1,2,3/7,8-PnCDD	6.84	4%	6.59	9%	6.55	13%	6.50	16%	7.06 ^a	6.14 ^c
1,2,3,4,7,8-HxCDD	7.52	4%	7.20	6%	6.92	8%	6.80	17%	7.54 ^a	6.45 ^c
1,2,3,4,6,7,8-HpCDD	7.84	3%	7.55	7%	7.28	12%	7.02	16%	7.83 ^a	6.69 ^c
OCDD	8.07	5%	7.97	8%	7.73	8%	7.45	22%	8.32 ^a	7.11 ^c
PCB 104	6.29	13%	5.78	10%	5.80	10%	5.48	19%	5.81 ^b	5.49 ^d
PCB 103	6.69	9%	6.19	12%	6.19	6%	5.89	23%	6.22 ^b	5.88 ^d
PCB 136	6.73	8%	6.25	7%	6.10	7%	5.86	24%	6.22 ^b	5.88 ^d
PCB 78	7.17	17%	6.76	13%	6.65	11%	6.27	9%	6.35 ^b	6.00 ^d
PCB 182	7.47	6%	7.06	8%	6.91	12%	6.60	19%	7.20 ^b	6.63 ^c
PCB 204	7.44	9%	7.15	4%	6.96	8%	6.84	23%	7.30 ^b	6.74 ^c
PCB 206	8.04	5%	7.80	9%	7.72	6%	7.42	18%	8.09 ^b	7.37 ^c
PCB 209	8.06	7%	7.77	5%	7.72	10%	7.49	19%	8.18 ^b	7.53 ^c

^a Data from Åberg et al. (2008) for all PCDDs except PnCDD. Log K_{OW} for 1,2,3,7,8-PnCDD is the average of all data reported by Mackay et al. (1992).

^b Hawker and Connell (1988).

^c Grant et al. (2016), determined with the same PDMS fibers as used in this study.

^d Smedes et al. (2009).

estimates for the various surfactant or surfactant mixture compositions ranged from 0.67 to 0.79 with $r^2 > 0.91$ and $S_{y,x} < 0.1852$. The relationships for single surfactant solutions are consistent with previous observations for SHOCs (Schacht et al., 2016) (SI – Section S9, Fig. S5), however those for the surfactant mixtures are presented for the first time. The tendency for SHOCs to partitioning into micelles increases with their increasing hydrophobicity (Zhou and Zhu, 2005). The evidence from this work though suggests that the relationship of $\log K_{MI}$ with $\log K_{OW}$ from one contaminant group e.g. PCDDs for a particular surfactant or surfactant mixture cannot be used to estimate K_{MI} data for other SHOC groups e.g. PCBs with sufficient accuracy.

Moreover, while the linear nature of the correlations with $\log K_{OW}$ suggests that prediction of K_{MI} values for contaminants with mixed surfactants is possible, a training data set is necessary since the relationship is specific to a particular SHOC group, the components of the surfactant binary mixture and their proportion in micelles.

Parameters relating to binary surfactant mixtures (e.g. CMC_{Mix} , total surfactant concentration and stoichiometric ratio) and SHOCs (K_{MI}) are important in the evaluation of the fate and transport of SHOCs in the subsurface environment. This work provides new methods and preliminary results to facilitate this. Due to diverse surfactant applications and release in urban, agricultural and industrial settings, understanding the effects of surfactant mixtures and contaminant properties on SFT inform not only surfactant-based remediation but provide insight into the potential and often unexpected environmental mobility of hydrophobic contaminants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.05.021>.

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