A novel method to quantify the amount of surfactant at the oil/water interface and to determine total interfacial area of emulsions

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Abstract

We present a methodology to quantitatively determine the fraction of sodium dodecyl sulfate (SDS) that partitions to the oil/water interface in oil-in-water macroemulsions and calculate the total interfacial area (TIA) through the novel use of filtration through nanoporous membranes. Ultrafiltration was carried out in centrifuge tubes having nanoporous filters with a 30,000 molecular weight cutoff (MWCO), so that emulsion droplets would not pass through, and only SDS (as monomers and micelles) that is in the bulk water phase (i.e., not at the interface) could pass through. The concentration of SDS in the filtrate was determined and used to calculate the TIA for each system. The mean droplet diameter of the emulsions was measured by light scattering. We analyzed the effects of total SDS concentration and oil chain length on the amount of SDS that partitions to the interface, the TIA, and the droplet diameter. The results showed that partitioning of SDS to the oil/water interface increases with increasing total SDS concentration in emulsion systems (i.e., the more SDS we add to the bulk solution, the more SDS partitions to the oil/water interface). However, the surface-to-bulk partition coefficient (i.e., the SDS concentration at the interface divided by the SDS concentration in the aqueous phase) remains the same over the entire concentration range (8–200 mM). The results showed a chain-length compatibility effect in that the minimum amount of SDS partitioned to the interface for C_{12} oil. The droplet size measurements revealed a maximum size of droplets for C_{12} oil. Penetration of oil molecules into SDS film at the interface has been proposed to account for the maximum droplet size and minimum partitioning of SDS at the oil/water interface for C_{12} oil + SDS emulsion system. The TIA, as determined from our ultrafiltration method, was consistently two orders of magnitude greater than that calculated from the droplet size measured by light scattering. Possible explanations for this disparity are discussed.
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1. Introduction

Macroemulsions, which we will refer to simply as "emulsions," are generally defined as heterogeneous systems of one liquid dispersed in another in droplet form with droplets sizes that typically range from 1–100 μm in diameter and with each droplet having a monolayer of surfactant or emulsifier molecules as a coating [1]. In most instances, the two liquid phases are immiscible, chemically unreactive, and the systems that they form are thermodynamically unstable [2]. Emulsions may consist of oil droplets dispersed in a continuous water phase (oil-in-water) or of water droplets dispersed in a continuous oil phase (water-in-oil). The type of emulsion that is formed depends on many factors including the oil/water ratio, the molecular structure and concentration of the surfactant, the presence or absence of electrolytes, temperature, and pressure [3].

Emulsion stability is dependant upon a variety of factors including the physical nature of the interfacial film, the presence

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of electrostatic or steric barriers on the droplet, the viscosity of the continuous phase, the droplet size distribution, oil/water ratio, and temperature [4]. Emulsion stability is also related to the amount of surfactant that adsorbs at the interface. When more surfactant adsorbs at the interface, the interfacial tension is decreased, and the surfactant molecules act as a barrier delaying the coalescence of droplets by electrostatic and/or steric repulsion [3].

Emulsions typically require the input of energy into the system for their formation. The energy supplied to the system acts to disperse one liquid into the continuous phase as droplets, which correspondingly increases the interfacial area significantly. The total interfacial area that is generated is related to the amount of energy put into the system as determined by Eq. (1) [5]:

$$W = \gamma(\Delta A), \tag{1}$$

where γ is the interfacial tension and ΔA is the change in interfacial area. For a given amount of work, the only way to increase the interfacial area (ΔA) would be to decrease the interfacial tension (γ).

Emulsions have a wide variety of applications including cosmetics, pharmaceutics, foods, paints, polishes, pesticides, and metal cutting oils. Due to this multitude of applications, emulsions have been extensively investigated over the years, and as such their structure is relatively well understood. However, to our knowledge, there are very few methods available to quantitatively determine the amount of surfactant that resides at the interface of the emulsion droplet relative to the surfactant concentration in the continuous phase and these methods are often quite complicated [6,7].

Here, we present, for the first time, a simple and direct method to quantify the amount of surfactant, sodium dodecyl sulfate (SDS), that partitions to the oil/water interface of oil-in-water emulsions of SDS, alkane oils, and water. We simply filter the emulsion, by centrifugation, through nanoporous filters having a 30,000 molecular weight cutoff (MWCO). The filtrate is then analyzed to determine the surfactant concentration. This concentration is considered to be the bulk surfactant concentration and the remaining surfactant is assumed to be adsorbed at the oil/water interface as SDS does not partition into oil. Assuming that the space occupied by each individual surfactant molecule at the oil/water interface is very close to area/molecule of the surfactant determined from Gibbs adsorption isotherm at the oil/water interface, we can calculate the total interfacial area (TIA) by multiplying the area/molecule by the number of molecules at the oil/water interface as determined from the ultracentrifugation and subsequent filtrate analysis of SDS. It has been shown that filtration through nanoporous membranes is a viable method to determine the monomer concentration of various surfactant systems, including SDS, Triton X-100, and Chaps (3-[(3-cholamidopropyl)-dimethylammonio]-1-propanesulfonate) [8]. However, this is the first time that nanoporous membranes have been utilized to provide information about the TIA and the adsorption isotherm in emulsion systems.

2. Experimental

2.1. Materials

Ultrapure sodium dodecyl sulfate (SDS) from MP Biomedicals, Inc. (Solon, OH) was used as received. Sodium octyl sulfate, sodium decyl sulfate, and tetradecyl sodium sulfate were purchased from Sigma Aldrich and used without further purification. The following chemicals were also used without further purification: hexane, octane, decane, dodecane, tridecane, tetradecane, pentadecane, and hexadecane. 1-Octanol, 1-decanol, 1-dodecanol (Acros Organics, New Jersey), 1-tetradecanol, 1-hexadecanol, and 1-octadecanol were used as purchased. Double distilled, deionized Millipure water was utilized for all solutions.

3. Emulsion preparation

3.1. Surfactant concentration experiments

To investigate the effect of surfactant concentration on partitioning at the oil/water interface, oil-in-water emulsions were prepared by placing 1% (v/v) hexadecane into solutions of SDS at concentrations ranging from 8 to 200 mM. The solution was then mixed on a Vortex hand mixer (Fisher Vortex Genie 2) at the highest setting (8) for 1 min.

3.2. Oil chain length experiments

To investigate the effect of oil chain length on surfactant partitioning to the oil/water interface, 50 mM solutions of SDS were prepared, and 1% (v/v) of the oil phase was subsequently added. The solution was then mixed on a Vortex hand mixer (Fisher Vortex Genie 2) at the highest setting (8) for 1 min.

3.3. Methods

Centricon YM-30 ultracentrifugation filter tubes, having a 30,000 molecular weight cutoff (MWCO), were purchased from Fisher Scientific. Two milliliters of the emulsion solution were placed into the top portion of the ultracentrifugation tubes and subsequently centrifuged at ∼900g for approximately 25 min so that less than 10% of the total solution volume was collected as filtrate to minimize the deviation from the equilibrium concentration. All samples were centrifuged in a bench top IEC clinical centrifuge (Damon/IEC Division, Needham Hts., MA). The filtrate was collected in the bottom attachment and diluted to the micromolar concentration regime for analysis by a slightly modified dye complexation method [9] and compared to a previously prepared calibration curve. Each data point in the graphs represents an average of four individual samples in different sample tubes.

Methylene blue dye, chloroform, sodium phosphate monobasic, and sulfuric acid were purchased from Fisher Scientific. Methylene blue reagent was prepared according to standard preparation procedure [10]. Two milliliters of methylene blue reagent were added to two milliliters of the diluted filtrate

from the ultrafiltration experiments. Two milliliters of chloroform were added and the solution was shaken on a Vortex mixer for approximately thirty seconds. Any SDS that was in the filtrate complexed through electrostatic interaction with the positively charged methylene blue, making it oil soluble. The SDS/dye complex would then partition into the chloroform organic phase. The solution was allowed to phase separate and the organic phase was removed and placed into a separate test tube. This process was repeated two more times and the organic phase was then analyzed by UV–visible spectrometry at 652 nm and the SDS concentration was determined upon comparison with a calibration curve. All extractions were carried out in a fume hood. A Hewlett Packard HP 8453 UV–vis spectrometer was used for all UV–vis analysis.

Droplet size analysis was performed on a Brookhaven Zeta-Plus particle size analyzer. The refractive index of the dispersed phase is input into the software. The emulsion sample is placed into a cuvet and inserted into the instrument. The droplet diameter is determined by means of light scattering.

4. Results and discussion

As previously mentioned, emulsions have been thoroughly studied throughout the years and there is quite a bit of general knowledge available regarding methods to manipulate emulsion size and stability. According to Eq. (1) above, the only method by which to increase interfacial area for a given amount of work is by decreasing the interfacial tension. The primary use of surfactants is to reduce the surface and/or interfacial tension of a given solution. This property of a surfactant is directly dependent upon its ability to partition to the interface, which is reflected by the surface excess, Γ [4]. This relationship between surface or interfacial tension and surface excess is represented by the Gibbs equation, as follows:

$$d\gamma = -\sum_i \Gamma_i \, d\mu_i, \qquad (2)$$

where $d\gamma$ is the change in surface or interfacial tension of the solvent, Γ_i is the surface excess concentration of any component of the system, and $d\mu_i$ is the change in chemical potential of any component of the system (a more usable form of Eq. (2) is given in Eq. (4)).

Over the years various efforts have been made to investigate adsorption of surfactants at oil/water interfaces [6,7]. Staples et al. [7] have investigated the adsorption of mixed surfactant at the oil/water interface through the use of small-angle neutron scattering (SANS) in combination with hydrogen/deuterium isotopic substitution. While these studies have been insightful in many regards, they can be rather complicated and can require the use of complex and costly instruments. It should be noted that measuring surfactant adsorption at the oil/water interface in non-disperse (i.e., two separate phases in contact) systems through interfacial tension determination is relatively easy. However, when the oil/water system is dispersed, it is very difficult to measure the concentration of surfactant in the oil phase, water phase, and at the interface. We have developed a novel ultrafiltration methodology, illustrated in Fig. 1, that will
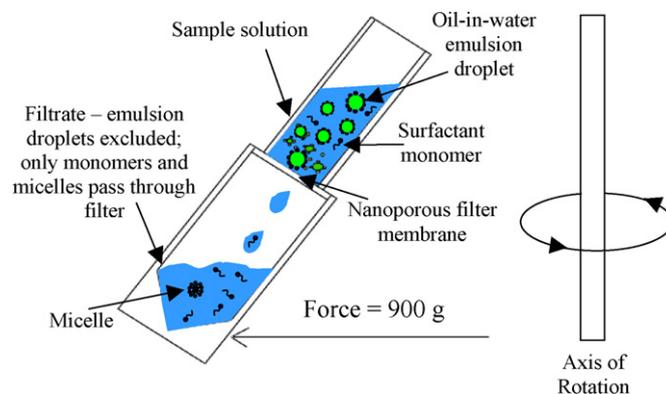

Fig. 1. Schematic depiction of filtration of oil-in-water emulsion through nanoporous filter membrane. Emulsion droplets are retained in the filtrand (top portion) and only surfactant monomers and micelles are small enough to pass through the filter pores.

allow us to quantitatively determine how much surfactant partitions to the oil/water interface and how much remains in the bulk (aqueous) phase.

We first investigated the effect of surfactant concentration on partitioning to the oil/water interface. Emulsion solutions of 1% hexadecane in increasing concentrations of SDS were prepared and filtered through the 30,000 MWCO filters (see Fig. 1). It is well recognized that SDS does not dissolve in pure hexadecane. Therefore, the emulsions produced by SDS + hexadecane + water system involve partitioning of SDS only in the aqueous phase and at the interface. Since SDS has an aggregation number of ∼65 molecules/micelle and a molecular weight of 288, we know that any micelles (MW of SDS micelle = 18,720) that may be present in the emulsion should freely pass through the 30,000 MWCO filters. To ensure that micelles do indeed pass through the 30,000 MWCO filters, a control experiment was done where *no* oil was present (i.e., only micelles of SDS are present in the solution). The micellar solutions were filtered through the 30,000 MWCO filters and the SDS concentration in the filtrate was determined for each initial SDS concentration. Fig. 2 shows that approximately 98.7% of the surfactant passes through the filter (i.e., nearly all micelles pass through the filter). Given this fact, the 30,000 MWCO filters can be utilized to determine the amount of surfactant at the oil/water interface of emulsions and it can be assumed that all of the micelles are allowed to pass through the pores into the filtrate. As shown in Fig. 3, for a 1% (v/v) hexadecane-in-water emulsion, the concentration of SDS in the filtrate increases linearly with increasing total SDS concentration.

Since the 30,000 MWCO filters allow micelles to pass through into the filtrate, the SDS concentration that is not in the filtrate must be present at the oil/water interface since SDS does not partition into hexadecane. The slope of the line represents the fraction of SDS that is in the filtrate. The take home message here is that in emulsions of 1% hexadecane in SDS solutions, approximately 40% of the surfactant resides at the oil/water interface of the emulsion droplets and the remaining 60% remains in water in this concentration range. This is indicative that as we increase the concentration of SDS in the aqueous phase, more SDS partitions into the interface. How-
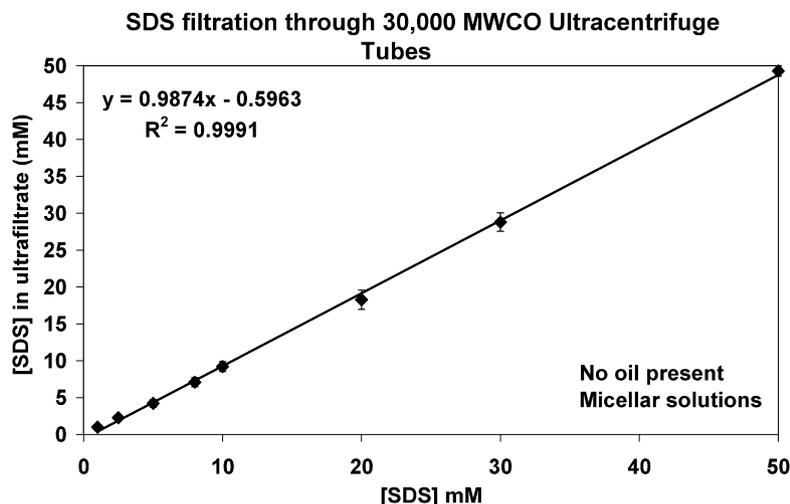
Fig. 2. Filtration of SDS through 30,000 MWCO nanoporous membrane filter for SDS concentrations from 1 to 50 mM. Each point represents the average value of four samples of filtrate.
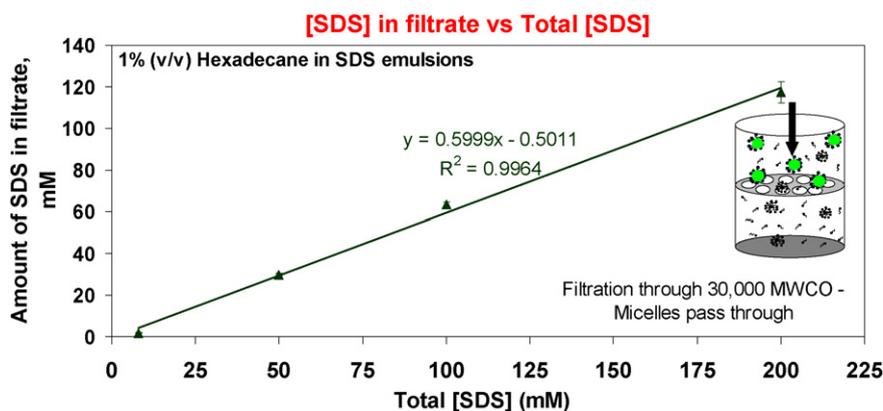

Fig. 3. Amount of SDS in filtrate as a function of total SDS concentration after filtration of 1% (v/v) hexadecane-in-water emulsions through 30,000 (YM30) molecular weight cutoff (MWCO) filters. Samples were centrifuged at $900g$ for 25 min. Each point represents the average value of four samples of filtrate. Schematic inset on right side depicts the transport of micelles through 30,000 MWCO filter.

ever, the surface to bulk partition coefficient (concentration at interface/concentration in aqueous phase) remains constant at 2/3 with 40% of total SDS at the interface and 60% of total SDS in the aqueous phase. This is possible only if the total interfacial area increases with total concentration of surfactant. Since the total volume of oil was fixed, increasing the total interfacial area implies a smaller droplet size with increasing SDS concentration. This was confirmed by the particle size measurements of the emulsions (see Fig. 4). As can be seen in Fig. 4 the droplet size decreases with increasing SDS concentration. This correlates well with the increasing amount of SDS at the hexadecane/water interface as the total SDS concentration is increased. The decrease in mean droplet diameter with increasing SDS concentration means that there must be an increase in the number of oil droplets and hence in the total interfacial area.

The results of these experiments raise an interesting observation. Equation (1), $W = \gamma \Delta A$, suggests that for a given interfacial tension and a given work value, the total interfacial area should be constant. Given that we are at SDS concentrations that are significantly higher than the cmc value, one might suspect that the interfacial tension would not change significantly
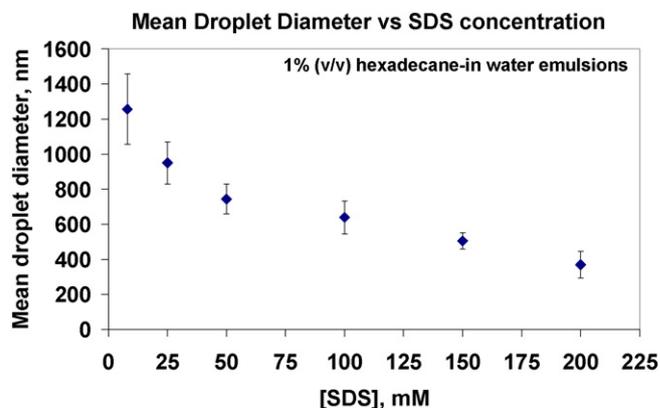

Fig. 4. Effect of SDS concentration on mean droplet diameter of 1% (v/v) hexadecane-in-water emulsions. Each point represents the average value of three emulsion samples.

with increasing SDS concentration. However, the droplet size results suggest that the interfacial tension must be changing significantly. This fact made us re-evaluate Eq. (1) and we realized that we were attempting to apply an equilibrium equation to a dynamic situation. As the emulsion is being generated, it is

the dynamic interfacial tension that is important in determining the total interfacial area that can be stabilized by the surfactant. Therefore, it would be more accurate under dynamic conditions for Eq. (1) to be rewritten as:

$$dW = \int_{t_0}^{t_f} \int_{\gamma_i}^{\gamma_f} d\gamma \, \Delta A \, dt, \qquad (3)$$

where the first integral runs from time, t_0 to time, $t_f = t_{\text{final}}$ which represents the time that it takes to generate the emulsion and the second integral represents the dynamic interfacial tension ($d\gamma$) and runs from γ_{initial} (γ_i) to γ_{final} (γ_f).

Given that we now have a method to measure how much surfactant is at the interface of these emulsion droplets, we can now approximate the total interfacial area by multiplying the area per molecule of each surfactant by the total number of molecules at the interface. The area/molecule at the interface can be calculated using the Gibbs adsorption isotherm [11]:

$$\Gamma = -\frac{1}{2RT} \frac{d\gamma}{d\ln C}, \qquad (4)$$

where Γ is the concentration of surfactant at the interface, R is the ideal gas constant, T is the temperature, γ is the interfacial tension at the oil/water interface, and C is the initial concentration of surfactant in the bulk solution. The area/molecule at the interface can be calculated by dividing the total interfacial area by the total number of surfactant molecules at the interface. An SDS area per molecule of 50 Å^2/molecule at the oil/water interface was used as reported in literature [12] and as suggested by the findings of Rehfeld [13]. The total interfacial area (TIA) values were calculated from the results of the filtration experiments and compared to values which were calculated from the measured droplet size. In order to determine the TIA from the mean droplet size, the following series of equations had to be solved. First, the volume of a single drop can be determined from:

$$V = \frac{4}{3}\pi r^3, \qquad (5)$$

where r = radius of droplet as determined from light scattering. Dividing the total volume of oil by the volume of a droplet as given by Eq. (5) will give the total number of droplets, N. The total interfacial area is then simply calculated from:

$$\text{TIA} = N 4\pi r^2, \qquad (6)$$

where r is the measured droplet size from light scattering measurements.

As can be seen from Table 1, the TIA that is calculated based on the filtration experiment is two orders of magnitude higher than the TIA from the droplet size measurement. It must be noted that the droplet size (from the dynamic light scattering results) that is used to determine the TIA is in fact a *mean* droplet size and that there is a size distribution associated with each of these emulsions. Therefore, the TIA calculated from light scattering measurements only provides an approximation of the TIA that will be sufficient for making order of magnitude comparisons in contrast to direct determination of surfactant at

Table 1
Total interfacial area with increasing SDS concentration for 1% (v/v) hexadecane-in-water emulsions

SDS concentration (mM)	Total interfacial area (cm^2/L) [from filtration results]	Total interfacial area (cm^2/L) [from light scattering droplet size]
8	1.831E+07	4.776E+05
50	5.982E+07	8.06E+05
100	1.088E+08	9.390E+05
200	2.461E+08	1.624E+06

the interface using filtration through nanoporous membranes. One other possible flaw of dynamic light scattering is that in an emulsion with a broad size distribution, larger droplets would dominate the light scattering and smaller droplets are ignored [14]. On the contrary, filtration through nanoporous membranes accounts for surfactant lost by adsorption on small as well as large droplets (i.e., it provides results that are nearly size independent). The magnitude of the difference in TIA for the two methods is significantly large. Given that the 30,000 MWCO filters retain nearly all droplets larger than approximately 5–6 nm, the TIA that is calculated from ultrafiltration method is significantly more accurate than the value that can be deduced from droplet size measurements using light scattering.

To give further clarity to our interpretation of the difference in the TIA values that are calculated from the two different results (filtration vs mean droplet size), we calculated the percentage of surfactant at the interface that is accounted for based on the mean droplet size that is reported and an SDS area per molecule of 50 Å^2/molecule. This was done by calculating how many molecules of SDS are at the interface by dividing the TIA (calculated from mean droplet size measurement) by the SDS area per molecule (50 Å^2/molecule). This value (molecules of SDS at interface according to droplet size measurements) was then divided by the number of SDS molecules at the interface as determined by the filtration experiments. This calculation yields the fraction of SDS at the interface that is accounted for and multiplication by 100 gives the percentage. It was found that only about 0.5–2% of the surfactant is accounted for when the mean droplet size is used to calculate the TIA.

Another novel aspect of our filtration methodology is that the resulting TIA values can be used to determine an adsorption isotherm for SDS in disperse systems. This adsorption isotherm is determined by dividing the average SDS concentration at the interface (which is calculated by subtracting the filtrate SDS concentration from the initial total SDS concentration) by the calculated TIA. This value was determined for SDS total concentrations ranging from 8 to 200 mM and in each case the adsorbed amount, Γ_{ads}, was found to be constant, at 3.354×10^{-10} mol cm^{-2} as shown in Fig. 5. This value is in good agreement with that reported in literature [7]. Staples et al. [7] plotted the SDS adsorption isotherm at the hexadecane emulsion–water interface as determined from small-angle neutron scattering (SANS) measurements and from surfactant electrode data in the SDS concentration range of 1 to 30 mM. In their results from SANS data, the adsorbed amount of surfactant at the oil/water interface increases linearly from 1 to 7 mM

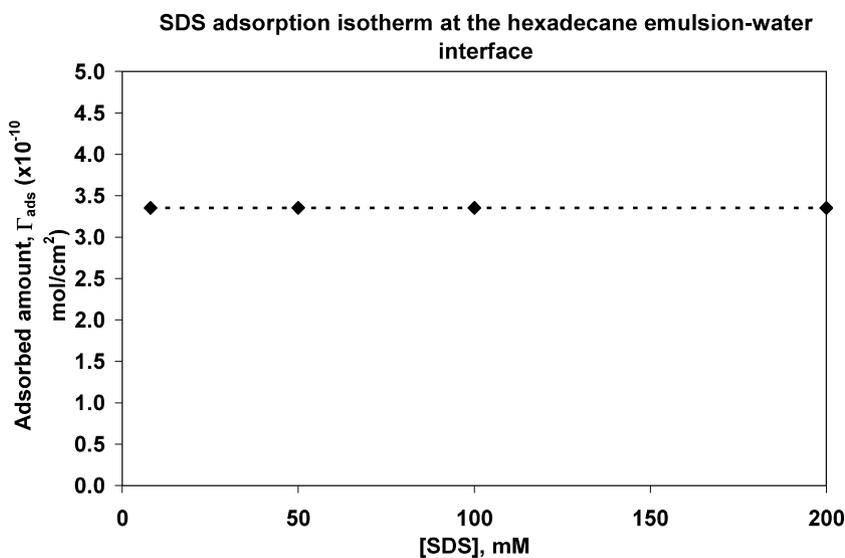**SDS adsorption isotherm at the hexadecane emulsion-water interface**

Fig. 5. Adsorption isotherm for SDS from 8 to 200 mM at the hexadecane emulsion–water interface. The adsorption isotherm was calculated for an assumed SDS area per molecule of 50 $Å^2$.

SDS, and beyond 7 mM SDS the adsorbed amount begins to level off at around 3.0×10^{-10} mol/cm^2. In their results from surfactant electrode data, the adsorbed amount of surfactant at the oil/water interface again increases linearly from 1 mM to around 9 mM SDS. Above 9 mM SDS the adsorbed amount is nearly constant at around 4.0×10^{-10} mol/cm^2. Our results in the concentration range of 8 to 200 mM falls directly in between the two reported results of Staples et al. within this concentration range.

From this methodology we are able to determine that for increasing concentration of SDS, the partition coefficient between the interface and the bulk phase remains constant, the total amount of SDS at the interface increases, the droplet size decreases, the number of droplets increases, the total interfacial area (as measured from the filtration data) increases. The total interfacial area (as measured from light scattering droplet size results) also increases as shown in the master diagram shown in Fig. 6 which correlates the trends among all of these properties of emulsions.

Next, we decided to investigate the effect of increasing the chain length of alkane oils on adsorption at the oil/water interface. We prepared emulsions of 1% alkane oil (octane to hexadecane) in 50 mM solutions of SDS (C$_{12}$SO$_4$). We then filtered these solutions (by centrifugation) through a nanoporous membrane filter (see Fig. 1) having a molecular weight cutoff (MWCO) of 30,000. This MWCO was chosen so that any micelles of these surfactants that may be present in the emulsion could pass through the pores and so that all emulsion droplets would be excluded by the filter. The SDS concentration in the filtrate was determined by the methylene blue dye complexation method [10] and used to determine the amount of surfactant that had partitioned to the interface. It was assumed that all surfactant that did not pass through the filter was at the oil/water interface. Fig. 7 shows the results of this analysis.

It is hypothesized that increasing the chain length of the oil in an analogous series of alkane oils will increase the driving
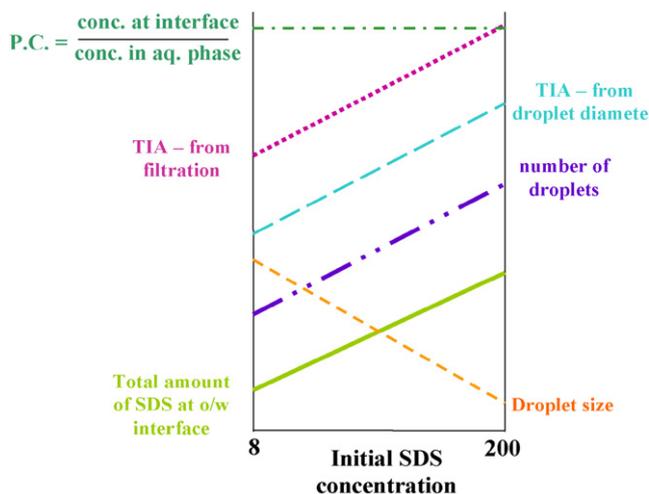

Fig. 6. Master diagram showing the changes in partition coefficient, amount of SDS at interface of oil-in-water emulsions, emulsion droplet size, number of droplets, total interfacial area (TIA, calculated from droplet diameter), and total interfacial area (calculated from filtration results) with respect to initial SDS concentration.

force for SDS surfactant to partition to the oil/water interface. This would lead to a greater surface excess (lower interfacial tension). We employed our methodology to test this fact and found that when the chain length of the oil is shorter than the chain length of the surfactant (SDS), increasing the oil chain length in fact, acts to decrease the surfactant partitioning (see Fig. 7). When the chain lengths of the oil and surfactant are equal, there is a minimum in surfactant adsorption at the interface, and as the oil chain length is increased beyond this point, the partitioning of SDS to the interface increases.

For the oil chain lengths that are less than or equal to 12 carbons, the partitioning of SDS decreases with increasing chain length, which is in agreement with the findings of Hallworth and Carless [15,16]. They found that for the shorter oil chain lengths ($<$C$_{12}$) the adsorption of SDS at the oil/water interface
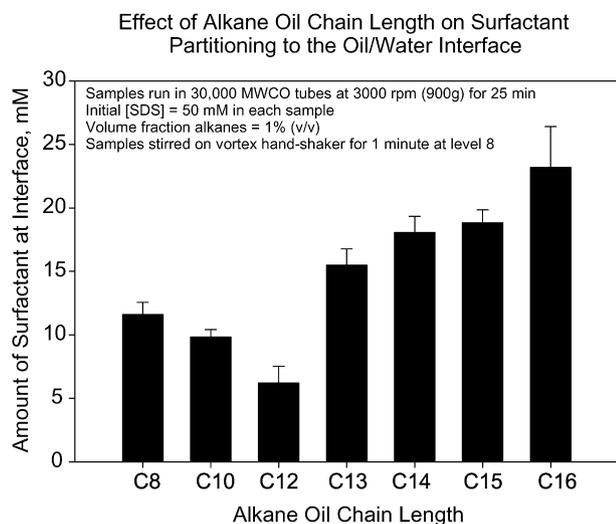
Fig. 7. Effect of oil chain length on SDS partitioning to oil/water interface. Oil chain length was varied from octane to hexadecane. Each bar represents the average of 4 filtrate samples.
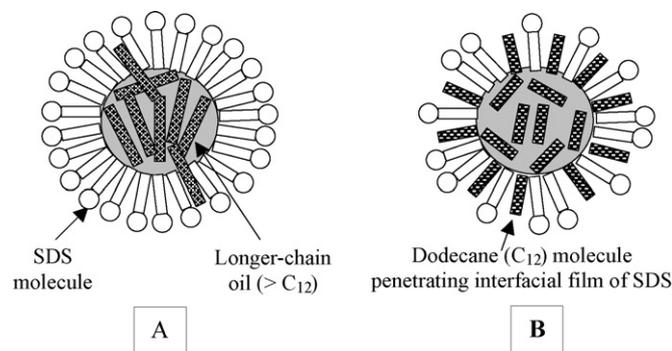

Fig. 8. Schematic depiction of emulsion droplets coated with (A) SDS alone with oil molecules more towards the interior of the droplet or (B) SDS with dodecane penetrating the interfacial space between SDS molecules and forming a rigid, cohesive interfacial film.
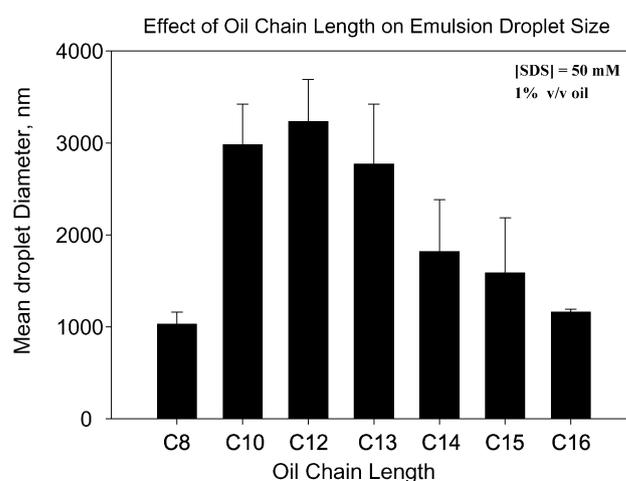

Fig. 9. Mean droplet diameter of oil-in-water emulsions as a function of oil chain length. Emulsions prepared from 50 mM SDS and 1% (v/v) oil. Each bar represents the average of 3 emulsion samples.

was the greatest for the shortest chain length (hexane). We believe that this phenomenon may be due to solubility of the SDS in shorter chain length oils. The minimum in partitioning that is seen when dodecane (C_{12}) is the oil phase is due to a chain length compatibility effect which leads to penetration of the oil molecules into the space between the hydrophobic tails of SDS molecules as depicted by Fig. 8. The oils with chain lengths greater than C_{12} presumably penetrate less into the interfacial film; the difference in the chain lengths between the oil and SDS would lead to tail wagging [17]. This would be unfavorable as compared to cohesive force between oil molecules, so the longer-chain oils remain more in the interior of the droplets. In other words, maximum penetration of oil in the interfacial monolayer occurs when the oil and the surfactant molecules have the same chain length. This is in agreement with several observations made by various researchers [17–25].

Chain length compatibility is a phenomenon that can exhibit its effects in foam stability [19], evaporation of water through monolayers [26], micellar stability [17], and even in changes in the area per molecule of surfactants [26]. Over the years it has been shown that chain length compatibility between the oil phase and the surfactant can also play a major role in boundary lubrication [18], solubilization of water into water-in-oil microemulsions [19,27,28] and in emulsion formation and stabilization [21].

The increase in SDS adsorption with increasing chain length beyond C_{12} oil (dodecane) reflects the findings of McClements and coworkers [29]. They showed that the Ostwald ripening rates decreased with increasing oil chain length for 5 wt% oil-in-water emulsions stabilized with 20 mM SDS. Ostwald ripening is a destabilization process in emulsions by which larger emulsion droplets grow at the expense of the smaller droplets [30]. This suggests that with increasing chain length, the emulsions become more stable against coalescence, which could be due to the adsorption of more surfactant at the interface which will create greater Coulombic repulsion between adja-

cent droplets. In order to further clarify how oil chain length affects SDS partitioning to the interface, the emulsion droplet size was measured and plotted in Fig. 9. The plot shows that the largest particle size is obtained for the case when the oil phase is dodecane (C12), which also corresponds to the lowest partitioning of SDS at the interface. Also, for C12–C16, the partitioning increases and the droplet size decreases.

The total interfacial area was calculated from the filtration results and from the mean droplet size results, and once again, the values were found to be approximately two orders of magnitude higher when calculated from the filtration results as can be seen in Table 2. Therefore, we have shown that filtration of emulsions through nanoporous filters and subsequent determination of the amount of surfactant at the interface provides a novel, more reliable, and effective method by which to approximate the total interfacial area (TIA) in emulsion systems.

5. Summary

We have, for the first time, developed a simple and direct method to quantitatively determine the amount of surfactant that partitions to the oil/water interface and effectively used

Table 2
Total interfacial area (TIA) as a function of oil chain length for oil-in-water emulsions prepared from 50 mM SDS

Oil chain length	Total interfacial area (cm^2/L) [from filtration results]	Total interfacial area (cm^2/L) [from light scattering droplet size]
C_8	3.663E+07	5.825E+05
C_{10}	2.814E+07	2.014E+05
C_{12}	1.855E+07	1.855E+05
C_{13}	4.623E+07	2.164E+05
C_{14}	5.387E+07	3.297E+05
C_{15}	5.619E+07	3.777E+05
C_{16}	5.982E+07	8.06E+05

these results to calculate the total interfacial area of a given oil-in-water emulsion. By using nanoporous filter membranes having a 30,000 molecular weight cutoff (MWCO) through which emulsion droplets could not pass, we were able to determine the free concentration of sodium dodecyl sulfate (SDS) (i.e., the concentration that was not at the interface of the oil droplets). We have assumed that the amount of surfactant that is not in the filtrate is adsorbed at the oil/water interface of emulsion droplets.

In this manuscript, we first investigated the effect of surfactant concentration on partitioning to the oil/water interface. We found that the partitioning of surfactant to the interface increases linearly with increasing total surfactant concentration. By filtering the samples through the 30,000 MWCO filters, we were able to ensure that micelles would pass through the filter and thereby determine the amount of surfactant that is present at the oil/water interface. We determined that for solutions of 1% (v/v) hexadecane in SDS, approximately 40% of the surfactant in the solutions is present at the oil/water interface. We have also shown that mean droplet size decreases with increasing SDS concentration as expected based on the filtration results.

The total interfacial area was calculated from the partitioning results and compared to calculations that were based on the mean droplet size measurements. It was shown that the total interfacial area that was calculated from the SDS partitioning determination was approximately two orders of magnitude greater than the total interfacial area that was calculated from the mean droplet size. This disparity is due to the fact that the droplet size measurement is a mean size and since there is a size distribution of droplets, this value will not lead to a very accurate total interfacial area. Our method of determining total interfacial area based on the amount of SDS that partitions to the oil/water interface of droplets is much more accurate because it accounts for all droplet sizes down to ∼5 nm. We also used our results to determine the adsorption isotherm of SDS in a hexadecane-in-water emulsion and found that our values are in good agreement with results that have been reported in literature using SAXS and SANS methods.

We also evaluated the effect of the oil chain length for a series of alkane oils on the partitioning of SDS to the interface. We have shown that for oil chain lengths from octane (C_8) to dodecane (C_{12}), the partitioning of SDS decreases with increasing oil chain length. This has been attributed to solubilization of the SDS into the shorter chain length oils (C_8–C_{10}). Partition-

ing of SDS at the oil/water interface increases with increasing oil chain length from dodecane (C_{12}) up to hexadecane (C_{16}). The minimum in partitioning at C_{12} oil is due to a chain length compatibility effect by which there is penetration of oil molecules to the interface so that less SDS can partition. As the oil chain length is increased beyond C_{12}, the partitioning of SDS to the interface increases because the oil phase penetrates less and less into the interface as the chain lengths become more incompatible. This results in lower interfacial tension and higher interfacial area with increasing oil chain length.

The droplet size was measured for the emulsions as a function of oil chain length and correlated to the partitioning results. The mean droplet diameters correlated well with the partitioning results. The greatest mean droplet diameter was found when the oil phase was dodecane (C_{12}), which directly corresponds to the least partitioning of SDS for dodecane. The droplet size increased from the octane (C_8) emulsion up to the dodecane emulsion and decreased from the dodecane emulsion to the hexadecane (C_{16}) emulsion (i.e., the maximum droplet size was found when the chain lengths of the oil and surfactant are equal, at C_{12}).

This approach is exciting in that it provides a simple and direct means to determine the amount of surfactant that partitions to the oil/water interface in emulsions and how much remains in the bulk aqueous phase and a means to determine the TIA and corresponding adsorption isotherm. This methodology has the potential to be expanded to apply to any dispersed system (L/L or S/L) where the surfactant concentration can be determined in the micromolar regime in the continuous phase and where the area per molecule of the surfactant is known or can be determined using Gibbs equation or other methods.

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