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Interfacial vs Bulk Phenomena Effects on the Surface Tensions of Aqueous Magnetic Surfactants in Uniform Magnetic Fields

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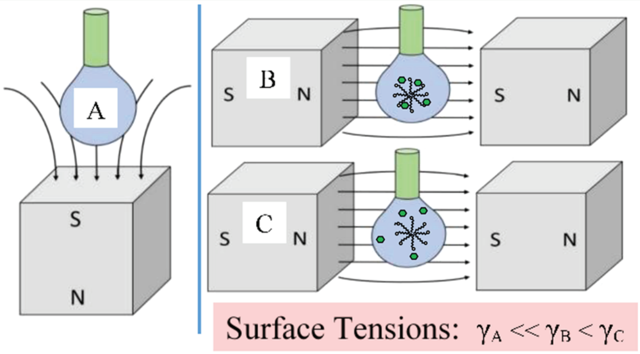

ABSTRACT: The literature clearly reports that magnetic surfactant systems respond to magnetic fields. This manuscript investigates if the responses are because the magnetic fields directly alter the interfacial properties or if the surface-active properties are independent of the paramagnetic fluid responses. It uses uniform and gradient magnetic fields to determine the magnetically induced changes to the surface tensions independent of bulk paramagnetic fluid effects for ionic magnetic surfactants. The magnetically induced decrease in surface tensions is small compared to the bulk paramagnetic fluid effects. The reported decrease in surface tensions is significantly smaller than those previously found in the literature, which reported a combined interfacial and bulk paramagnetic effect. The magnetically induced surface tension changes are a function of the degree of association, α, of the magnetic moiety with the surfactant's amphiphilic structure. Therefore, the proposed answer to the question is that as α approaches zero, the magnetic properties of the magnetic surfactant system approaches the behavior of an ordinary paramagnetic fluid. For magnetic surfactants with α approaching one, there is a measurable interfacial response. For example in this study, a magnetic surfactant with $\alpha = 0.92$ had a 2.5 times greater magnetically induced change in surface tension compared to a magnetic surfactant with α = undetectable, even thought they had similar magnetic moments.

■ INTRODUCTION

In 2012, Brown et al. introduced a new class of surfactants that exhibited an apparent reduction in surface tension at the air−water interface in response to an external magnetic field.[1] These magnetically responsive surfactant systems combine the traditional amphiphilic structure and properties of surfactants with a magnetic moiety such as a high-spin transition metal[2] or lanthanide[3] cations. Potential applications of this new class of surfactants, a.k.a. magnetic surfactants, include aqueous nanomaterial recovery,[4] protein separations,[5] and capture/release of DNA.[6] The literature has also investigated the utilization of external magnetic fields on magnetic surfactants to alter surface tensions[1,7] or the boundary between two phases such as microemulsions.[8]

Research clearly shows that magnetic surfactant systems do respond to external magnetic fields. However, some researchers have questioned if the responses are because the magnetic fields directly alter the interfacial properties[1] or because the surface-active properties are independent of the paramagnetic fluid responses.[7] Answering this question is a challenge. The data and discussion that follows is the second study in our work to isolate the magnetic surface-active responses from the paramagnetic fluid responses to systematically answer this question. In our first study, we examined the paramagnetic fluids created by dissolving magnetic surfactants into water; specifically, we looked at the degree of association of the magnetic moiety with the amphiphilic structure and the surfactant/fluid interface (i.e., micelles).[9]

Our objective in this second study was to measure magnetically induced changes in the interfacial surface tension independent of bulk paramagnetic fluid effects. In order to explain our experimental design and procedures to measure these two effects separately, the remainder of this Introduction will review the underlying physics of the relevant systems.

A paramagnetic fluid becomes magnetized in the presence of a magnetic field and loses its magnetic properties with the removal of the magnetic field. Paramagnetic fluids can be suspensions of nanoferromagnetic particles or a liquid of chemicals with magnetic moieties on the molecular scale.[10] In

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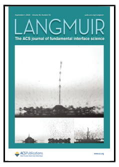

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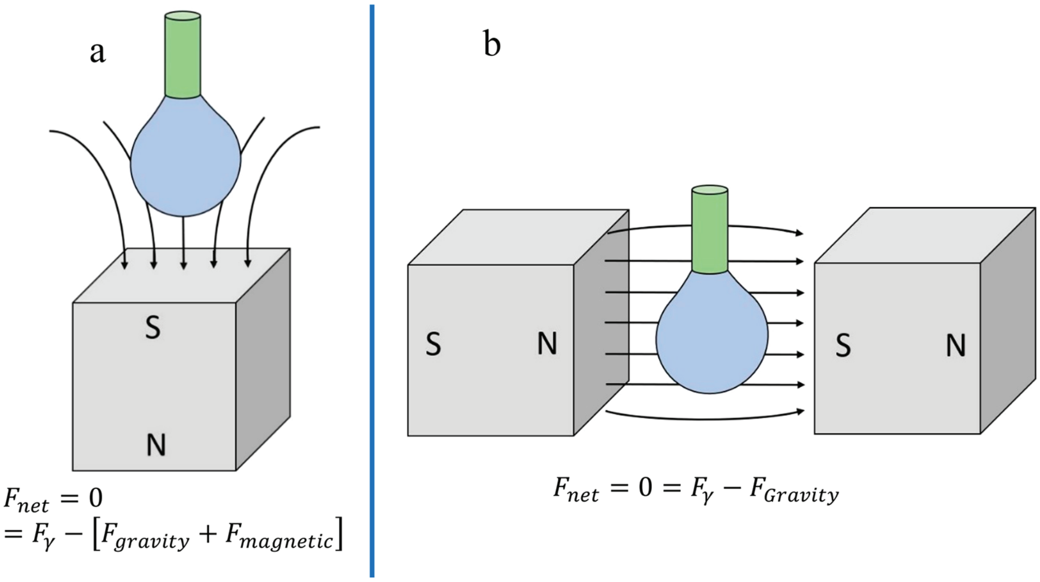

Figure 1. Two types of external magnetic fields interacting with a pendant drop and their associated force balances: (a) gradient field and (b) uniform field. F_γ is the surface tension force holding the drop to the dispensing needle. $F_{gravity}$ denotes the force of gravity acting upon the drop and $F_{magnetic}$ denotes the force arising from the magnetic gradient acting upon the drop in panel a.

the case of liquid chemicals, magnetic moieties are atomic-sized magnetic dipoles that are randomly aligned and nonmagnetic unless an external magnetic field aligns the randomly distributed dipoles within the liquid.[10] Aqueous solutions of magnetic surfactants are paramagnetic fluids.

Thus, the alignment of magnetic dipoles of a magnetic surfactant solution is one consequence of imposing an external magnetic field on the paramagnetic surfactant system. There are also force generation and energy (i.e., thermodynamic) consequences. Molecularly the alignment reduces the degrees of freedom of the magnetic dipoles. If the magnetic dipoles are strongly associated with the amphiphilic structure, then the degrees of freedom of the surfactant molecule is decreased. In other words, molecularly a magnetic surfactant in a magnetic field has less modes of random movement. In molecular thermodynamics, this reduction in degrees of freedom of magnetic surfactants at an interface represents an increase in system order or a decrease in entropy, *S*. To illustrate the potential impact on the interfacial surface tension, γ, start with the isothermal change in Gibbs energy (dG) for a change in interfacial area:

$$dG = dH - TdS \tag{1}$$

where the change in enthalpy, dH, results from the work done to change the interfacial area (dA):[11]

$$dH = \gamma dA \tag{2}$$

Plugging eq 2 into eq 1 and rearranging gives

$$\gamma = \frac{dG}{dA} + T\frac{dS}{dA} \tag{3}$$

Equation 3 relates the surface tension to temperature, entropy, and Gibbs energy with respect to the interfacial area. As an external magnetic field imparts order to the magnetic surfactant molecules, the system becomes more ordered and the change in entropy (dS) is negative. This could result in a surface tension decrease in an external magnetic field.

The force generation consequence of an external magnetic field aligning magnetic dipoles has a direct impact on experimental design.[10] In general, the literature measurements of magnetic surfactant surface tensions inside and outside of magnetic fields use the pendant drop technique pioneered by Andreas et al.[12−14] Figure 1 shows two of the many potential ways of putting a pendent drop inside of a magnetic field. Figure 1a has been more commonly used by other researchers[1,7] vs the arrangement in Figure 1b.[15] When considering the magnetic field at one end, or pole, of a permanent magnet (Figure 1a), the magnetic field strength is inversely proportional to the square of the distance from the pole. This creates a gradient in magnetic field strength. Figure 1b shows a magnetic field with a constant field strength in the region of the pendent drop. Two magnets placed as illustrated can create this constant or uniform magnetic field.[16] Both the gradient and uniform magnetic fields will align magnetic dipoles in a paramagnetic fluid or magnetic surfactant solution creating a magnetized material. The difference is that a magnetized material experiences a magnetic force in the direction of increasing magnetic field strength:

$$\mathbf{F}_{\text{magnetic}} = \nabla(\mathbf{m}_{\text{dipole}}\cdot\mathbf{B}) \tag{4}$$

where $\mathbf{F}_{\text{magnetic}}$ is the force arising from the magnetic strength gradient in Newtons, $\mathbf{m}_{\text{dipole}}$ is the magnetic dipole moment in Amp(m^2), $\mathbf{B}$ is the magnetic flux density in Tesla, and ∇ is the grad operator. Since Figure 1a has a $\nabla\mathbf{B}$, an induced $\mathbf{F}_{\text{magnetic}}$ will try to pull the drop toward the magnet. However, the drop in Figure 1b would experience a negligible $\mathbf{F}_{\text{magnetic}}$ since it is in a uniform gradient field ($\nabla\mathbf{B} \approx 0$).

The pendant drop technique measures the changes in the shape of the drop to determine changes in the surface tension of the solution. For pendant drop experimental setups, using a single magnet placed directly under the hanging drop would induce a downward force, $\mathbf{F}_{\text{magnetic}}$, causing an elongation in the drop's shape. Because the shape of the drop is used to determine the surface tension, the magnetic response at the interface is confounded by this $\mathbf{F}_{\text{magnetic}}$. Separating the elongation of the drop because of magnetic changes in surface tension from the elongation caused by F_{magnetic} is complicated.

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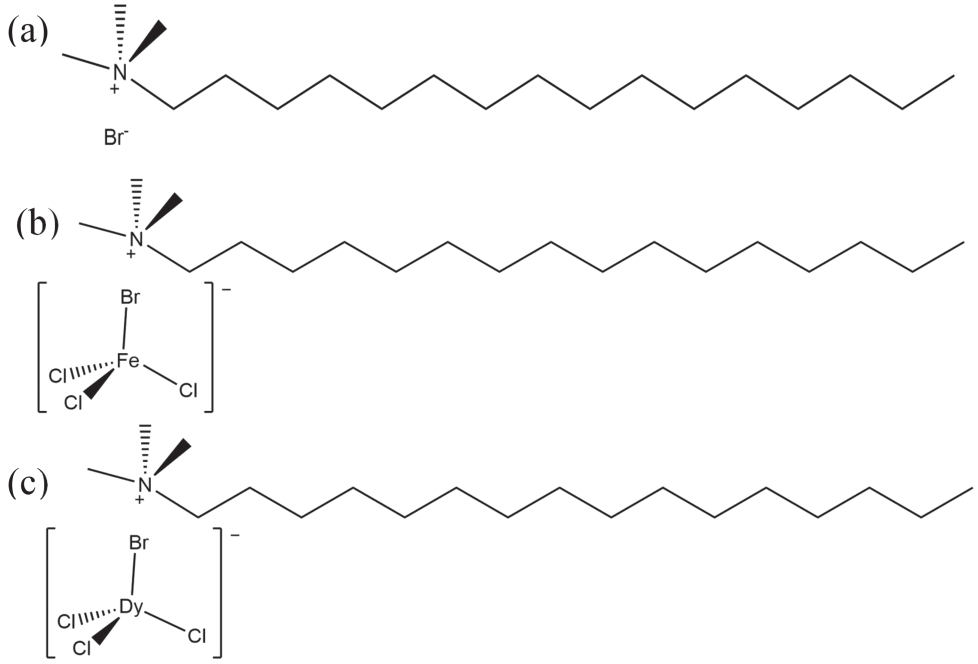

Figure 2. Molecular structures of (a) C_{16}TAB, (b) C_{16}TAFe, and (c) C_{16}TADy.

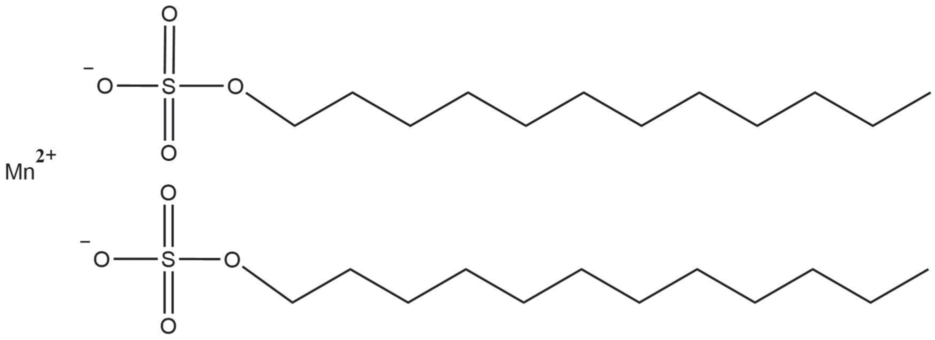

Figure 3. Molecular structure of manganese didodecyl sulfate (MnDDS).

This complication is minimized in a pendant drop experimental setup with uniform magnetic fields (Figure 1b). Hayakawa et al. used experimental set-ups similar to Figure 1b to distinguish between the bulk and surface effects of moderate magnetic fields (0.14 T) on a solution of $HoCl_3$.[15] The main differences between the Hayakawa et al. experiments and ours were the addition of the amphiphilic structure of the surfactants and the use of larger magnetic fields (up to 0.68 T).

We, therefore, used experimental setups similar to Figure 1b to measure the magnetically induced changes to surface tension and setups similar to Figure 1a to measure bulk paramagnetic effects. The nature of the paramagnetic fluids created by dissolving magnetic surfactants into water, determined in our previous study,[9] also guided our experimental plan.

■ EXPERIMENTAL SECTION

Materials and Synthesis. Iron(III) chloride hexahydrate ($FeCl_3$) 98% and cetyltrimethylammonium bromide (C_{16}TAB) 99% were purchased from Sigma-Aldrich. Dysprosium(III) trichoride ($DyCl_3$) 99% was purchased from Alfa Aesar. Sodium dodecyl sulfate, 99%, was purchased from ACROS Organics. Anhydrous manganese(II) chloride, 99%, was purchased from American Elements. Distilled water was purchased for use in making aqueous surfactant solutions. All reagents were used as received.

The cationic surfactant C_{16}TAB (1.50 g, 4.12 mmol) was dissolved in 10 mL of methanol. An equimolar amount of the corresponding metal halide ($FeCl_3$ or $DyCl_3$) was dissolved separately in 5 mL of methanol. The metal halide solution was added to the surfactant solution, immediately forming a precipitate. The resulting solution was mixed vigorously and then allowed to separate into two phases. The resulting two-phase solution was stored overnight at −20 °C and then vacuum filtered. The product was purified via recrystallization from methanol two more times for a yield of 35%. The molecular structures of C_{16}TAB and the corresponding products cetyltrimethylammonium−iron(III) monobromotrichloride (C_{16}TAFe) and cetyltrimethylammonium−dysprosium(III) monobromotrichloride (C_{16}TADy) are in Figure 2.

Manganese didodecyl sulfate (MnDDS) was synthesized by modifying a previously reported literature method.[17] Briefly, sodium dodecyl sulfate was dissolved in distilled water to form a concentrated solution before an excess of concentrated aqueous manganese chloride solution was added. The solution was then stored at 5 °C until crystals formed. The crystals were recovered by vacuum filtration and then purified by recrystallization three times from distilled water. The structure of the product MnDDS is in Figure 3.

Tensiometry. Critical micelle concentration (CMC) measurements outside of magnetic fields were conducted using an Attension Sigma701 Tensiometer (Biolin Scientific, Sweden) using a platinum

Du Nouy ring. The Du Nouy ring was cleaned with ethanol, DI water, and then flame heated to red-hot between each measurement. The procedure for determining the surface tensions and CMCs started with aqueous surfactant solutions and measured the changes in surface tension with changing concentration. The changing concentrations resulted from dilution with distilled water. The concentrations of the starting solutions were greater than the expected surfactant CMC; specifically, the starting concentrations were 3.5 mM for MnDDS, 11 mM for C_{16}TAFe, and 11 mM for C_{16}TADy. The data were graphed as surface tension vs surfactant concentration and are in the Supporting Information, Figures S1−S4. The graphs had two sections, first the reduction in surface tension with increasing concentration followed by a plateau of constant surface tension with increasing total concentration. The CMC is at the intersection of a horizontal line determined by the plateau region with a linear regression line determined by the region of reducing surface tension near the plateau section.

Magnetic Strength Measurements. Magnetic field strengths were measured using a Hirst model GM08 Gmeter (Hirst Magnetic Instruments, Ltd., U.K.) with a transverse Hall probe (model PT 6324). In all cases, the transverse probe was aligned perpendicular to the magnetic field. In the case of the single magnet set-ups (Figure 1a), the magnetic field strength at the point of the hanging drop's connection with the dispensing needle was recorded along with the value at the surface of the magnet. In the case of the uniform field, the value at the location of the center of the pendant drop was recorded.

Pendant Drop Goniometry. Figure 1a illustrates the experimental setup for measuring the drop elongation inside of a gradient magnetic field. For measurements within uniform external magnetic fields, we designed a jig (Figure 4) to hold two permanent magnets apart while accommodating access for the pendant drops of aqueous magnetic surfactant solutions. Olympus Stream Essentials software, Version 1.9.4, evaluated digital pictures of magnetic solution pendant drops inside and outside of magnetic fields of varying strengths. Drops of aqueous magnetic surfactant solutions were dispensed using a Razel model R-100 syringe pump. After dispensing, the drop was aged for 60 ± 10 s before being photographed with a 2-megapixel AmScope UWT 500X USB microscope camera.

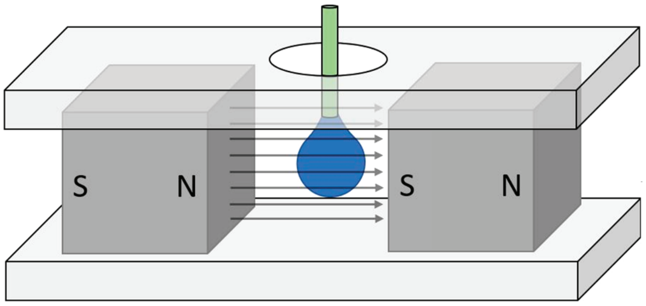

Figure 4. Uniform magnetic field jig. Each magnetic jig held two cubic magnets between aluminum plates. Magnets were arranged so that the magnetic field lines between the two magnets would be parallel, creating a uniform field. A hole in the upper aluminum plate allowed a needle through to dispense the aqueous magnetic surfactant solution.

For each magnetic surfactant tested, at least two concentrations above the CMC and at least two concentrations below the CMC were examined to determine if the CMC changes significantly inside of a magnetic field. At each concentration and magnetic field strength, six drops were evaluated, with the average surface tension and the standard error of the mean reported. Five uniform magnetic field jigs (Figure 4) were constructed with the following field strengths in Teslas: 0.46, 0.48, 0.52, 0.60, and 0.68. The cube permanent magnets used in the gradient magnetic field and uniform magnetic field jigs were neodymium magnets sourced from K&J Magnetics, Inc., Pipersville, PA, USA.

The analysis of the Pendant Drop data started with a force balance applied to a stable hanging drop. For example, using Figure 1b, a hanging pendant drop at equilibrium will have the surface tension force ($\mathbf{F}_\gamma$) counteracted by the gravity force, $\mathbf{F}_{\text{gravity}}$, in the absence of other forces

$$\mathbf{F}_{\text{net}} = 0 = \mathbf{F}_\gamma - \mathbf{F}_{\text{gravity}} \tag{5}$$

Since the definition of surface tension, γ, is force per unit length

$$\gamma = \frac{\mathbf{F}_\gamma}{L} = -\frac{\mathbf{F}_{\text{gravity}}}{L} \tag{6}$$

The shape of the drop is a function of the γ and the gravity force. Andreas et al.[12] used this functionality of the drop shape to calculate γ from the drop's mass and shape via:

$$\gamma = -\Delta\rho g D^2\left(\frac{1}{H}\right) \tag{7}$$

where $\Delta\rho$ is the difference in density between the surfactant solution (ρ_{A}) and the air (ρ_{B}), g is the acceleration due to gravity, D is the diameter of the drop at the widest point, and the quantity $1/H$ is computed using the empirical relation given by Drelich et al.[13]

$$\frac{1}{H} = \frac{B_4}{S^a} + B_3S^3 - B_2S^2 + B_1S - B_0 \tag{8}$$

with

$$S = \frac{d}{D} \tag{9}$$

where D is the equatorial diameter of the drop, d is the diameter of the drop measured a distance D from the base of the drop, and the B's are empirical constants tabulated in Drelich et al.[13] Figure 5 shows a schematic of the variables measured to calculate surface tension using eqs 7 through (9). D_{out} is the outer diameter of the dispensing needle, used to scale the other values from pixels to millimeters.

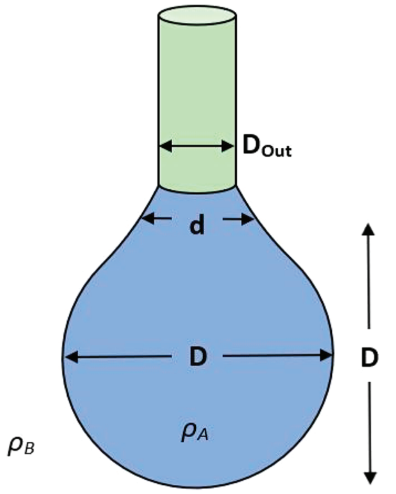

Figure 5. Variables measured in shape-dependent pendant drop technique. D is the equatorial diameter of the drop, while d is a diameter measured a distance D from the drop's base. ρ_{A} and ρ_{B} are the densities of the drop and the surrounding fluid, respectively. D_{out} is the diameter of the dispensing needle, used to scale D and d.

The force balance for a hanging pendant drop inside of a gradient (Figure 1a) is

$$\mathbf{F}_{\text{net}} = 0 = \mathbf{F}_\gamma - \mathbf{F}_{\text{gravity}} - \mathbf{F}_{\text{magnetic}} \tag{10}$$

This means that, to accommodate $\mathbf{F}_{\text{magnetic}}$ and keep the drop at equilibrium ($\mathbf{F}_{\text{net}} = 0$), $\mathbf{F}_\gamma$ must become larger than the $\mathbf{F}_\gamma$ in Figure 1b or eq 5. $\mathbf{F}_\gamma$ becomes larger by increasing the length of the drop altering the shape of the drop. Since eqs 7−9 assume that $\mathbf{F}_{\text{magnetic}} \approx 0$, they will calculate an observed surface tension less than the actual surface tension, γ, for experimental setups similar to Figure 1a.

■ RESULTS AND DISCUSSION

Critical Micelle Concentration Data. We used the Du Nouy ring technique to establish a baseline for the CMC's and surface tensions of the magnetic surfactants. These values also helped with the uncertainty analysis of the data obtained from the pendant drop tests. Table 1 contains our CMC values and literature values for comparison. Our values are in good agreement with literature values for C_{16}TAB and MnDDS. The figures of surface tension vs concentration used to calculate our CMC's for all four surfactants are in the Supporting Information, Figures S1−S4.

Table 1. CMC's and Associated Surface Tensions of Tested Surfactants Outside of Magnetic Fields Determined by Du Nouy Ring Method

	this study		literature
surfactant	γ at CMC (mN/m)	CMC (mM)	CMC (mM)
C_{16}TAB	37.2	0.95	0.98 (Rosen[18])
C_{16}TAFe	39.1	0.69	
C_{16}TADy	37.0	0.69	
MnDDS	33.8	1.4	1.2 (Miyamoto[17])

The CMC's for both C_{16}TAFe and C_{16}TADy were 0.26 mM lower than the 0.95 mM for C_{16}TAB. One explanation for this is the much larger counterion size in C_{16}TAFe and C_{16}TADy relative to C_{16}TAB (see Figure 2). The similar CMC's of C_{16}TAFe and C_{16}TADy are consistent with the work of Brown et al., who reported that the CMC's of cationic surfactants do not change significantly between similar magnetically active polyatomic anions.[1]

Uniform Magnetic Field Impact on Surface Tension. Energy transferred to a system by a magnet could have a power-law relationship with the magnetic field strength.[10] Therefore, to see if magnetic field impacts on surface energies, i.e., surface tensions, also have a power-law relationship, we tested three to six uniform magnetic field strengths ranging from 0 to 0.68 T. The results of these multiple field strength tests vs magnetic surfactant solution concentration are in the Supporting Information, Tables S1 and S2. For clarity, Figures 6−9 only show the extreme range of the field strengths: 0 and 0.68 T. The range of changes in surface tension reported in the Supporting Information tables was not large enough to determine if there is, or is not, a power-law relationship with the strength of the magnetic field.

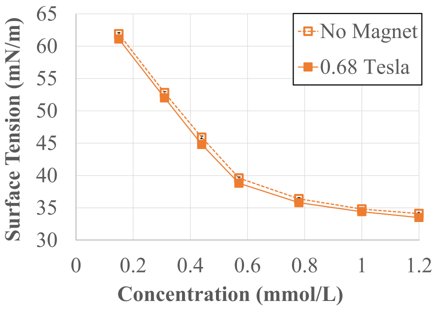

Figure 6. Surface tension decrease of C_{16}TAFe solutions inside of a 0.68 T uniform field. Distance between markers of equal concentration shows the change in surface tension. Error bars contained within markers and denote the standard error of the mean. Lines added to guide the eye.

The results for C_{16}TAFe and C_{16}TADy are in Figures 6 and 7, respectively, with the gap between the empty and filled markers being the magnetic impact on the surface tension from a uniform magnetic field. The data show no observable change in the CMC inside of a uniform magnetic field for either C_{16}TAFe or C_{16}TADy. Also, both C_{16}TAFe and C_{16}TADy show little change in surface tension because of the 0.68 T uniform field, experiencing an average observed reduction in surface tension of 1.7% and 2.1%, respectively. The higher magnetic response of C_{16}TADy is consistent with the higher effective magnetic moment of dysprosium compared to iron. The magnetic moment of Dy^{3+} is 10.65 μ_B while the value for Fe^{3+} is 5.92 μ_B.[19]

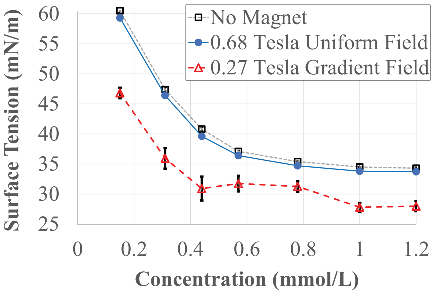

Figure 7. Surface tension decrease of C_{16}TADy solutions inside of a 0.68 T uniform field (filled circles with solid line), in a gradient field of 0.27 T (triangles with dashed line), and in the absence of an external magnetic field (empty squares with dotted line). Error bars denote the standard error of the mean. Lines added to guide the eye.

The reduction in surface tensions for both C_{16}TAFe and C_{16}TADy are not functions of the surfactant concentrations. When comparing a 0.68 T uniform field vs no magnetic field over the concentration range of 0.15−1.2 mM, C_{16}TAFe had an average decrease in surface tension of 1.6% with a st. dev. of 0.3%. Similarly, the decrease in surface tension for C_{16}TADy was 2.1% with a st. dev. of 0.4% for concentrations ranging from 0.15 to 1.2 mM.

MnDDS has a greater response to a uniform magnetic field, Figure 8, than either of the cationic magnetic surfactants. The change in surface tensions ranged from 0.9−2.1 mN/m or an average observed change of −4.2%. This is a 2.5 times greater average change in surface tension (4.2% vs 1.7%) compared to

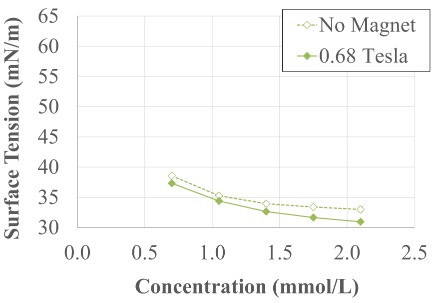

Figure 8. Surface tension decrease of MnDDS solutions inside of a 0.68 T uniform field. Distance between markers of equal concentration shows the change in surface tension. Error bars denote the standard error of the mean. Lines added to guide the eye.

C_{16}TAFe even though Fe^{3+} and Mn^{2+} have the same number of unpaired electrons and, therefore, similar effective magnetic moments. Using a common concentration of 1.0 mM as an example, MnDDS had over 2.2 times greater response to a 0.68 T uniform field compared to C_{16}TAFe, even though the two surfactants had magnetic elements with near identical magnetic moments. Furthermore, the greater change in surface tensions of MnDDS compared to C_{16}TADy is inconsistent with the higher magnetic moment of Dy^{3+} (10.65 μ_B) compared to Mn^{2+} (5.8 μ_B),[19] insinuating that another phenomenon is at play in our measurements of surface tension in response to uniform magnetic fields.

We also exposed the nonmagnetic surfactant C_{16}TAB to the same experimental procedures as discussed above for the magnetic surfactants. The results presented in Figure 9 shows that the 0.68 T uniform field has no significant impact on the solution's surface tension. For most of the data points, there are no statistical differences between the magnetic field data and the no magnetic field data. There appears that there might be a slight increase in surface tension inside the magnetic field. This increase in surface tension is counter to that observed for the magnetic surfactants. Degen et al. also reported a slight increase (0.8%) in the surface tension of the similar but shorter tailed nonmagnetic surfactant C_{12}TAB.[7] The increase in surface tension report by Degen et al. was the same increase they report for pure water, 0.3 mN/m, which is similar to the average difference (0.4 mN/m) between our two data sets in Figure 9 for C_{16}TAB.[7]

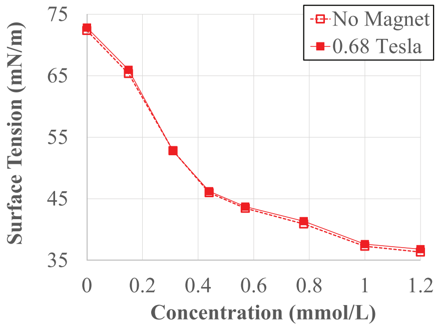

Figure 9. Surface tension behavior of nonmagnetic surfactant C_{16}TAB solutions inside of 0.68 T uniform field. Note that the no magnetic field and 0.68 T field data overlap showing no response. Lines added to guide the eye.

Uniform vs Gradient Magnetic Fields. Figure 6 shows an average reduction in surface tension inside of a 0.68 T uniform magnetic field of 1.7% for C_{16}TAFe. This value is significantly less than the observed reductions reported by Brown et al., who reported a 9.4% reduction for C_{12}TAFe in a 0.44 T field.[20] The difference in observed reduction in surface tensions comes from the type of field used. The Brown et al. experimental setup was similar to Figure 1a. Figure 7 further illustrates the difference a uniform vs gradient magnetic field makes in the observed reduction in solution surface tension. We tested the response of C_{16}TADy (Figure 7) over a range of concentrations via the pendant drop method within both a uniform magnetic field of 0.68 T and a gradient magnetic field of 0.27 T (measured at the attachment of the drop to the dispensing needle) with 0.6 T at the magnet's surface.

Based on the data shown in Figure 7, there is a significant difference in the surface tension observed in the uniform field compared to the gradient field. The uniform field produces observed surface tensions that are reduced by 2.1% compared to a system not exposed to a magnetic field. The gradient field, however, produces considerably lower observed surface tensions at all concentrations despite having less than half the magnetic strength of the uniform field. The observed reductions in surface tensions ranged from 4.7−13.7 mM/m with an average reduction of 19%. The much larger observed reduction in surface tension seen in the gradient field comes from the gradient stretching the drop, thereby, producing a greater change to the shape of the drop. This greater change in shape is consistent with the idea of the drop being pulled downward by bulk magnetic attraction, rather than a phenomenon occurring at the interface. As discussed in the introduction, the gradient field data confounds the bulk paramagnetic fluid effect with changes in the surface tension whereas the uniform field data isolates the magnetically induced change to surface tension.

Correlation between Surface Tension Changes and Magnetic Moiety Degree of Association. The surface tension reductions in a uniform magnetic field of the anionic surfactant (MnDDS) are twice the reductions for the cationic surfactant (C_{16}TADy) even though the magnetic moment of Mn^{2+} is one-half of the magnetic moment of Dy^{3+}. Mn^{2+} and Fe^{3+} have similar magnetic moments; yet, MnDDS has a 2.5 times greater reduction in surface tension compared to the cationic surfactant C_{16}TAFe. As we alluded to earlier, there appears to be an additional phenomenon at play that is complicating the analysis of the magnetic surfactant behavior. We hypothesize that the reason for the discrepancy in the surface tension reductions vs magnetic moments is due to the propensity of the magnetic moiety to dissociate from the amphiphilic portions of the surfactant, leaving it with fewer magnetically responsive moieties than expected. This instability of the magnetic moiety was the focus of our previous study[9] in which we explored the degree of association, α, of the magnetic moiety with the surfactant's amphiphilic structure using solution conductivity, cyclic voltammetry (CV), sampled current voltammetry (SCV), and solution pH measurements. Table 2 gives the average reduction in surface tensions of the representative cationic (C_{16}TAFe) and anionic (MnDDS) magnetic surfactants along with the degree of association, α, of the magnetic moiety with the surface-active moiety.

Table 2. Reduction in Surface Tensions vs the Magnetic Moiety's Magnetic Moment and Degree of Association with the Surfactant's Amphiphilic Structure

magnetic surfactant	average % reduction in surface tension	degree of association, α[9]	magnetic moment
C_{16}TAFe	1.7%	undetectable[a]	5.9 μ_B
MnDDS	4.2%	0.92	5.8 μ_B

[a] Undetectable = the specific conductivity produced a nonquantifiable value for α. Other tests, however, show that the paramagnetic ions do not associate with the surfactant. See Fortenberry et al.[9]

C_{16}TADy has a paramagnetic metal halide counterion. The instability of metal halide ions in aqueous solutions is well documented.[9] Studies of magnetic surfactants with metal halides based on Fe, Co, and Gd found that the metal halide anions of C_{16}TAFe, C_{16}TACo, and C_{16}TAGd do not act as counterions to the cationic surfactants in aqueous tests leading to undetectable degrees of associations between the magnetic moiety and the surface-active moiety.[9]

Based on the degree of association of the magnetic moiety reported in Table 2 and in our previous study,[9] the magnetic moiety is more likely to dissociate from C_{16}TAFe or C_{16}TADy than MnDDS. As a greater fraction of the magnetically active elements dissociates from the surfactant, the response of the interface to external magnetic fields may decrease. As α approaches zero, the magnetic properties of a magnetic surfactant solution approach the behavior of an ordinary paramagnetic fluid. Therefore, the conclusion of Degen et al. that the interfacial and magnetic properties are separate phenomena[7] applies to magnetic surfactant systems with small values of α. Thus, we submit that the interfacial response of a magnetic surfactant to a magnetic field correlates to the degree of association, α. Specifically, MnDDS shows a greater reduction in surface tension within a uniform magnetic field than either C_{16}TAFe or C_{16}TADy even though Mn^{2+} has a much lower magnetic moment than the Dy^{3+}. One potential explanation for this correlation is that magnetic surfactants with high degrees of association, α, may have more magnetic moieties at the interface, allowing for a greater response of the interface to a magnetic field.

■ SUMMARY AND CONCLUSIONS

By using a pendant drop technique to expose magnetic surfactant solutions to both uniform and gradient magnetic fields, we were able to measure magnetically induced changes to the interfacial surface tension independent of the bulk paramagnetic fluid effect. The magnetically induced changes to the surface tension are measurable; however, the changes were small compared to the bulk paramagnetic fluid effects. In the case of C_{16}TADy, the bulk paramagnetic fluid effect created an observed reduction in surface tension of 19% compared to 2.1% reduction when we measured the magnetically induced changes independent of the bulk paramagnetic fluid effect. Furthermore, the magnetically induced changes to the surface tension is a function of the degree of association, α, of the magnetic moiety with the surfactant's amphiphilic structure. For example, even though Fe^{3+} and Mn^{2+} have similar magnetic moments, the magnetically induced change in the surface tension of C_{16}TAFe was 40% of the reduction measured for MnDDS. However, the degree of association, α, for C_{16}TAFe is undetectable while α for MnDDS is 0.92. This suggests a need to rethink the molecular structures used in future research and development of magnetic surfactant applications that moves away from cationic surfactants with metal halide ions[9] toward anionic surfactants such as MnDDS or type II metal surfactants, which have metal chelating surfactant head groups.[22]

We showed that the type of magnetic field (uniform vs gradient), in addition to its strength, determines if the magnetic effect being quantified is the interfacial or bulk paramagnetic fluid effect. Within a uniform field, there is no gradient in field strength to induce a bulk force on the drop, meaning that any changes observed are changes in the interface alone. The reductions in surface tensions, in a uniform field, that we report for the cationic surfactants (C_{16}TAFe and C_{16}TADy) are roughly 1 order of magnitude lower than the values reported by Brown et al. for the analog cationic surfactants exposed to gradient magnetic fields.[1,21] The larger reported reductions by Brown et al. are for a combined interfacial and bulk paramagnetic fluid effect.

Degen et al. previously proposed that in magnetic surfactant solutions the surface-active properties and paramagnetic properties are separate phenomena.[7] We have shown that this proposal by Degen et al. applies to magnetic surfactants with small degrees of association, like the C_{16}TAFe. However, for magnetic surfactants with larger degrees of association, like MnDDS with $\alpha = 0.92$, there is a measurable magnetic interfacial phenomenon in addition to the bulk paramagnetic properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c01215.

> Tensiometer measured surface tension vs concentration results used to determine the CMC values reported in this manuscript and tables of the pendant drop goniometry data for magnetic surfactants within uniform magnetic field strengths ranging from 0–0.68 T (PDF)

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Notes

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