

Low Interfacial Free Volume of Stubby Surfactants Stabilizes Water-in-Carbon Dioxide Microemulsions

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A novel paradigm for the design of surfactants for water/CO₂ (W/C) microemulsions is presented. The paradigm focuses on the fractional free volume (FFV) available to CO₂ at the interface. The FFV is an unambiguous geometric parameter that is calculated directly from surfactant tail geometry and surface coverage. We present an analysis of recent experimental studies indicating that low FFV is a necessary, although not sufficient, condition for W/C microemulsion formation and that both microemulsion and macroemulsion stability correlate qualitatively with FFV. This correlation is understood by noting that a decrease in FFV tends to favor the factors that stabilize W/C microemulsions, namely, decreased interfacial tension, reduced overlap between tails (weakening attractive interdroplet interactions), and increased interfacial curvature. These factors are more challenging to achieve in CO₂ than in alkane solvents, implying that low FFV is especially important for W/C microemulsions.

Introduction

Microemulsions and emulsions stabilized with surfactants at the water/CO₂ (W/C) interface are of interest in protein separation and enzymatic catalysis,^{1,2} heterogeneous organic synthesis and polymerization,^{3,4} synthesis of templated nanoscale materials,⁵ and cleaning of fabrics⁶ and microelectronic devices.⁷ CO₂ is an environmentally friendly substitute for organic solvents commonly used in these processes. However, to date, primarily fluorinated surfactants, including fluoroalkanes^{8,9} and fluoroethers,¹ have been found suitable for forming W/C microemulsions and emulsions. Novel concepts are needed to discover how to design hydrocarbon surfactants for these emulsions, as they are far less expensive and less toxic than fluorinated surfactants.

A variety of strategies have been attempted for the design of both low- and high-molecular weight (MW) molecules that may be used as “CO₂-philic” tails in surfactants. The quadrupole moment of CO₂ has been shown to influence the solubility of certain polar polymers.¹⁰ Possible specific interactions between CO₂ and fluorinated solutes have been investigated by measuring ¹⁹F chemical shifts.¹¹ The strength of such interactions with fluoroalkanes was found to be significant in one *ab initio* study¹² but was much smaller in other studies.^{13,14} O'Neill et al. found that the solubility of polymers increased as their cohesive energy densities decreased, consistent with the extremely low polarizability/density and van der Waals forces for CO₂.¹⁵ Sarbu et al. raised solubilities of copolymers in CO₂ by designing one monomer that had low cohesive energy density and large free volume and a second that provided specific acid–base interactions with CO₂.¹⁶ Such strategies based on polar or specific interactions are being actively pursued. However, they have not

yet led to the design of highly interfacially active hydrocarbon surfactants capable of forming W/C microemulsions, suggesting that the critical factors needed have not yet been delineated and may lie primarily elsewhere. The formation of W/C microemulsions with hydrocarbon surfactants becomes possible with methylation, for example, with surfactant tails including propylene oxide,¹⁷ sodium bis(3,5,5-trimethyl-1-hexyl)sulfosuccinate,¹⁸ poly(ethylene glycol) 2,6,8-trimethyl-4-nonyl ether,¹⁹ or an ethylene oxide–propylene oxide copolymer dodecyl ether.²⁰ However, the fundamental mechanistic reasons for this improvement are not well-understood.

W/C systems differ from traditional oil/water systems with regard to the area per surfactant molecule at the interface. The neat interfacial tension for the W/C interface is typically 20–30 mN/m²¹ versus a much larger value of 50 mN/m for the water–oil interface. The smaller driving force for adsorption at the W/C interface due to lower interfacial tension implies that the area per headgroup will be much larger (typically 100 Å²/molecule)²² than at an oil/water interface (typically less than 50 Å²/molecule), and this difference has been seen experimentally.²¹ As a result of this enormous difference, new strategies will be needed to design surfactants for the W/C interface.

On the basis of recent computer simulations,²³ the energetic interactions between surfactant tails and CO₂ appear similar for an ineffective hydrocarbon and an effective fluorocarbon phosphate surfactant. The only chemical difference between these surfactants is the substitution of hydrogen for fluorine.²³ It is also apparent from the simulations that the fluorocarbon surfactant occupies more space at the interface. Calculations with simple molecular models²⁴ alone show that the fluorocarbon tail occupies 516 Å³ whereas the hydrocarbon occupies only 361 Å³. Because the thickness of the surfactant layers is similar, there is less free volume laterally in the tail region of the fluorocarbon surfactant compared to its hydrogenated analogue. These simulations²³ suggest that the feature distinguishing hydrocarbon and fluorocarbon surfactants is a better separation of CO₂ and water by the bulkier fluorocarbon tails, which leads

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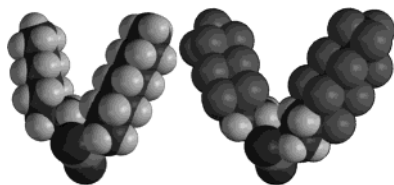


Figure 1. Structures illustrating the difference in free volume in the tail region for a surfactant with relatively high free volume (left, DiH8; FFV = 0.61, see eq 2) and a surfactant with relatively low free volume (right, DiF8; FFV = 0.45). The bulky fluorine atoms in DiF8 decrease the volume available to solvent, compared to DiH8.

to a lower interfacial tension with fluorocarbon surfactants. Figure 1 shows two surfactants with different amounts of free volume in the tail region.

The traditional concept of free volume is an excellent means to quantify the bulkiness of a surfactant. Free volume at an interface would measure how much space is available for CO₂ and water to interpenetrate, lessening the separation and increasing the interfacial tension. Such packing of a surfactant into micelles and microemulsions at an oil–water interface has been considered.²⁵ A useful geometric measure is the Israelachvili ratio, $\eta = V_t/l_t A_h$. This ratio has the structure of an occupied volume. V_t is an approximation of how much volume the surfactant tails occupy, and $l_t A_h$ is an estimate of how much volume is allocated to each surfactant molecule at the interface. In the field of polymer science it has been long recognized that free volume is an important quantity in determining the permeability of polymers.²⁶ Free volume in polymer systems is practically defined as²⁷

$$\text{FFV} = 1 - \frac{1.3V_w}{V_m} \quad (1)$$

where V_w is the van der Waals volume of the polymer and V_m is its molar volume. On the basis of η and eq 1, we can define the fractional free volume (FFV) for a surfactant system to be

$$\text{FFV} = 1 - \frac{V_t}{tA_h} \quad (2)$$

where V_t is the van der Waals volume of the surfactant tail, t is the thickness of the interface, and A_h is the interfacial area per headgroup.

In this article, we propose a new paradigm for microemulsion and emulsion formation and stability in CO₂ based on the effect of surfactant tail molecular architecture on interfacial packing discussed above. We hypothesize that the free volume on the nonaqueous side of the W/C interface (the volume not occupied by surfactant tails) plays a greater role for the W/C versus the water–oil interface. Microemulsion formation involves several important factors, including reducing the interfacial tension to below 1 mN/m,²² achieving the preferred curvature as influenced by the hydrophilic–CO₂-philic balance (HCB),^{21,28} and avoiding a phase separation due to attractive interdroplet tail–tail interactions.²⁹ As explained above, a decrease in FFV lowers the interfacial tension by aiding separation of the very small, penetrating CO₂ molecules from water. Second, stubby surfactant tails with low FFV are needed to increase the area on the tail side of the monolayer to compensate for the unusually large A_h and bend the interface about water. Finally, the overlap of tails by interpenetration on two approaching droplets is reduced with a lower FFV. Minimization of contact between tail segments is especially important in CO₂, given the weak CO₂–tail interactions relative to tail–tail interactions. Even for

surfactants with perfluoropolyether tails with relatively weak tail–tail interactions, interdroplet interactions in W/C microemulsions are about 3 times stronger than for water-in-alkane microemulsions stabilized by AOT (Aerosol-OT, sodium bis-(2-ethyl-1-hexyl)sulfosuccinate).²⁹ For water–oil microemulsions, the magnitude of the FFV is not as important a factor because tail solvation is much more effective, favoring lower interfacial tensions and weaker interdroplet interactions. In W/C macroemulsions interdroplet interactions are the most important factor, as the interfacial tensions do not need to be as low as in microemulsions and the interface is much less curved. In this paper we will use calculated FFV values and experimental data to show that a low FFV is a necessary, although not sufficient, condition for W/C microemulsion formation and that microemulsion and macroemulsion stability are correlated qualitatively with FFV.

Calculation of the Free Volume

To implement a simple calculation of FFV, the interfacial thickness can be estimated as the gas-phase length of the tail. The solvated length may be slightly different from the gas-phase length, but for short tails the difference is small. For double-tail surfactants, the gas-phase length is averaged over both tails. For this simple approximation, we will assume that other factors, such as surfactant tilt relative to the interfacial normal, head-group effects, and differences between the gas-phase length and the solvated length affect all surfactants equally. A better estimate of the thickness of the interface could be obtained from computer simulation at the W/C interface, but our current goal is to avoid this time-consuming approach to develop the conclusions of this study.

Table 1 shows the free volumes calculated using eq 2 for a number of surfactants, assuming a constant interfacial area of 100 Å² per headgroup, consistent with most experimentally measured areas in CO₂. It is reasonable to fix this value, as the goal is to learn how to design surfactant tails for CO₂, not an attempt to consider the totality of surfactant design. The gas-phase lengths have been calculated using geometries derived from molecular mechanics created with SPARTAN.²⁴ The molecule is created with all bonds in a trans conformation. Subsequently, an energy minimization is performed using the classical MMFF94 force field. SPARTAN reports both the length between the headgroup and the last atom in the tail and the volume of the molecule. The position of the headgroup is chosen to be the first oxygen in poly(ethylene glycol) headgroups or the central atom in an ionic headgroup, for example, C for COO[−] and P for PO₄[−].

Surfactant Performance in Microemulsions

Here, we demonstrate a correlation between the FFV and experimental studies of the effectiveness of alternative tails in stabilizing microemulsions. To separate the effects of headgroup on A_h , we examine homologous series of surfactants for a given headgroup type. Note that some of the reported FFV values arise from calculations based on molecules of a potentially slightly different length than those used in the laboratory. These values are noted in the table.

Surfactant performance in W/C microemulsions, that is, higher water-to-surfactant molar ratio (W_o) or a lower pressure (solvent density) requirement, does show a general trend with FFV (see Table 1). All modeled tails that are known to form microemulsions have fractional free volumes less than 0.6. Furthermore, within several classes of surfactant headgroups,

TABLE 1: Calculated Tail Fractional Free Volume (FFV^a) Correlates with Surfactant Performance
W/C Microemulsions

surfactant	FFV	T (°C)	P (bar)	surfactant concentration (wt %)	water dispersed (wt %)	performance ^b	
						uncorrected W_o	corrected W_o (per EO)
Nonionic							
TMN-6	0.52	35	220	1	1.1 ^c	34	3
LS 54	0.57 ^d	35	218	1.45	0.5 ^e	12.3	1.6
C ₈ E ₅	0.71	60	345	2.5	0.52 ^f	4	0.32
C ₈ E ₅ + C ₅ OH ^g	0.71	60	345	2.5	1.9 ^f	15	2.32
Sulfosuccinate							
di-CF4 AOT	0.40	30	120	4.23	2.22 ^h	20	
AOT-TMH	0.42	33	500	4.39		forms reverse micelles ^{i,j}	
AOT	0.49	33	500			no significant aggregation ⁱ	
Other Anionic							
DiF8	0.45	30	148	2.5	2.5 ^k	45	
F ₇ H ₇	0.48	30	127	1.9	1.48 ^l	26	
12–8	0.52	28	149	2.5	2 ^k	34	
PFPE (672 MW) ^m	0.59 ⁿ	30	175	3.0	1.6 ^o	20	
DiH8	0.61					negligible, assumed	
PO ₅ ^p	0.78					negligible, assumed	
Dilute W/C Macroemulsions							
surfactant	FFV	T (°C)	P (bar)	surfactant concentration (wt %)	water dispersed (wt %)	performance ^b	
						stability time	droplet diameter (nm)
PFOMA- <i>b</i> -PEO	0.46 ^q	25	340	1	3 ^r	> 24 h ^s	73
AOT-TMH	0.42	35	310	0.1	1 ^t	> 170 min	50
PFPE (2500 MW) ^u	0.59 ⁿ	35	247	2.68	~5 ^v	~3 min	
M(D'E ₇)M trisiloxane	0.48	10	59	1	1 ^w	1 min ^s	
AOT	0.49				fails		

^a $\text{FFV} = 1 - V_t/tA_h$, where V_t is the van der Waals volume of the surfactant tail, t is the thickness of the interface (estimated as the gas-phase length of the tail), and A_h is the interfacial area per headgroup (assumed constant at 100 Å²). References for the experimental data are noted in the "water dispersed" column. ^b For a microemulsion, the performance value is the uncorrected water-to-surfactant molar ratio (W_0) (and for nonionics, the corrected²⁹ water-to-EO group molar ratio). For a macroemulsion, the value is the time of stability (and for miniemulsions, the droplet size). ^c Reference 19. ^d LS 54 FFV is estimated as $1 - [(1 - \text{FFV}_{n-\text{C}_{12}}) + (1 - \text{FFV}_{\text{PPO}_5})] = 1 - [(1 - 0.79) + (1 - 0.78)]$. ^e Reference 32. ^f Reference 33. ^g *n*-Pentanol cosurfactant (5.8 mol %) was used and is not included in the FFV calculation. ^h Reference 36. ⁱ Reference 30. ^j AOT-TMH also forms a somewhat polydisperse W/C miniemulsion with modest stability. ^k Reference 9. ^l Reference 37. ^m The PFPE structure is $\text{CF}_3-(\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3))_n-(\text{O}-\text{CF}_2)_m-\text{COO}^- \text{NH}_4^+$ with $n \approx 3$ and $m \approx 2$. ⁿ PFPE FFV is calculated for $n = 3$ and $m = 1$ (695 MW). ^o Reference 38. ^p The tail PO_5 is the pentamer of propylene glycol. ^q PFOMA FFV is calculated for a FOMA dimer. ^r Reference 42. ^s Nonfloculated. ^t Reference 18, 0.1 M NaCl. ^u The PFPE structure is $\text{CF}_3-(\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3))_n-(\text{O}-\text{CF}_2)_m-\text{COO}^- \text{NH}_4^+$ with $m = 1$. ^v Reference 40, 5 vol % 0.01 M NaCl. ^w Reference 43.

decreasing FFV is associated with improvement in W/C microemulsion performance.

Tail branching is already appreciated to increase the interfacial activity (lower the interfacial tension) of hydrocarbon surfactants at the W/C interface.^{17–19,30} Because surfactant tails are solvated less effectively by CO₂ than by alkanes, it is more challenging to achieve low interfacial tensions in CO₂-based systems. Thus, tail branching (low FFV) is particularly important for CO₂. Because branched tails are bulkier than linear alkanes, the tails on two approaching microemulsion droplets may be expected to interpenetrate each other less effectively. The resulting weaker interactions between droplets is one element that would lead to a more stable microemulsion. The FFV of nonionic hydrocarbon surfactants is, in fact, shown to decrease as tail branching increases, as seen in Table 1. A branched and highly methylated tail gives Tergitol TMN series poly(ethylene glycol) 2,6,8-trimethyl-4-nonyl ether surfactants a relatively low FFV of 0.52. A 1 wt % solution of TMN-6 (approximately 8 ethylene oxide residues, C₂₈H₅₈O₉) can solubilize a slightly greater amount of water than its own weight, with a W_0 reaching 34.¹⁹ After accounting for the solubility of water in CO₂,³¹ the corrected W_0 is 28. The less-branched ABC triblock LS 54, approximately C₁₂H₂₅-(OCH₂CH₂)₅-(OCH(CH₃)CH₂)₄-OH, forms less-hydrated micelles in CO₂.³² Water solubilization is only 8

molecules for the head block of approximately 5 ethylene oxide residues (EO), which is approximately that amount of water required for EO group hydration alone. The performance of LS 54 (intermediate between TMN-6 and C₈E₅) corresponds with its FFV (also intermediate between TMN-6 and C₈E₅). The straight single C₈ tail of penta(ethylene glycol) *n*-octyl ether, C₈E₅, C₈H₁₇-(OCH₂CH₂)₅-OH, has the second-highest FFV (0.71) of any tail modeled. Significant *n*-pentanol cosolvent and relatively high pressure (345 bar) were required to give a W_0 indicative of microemulsion formation.³³ The cosolvent acts as a cosurfactant, as it is interfacially active. Perhaps by residing in the surfactant tail region,³³ the pentanol blocks some of the W/C interface in this high-FFV system and favors microemulsion formation.

The reason for the versatile and efficient performance of the sulfosuccinate AOT-type surfactants in W/O microemulsions has been studied extensively.^{34,35} Unfortunately, AOT does not form significant aggregates in CO₂ with or without added water, even at high densities (33 °C, 500 bar).³⁰ Though each AOT tail has only a single ethyl substituent, having two of these tails gives AOT a relatively low FFV of 0.49. Replacing the tails with trimethylated or fluorinated straight chains decreases the FFV to among the lowest values found. AOT-TMH (FFV 0.42), sodium bis(3,5,5-trimethylhexyl) sulfosuccinate, dissolves and

forms spherical reverse micelles (33 °C, 500 bar).³⁰ Furthermore, somewhat polydisperse W/C miniemulsions with modest stabilities may be formed with this surfactant.¹⁸ Therefore, the ability of AOT-TMH to stabilize the W/C interface far exceeds that of AOT. Although hydrocarbon sulfosuccinates are not known to stabilize microemulsions in CO₂, dual fluorinated straight C₅ tails enable di-CF₄ AOT (sodium bis(1*H*,1*H*-perfluoropentyl) sulfosuccinate) to form a microemulsion at a relatively low pressure (120 bar).³⁶ This behavior is consistent with di-CF₄ AOT having the lowest FFV (0.40) of any tail modeled.

Fluorination decreases the FFV and improves the water solubilization capability of other anionic surfactants. The highest corrected *W*₀ reported to date, 42, was obtained with the phosphate DiF₈, (C₆F₁₃CH₂CH₂O)₂PO₂[−] Na⁺.⁹ A 2.5 wt % solution disperses its own weight in water, at a fairly low pressure (148 bar at 30 °C). Performing slightly worse under similar conditions, a 2.5 wt % solution of the hybrid phosphate 12-8, (C₁₀F₂₁CH₂CH₂O)(C₈H₁₇O)PO₂[−] Na⁺, disperses 2 wt % water (*W*₀ = 34, uncorrected). As a hybrid, 12-8 has one fluorinated tail and one hydrocarbon tail. The slightly higher FFV of 12-8 (0.52 versus 0.45) corresponds to its lower *W*₀. F₇H₇, the first surfactant reported to form a W/C microemulsion,³⁷ has a similar performance and a similar FFV. The FFV of this hybrid sodium sulfate, (C₇H₁₅)(C₇F₁₅)CHSO₄[−] Na⁺, is taken as the average of the values for DiH₈ (the nonfluorinated analogue of DiF₈) and DiF₈. Slightly higher in FFV (0.59) and lower in performance is a PFPE (perfluoropolyether) carboxylate (672 MW, weight-average), which requires somewhat higher pressure (175 bar) to rival the performance of the phosphate and sulfate surfactants discussed thus far.³⁸ The PFPE structure is CF₃-(O-CF₂-CF(CF₃))_{*n*}-(O-CF₂)_{*m*}-COO[−] NH₄⁺ with *n* ≈ 3 and *m* ≈ 2, and the FFV is calculated for *n* = 3 and *m* = 1 (695 MW). A similar FFV is found for the twin tails of the hydrocarbon phosphate DiH₈, (C₈H₁₇O)₂PO₂[−] Na⁺. Nonfluorinated phosphates have been reported to be unable to support the formation of W/C microemulsions.³⁹ Finally, the highest FFV (0.78) is found for the tail PO₅, penta(propylene glycol), which is related to the PFPE tail. Neither DiH₈ nor PO₅ have bulky fluorine atoms to fill the tail region.

Macroemulsion Performance

The results above show that the readily calculated FFV offers a relatively quick and straightforward method for screening tail structures of small surfactants (MW under ~1000). A correlation of FFV and macroemulsion stability may also be rationalized. Formation of an emulsion requires work to expand the interfacial area between the two phases. Better separation of the bulk phases reduces the interfacial tension (IFT) and the corresponding work required to form an emulsion. Furthermore, the smaller the droplet size, the greater the interfacial area per unit volume and the lower the IFT required for formation. Finally, the contribution of the tails to interdroplet interactions must be sufficiently weak to prevent flocculation.^{40–42} A reduction in tail–tail overlap may be achieved with stubbier tails with a lower FFV. Thus, lower FFV should favor smaller droplets and greater emulsion stability.

Large polymeric surfactants, particularly those with significant side chains, present too many degrees of freedom to simulate repeatably, and a route to an analogue of the FFV is not clear. However, it is interesting to see whether oligomer FFV can be used to rationalize polymer behavior. Treatment of several oligomers shows that FFV is also related to emulsion performance (Table 1). PFOMA-*b*-PEO,⁴² poly(1,1-dihydroperfluorooctyl methacrylate)-*b*-poly(ethylene oxide), and M(D'E₇)M,

a trisiloxane with a head of 7 ethylene oxide residues, ((CH₃)₃-SiO)₂Si(CH₃)(CH₂)₃(OCH₂CH₂)₇OH,⁴³ are the only two surfactants known to form nonfloculated dilute W/C emulsions. PFOMA-*b*-PEO displays greatly superior stability (> 24 h). The FFV for the PFOMA segment is calculated for a FOMA dimer (FFV 0.46) and is similar to that of M(D'E₇)M (0.48). Higher FFV (0.59) and lower emulsion stability (1–3 min, flocculated) are seen for 2500 MW PFPE, which has structure CF₃-(O-CF₂-CF(CF₃))_{*n*}-(O-CF₂)_{*m*}-COO[−] NH₄⁺ with *m* = 1.⁴⁰ (The PFPE FFV is calculated for *n* = 3 and *m* = 1 (695 MW).)

The nonfloculated W/C emulsions formed by M(D'E₇)M⁴³ contrast with the flocculated emulsions formed by other siloxane-based surfactants, such as poly(dimethylsiloxane)-*b*-poly(methacrylic acid) (PDMS-*b*-PMA) and PDMS-*b*-poly(acrylic acid) (PDMS-*b*-PAA).⁴¹ A trimer of dimethylsiloxane has a FFV of 0.64, versus the M(D'E₇)M value of 0.48. Also, AOT fails to stabilize mini- or macroemulsions in CO₂, but as with microemulsions, replacing the 2-ethylhexyl tails with methylated chains decreases FFV and increases interfacial activity. AOT-TMH supports formation of a somewhat polydisperse dilute W/C miniemulsion stable for at least 3 h.¹⁸ Droplets were 50 nm in diameter (number fraction and volume fraction above 99%), with 300 nm and 4 μm droplets forming the remainder. These results further support the utility of the FFV concept. Refinement of this relationship will need to be aided by continuing use of quantitative experimental techniques, for example, turbidimetry, to study emulsion stability.^{18,42–44}

Conclusions

A readily calculated geometric surfactant parameter, the fractional free volume (FFV), has been defined and demonstrated to be remarkably useful in describing the behavior of surfactants at the W/C interface for stabilizing microemulsions and macroemulsions. This parameter builds on the Israelachvili ratio used for micelles and microemulsions and on free volume concepts from polymer science to define a fractional free volume at an interface. Several reasonable assumptions about the structure of the interface have been made to facilitate easy calculation of the FFV purely from the structure of the surfactant. These include the assumption of equal interfacial area per surfactant and the use of minimum-energy tail conformations to estimate the interface thickness. These assumptions allow for an unambiguous comparison of different surfactants. Motivated by computer simulation studies,²³ we have hypothesized that free volume plays an important role in surfactant performance at the W/C interface. A decrease in FFV will, in general, favor the factors that stabilize W/C microemulsions: a decrease in interfacial tension, an increase in preferred curvature about water, and less frustrated overlap between tails, thus weakening attractive interdroplet interactions.

The simulations suggest that free volume is a distinguishing characteristic between hydrocarbon and fluorocarbon surfactants, whereas the interaction energy of CO₂ with the tails and the degree to which CO₂ solvates the tails are not distinguishing. A review of experimental data presented here strongly supports this hypothesis that excellent surfactant performance at the W/C interface correlates with the FFV. This correlation is particularly strong within a series of surfactants with the same headgroup and is relatively strong even when comparing between headgroups. The recently discovered modest activity of certain hydrocarbon surfactants at water/CO₂ interfaces is consistent with their low FFV. Of course, the use of the FFV in isolation is not recommended, as the specific details of key factors such as interfacial tension, tail–tail interactions, HCB, and curvature

effects in a system containing CO₂ molecules can strongly affect surfactant performance. Nevertheless, the new paradigm embodied in the FFV shows great promise to guide the understanding of surfactant behavior and to rationalize the design of new surfactants for emulsions at the W/C interface and at other interfaces.

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