A molecular parameter to scale the Gibbs free energies of adsorption and micellization for nonionic surfactants*

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Abstract

Over the past forty years, there have been many attempts to develop molecular based models for the free energy of adsorption and micellization. Historically, molecular models for C_iE_j surfactants have suggested a correlation between the length of the chemical groups and thermodynamic parameters, e.g. the critical micelle concentration (CMC), the equilibrium constant (K), and the maximum surface concentration (Γ_∞). However, there are no current models to date that satisfactorily capture the large range of C_iE_j chemistry. In this paper, we propose a new thermodynamically consistent model that depends on two simple molecular parameters. More specifically, we combine the well-known linear dependence of CMC and K on the number of carbons, N_C, with a nonlinear dependence on the molecular hydrophobic mass fraction, y_{phob}. An extensive review of the C_iE_j literature is analyzed to parameterize and validate the models. The success of the model is demonstrated by the collapse of all experimental data onto master curves. These models represent the first successful phenomenological theory which is able to collapse a broad range of experimental data for C_iE_j surfactants. Furthermore, the free energy models are capable of predicting the maximum surface concentration at the air-water interface, thus providing a link between the physics of adsorption and self-assembly. This paper summarizes many years of experimental and theoretical understanding of surfactant structure-property relationships for C_iE_j's, and the resulting theory quantitatively explains many hypotheses on the effect of surfactant chemistry on interfacial thermodynamics. This theory is a step towards engineering interfacial thermodynamics by chemical design which enables prediction of interfacial properties of novel surfactants without extrapolation.

Keywords: surfactants, micellization, adsorption, structure-property relationships

1. Introduction

Understanding the link between the chemical structure of surfactants and their fundamental interfacial properties is essential for the design and selection of surfactants for industrial processes. Currently there are no comprehensive correlations between molecular parameters and experimentally determined interfacial parameters, e.g. critical micelle concentration (CMC), maximum surface

*This work is dedicated to the memories of Jacob N. Israelachvili (1944-2018) and Milton J. Rosen (1920-2020), whose pioneering works in the field of surfactant self-assembly [1, 2, 3, 4] and structure-property relationships [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20] laid the groundwork for the field of interfacial thermodynamics.

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concentration (Γ_∞), and the equilibrium adsorption constant (K_x). Several attempts to correlate CMC to molecular parameters using thermodynamic models, e.g. group contribution theory [21, 22, 23, 24, 25, 26] and statistical mechanics [27, 28, 29, 30], have resulted in unsatisfactory comparisons to experimental data. In this paper we demonstrate a simple correlation of thermodynamic parameters with the length of the hydrocarbon chain and the molecular hydrophobic mass fraction.

The most studied model surfactants are poly(ethylene glycol) monoalkyl ethers (C_iE_j) because of their simple chemistry and their use in a broad range of engineering systems [31]. The most successful attempt to correlate CMC of C_iE_j's with molecular parameters is the scaling of CMC with the number of alkyl repeat units, N_C, i.e. the hydrophobe, with a fixed number of ethylene glycol repeat units, N_{EO}, i.e. the hydrophile [32, 33]. However, it has been shown that this scaling does not capture the relationship of CMC with constant N_C and varying N_{EO}, see Figure S1 in the supplementary materials. Note that more complicated scalings with N_C and N_{EO} have been proposed with limited success [34, 24, 4, 35, 36, 37, 38, 39, 32]. However, no scaling to date is capable of broadly capturing/predicting the change in CMC with N_C and N_{EO}.

On the other hand, many studies have attempted to find correlations between the hydophilic-lipophilic balance (HLB) and surfactant properties as a function of chemistry. The HLB is an empirical construct put forth by Griffin in the mid 1950s [40], but does not refer in general to any one specific equation. While Griffin's definition had no thermodynamic rationale, later studies focused on developing an HLB definition that is thermodynamically consistent [41]. While HLB is mostly discussed with respect to emulsion stability, it has been successfully correlated with the CMC of fluorinated and ionic surfactants [42, 43], where the CMC is argued to go as the exponential of HLB. A good resource for HLB correlations can be found in Kruglyakov [41]. The HLB was also used by Israelachvili and co-workers [4] in the derivation of the aggregation number. The majority of HLB definitions show dependencies of key thermodynamic parameters on some relative ratio of the amount of hydrophobe to hydrophile. This work aims to develop consistent equations that capture the effects of N_C and the relative balance between length of hydrophile and hydrophobe to correlate thermodynamic parameters for micellization and adsorption.

We start by defining a new parameter that quantifies the mass fraction of hydrophobe to the mass of the surfactant molecule, y_{phob}. We propose that this parameter characterizes the balance between the hydrophobe and hydrophile for a given surfactant. Note that similar parameters have been proposed in the past [44]. We acknowledge that a partial molar volume could also be used, however, this requires an independent measure of molecular density, not readily available. Historically, our definition of y_{phob} is related to Griffin's original definition of HLB, i.e. HLB $\approx 20\ (1 - y_{phob})$ [40]. It is important to note that this relationship is only explicitly true for Griffin's definition. In the polymer literature, y_{phob} has been used to correlate the micellization propensity of polymers. For example, Widder et al. found that the hydration of an amphiphilic polymer goes inversely with y_{phob} such that interactions with water are favored over micellization [45].

In this paper, we propose a simple functional form of the free energies of micellization, ΔG^{mic}, and adsorption, ΔG^{ads}, on both N_C and y_{phob} with two fitting parameters. A wide range of experimental data for C_iE_j's ($N_C \geq 6$ and $N_{EO} \geq 1$) is aggregated and used to parameterize the models. The models are compared to experimental data, and show a collapse of thermodynamic parameters onto master curves. We then propose a theoretical dependence of Γ_∞ on ΔG^{mic} and ΔG^{ads} considering the Langmuir isotherm. The models for the free energies are tested and validated by comparison with experimental data of Γ_∞. When possible, we present comparisons of the new theory with previously reported models in the literature. Ultimately, we present a simple theory that

is capable of quantitatively explaining observed trends of thermodynamic parameters on surfactant chemistry.

2. Literature Review and Analysis

The surfactant data used in this paper represents a comprehensive set from the scientific literature. All attempts have been made to fully represent the available data for C_iE_j surfactants at the air-water interface at 25 °C, however the authors acknowledge that some data may be inadvertently missed. Among these sources, critical micelle concentrations are by far the most commonly available values. Some works include surface tension isotherms which include the CMC and surface tension as a function of surfactant concentration. Furthermore, dynamic interfacial tension is sometimes available. In the case where isotherm parameters were not reported, the authors digitized the experimental data for the purpose of performing a nonlinear least squares regression of the appropriate isotherm parameters. Table 1 summarizes the various references for surfactant data by chemistry, including the type of available data. Interestingly, there are numerous studies on the same C_iE_j's, while others remain uncharacterized.

The vast majority of studies determine the CMC from surface tension isotherms, i.e. the transition to a zero/small slope of γ versus $\log C$. The surface tension isotherms were measured using Wilhelmy plate [46] and du Noüy ring [47] tensiometers, drop weight method [48], pendant drop/bubble shape analysis [49, 50], and a microtensiometer [51]. Each of these methods have inherent experimental error, however, most sources report high degrees of internal reproducibility. Other methods reported include: calorimetry[52] and spectrophotometry [53]. The deviation between measurement types is expected to be small [53]. Therefore, the largest errors are likely to be derived from: (i) errors in solution concentration, (ii) system impurities/contamination, and (iii) systematic errors. An additional source of error is likely due to surfactant dispersity as a result of synthesis or imperfect purification. For instance, some groups report intensive fractionation to obtain high levels of surfactant purity [13], while others use technical grade surfactants with no purification stage [33]. We have chosen to report all datasets as individual experimental values rather than averaging or applying a filter. These decisions have been made to minimize any introduced bias into the data.

3. Results and Discussion

There are two free energies that govern the thermodynamics of surfactants in solution: the free energy of adsorption ΔG^{ads} and the free energy of micellization ΔG^{mic}. The previous scaling approaches with N_C and HLB suggest that the thermodynamics should depend on both y_{phob} and N_C, such that:

$$\Delta G^{mic} = f(N_c, y_{phob}) \tag{1}$$

$$\Delta G^{ads} = g(N_c, y_{phob}) \tag{2}$$

More specifically, f and g are both expected to depend linearly on N_C [39, 6, 32]. There is currently no proposed functional form of the dependence of f and g on y_{phob} that consistently captures experimental data for a wide range of C_iE_j chemistries.

Table 1: References to Experimental Data for Surfactant Thermodynamic Parameters

N_{EO}	N_C					
	6	8	10	12^4	14	16^4
1		[48][2] [54][3] [55][3]		[56][3] [54][3]	[57][2]	
2				[13][2] [56][2]	[57][2]	
3	[47][2] [58][3] [59][3] [54][3] [60][3] [55][3]	[58][3] [59][3] [54][3] [55][3]	[58][3] [61][3] [23][3] [55][3]	[13][2] [54][3] [55][3]	[57][2] [55][3]	[55][3]
4	[47][2] [53][3] [59][3] [54][3]	[59][3] [52][3] [55][3]	[53][2] [62][2] [59][3] [63][2] [64][3] [54][3] [24][3] [49][1] [50][1] [65][2]	[13][2] [59][3] [56][3] [54][3] [55][3] [46][2] [50][1] [66][2]	[54][3] [57][2]	
5	[47][2] [54][3] [60][3] [55][3]	[59][3] [54][3] [60][3] [52][3] [55][3]	[53][3] [61][3] [23][3] [60][3] [49][1] [55][3] [46][2]	[53][2] [67][2] [13][2] [59][3] [23][3] [49][1] [68][1] [55][3] [46][2]	[55][3]	
6	[47][2] [69][2] [61][3]	[70][3] [58][2] [61][3] [23][3] [55][3]	[53][2] [58][3] [61][3] [23][3] [71][2]	[70][2] [53][2] [58][3] [61][3] [59][3] [64][3] [63][2] [23][3] [55][3] [72][1] [50][1]	[61][3] [23][3]	[70][3] [53][2] [61][3] [23][3] [55][3]
7			[73][3]	[67][2] [13][2] [23][3] [55][3]		
8		[55][3]	[74][3] [75][2] [23][3] [49][1] [55][3] [51][1]	[74][3] [75][2] [13][2] [63][2] [64][3] [23][3] [49][1] [55][3] [50][1] [51][1]	[74][3] [75][2] [23][3] [55][3] [57][2] [50][1] [51][1]	[54][3] [55][3]
9		[58][3] [23][3] [55][3]	[58][3] [61][3] [23][3] [50][1]	[67][2] [23][3] [55][3] [76][1] [66][2]		[53][2] [23][3]
10				[55][3]		[77][3] [55][3]
12				[67][2] [55][3]		
13				[55][3]		
14			[71][2]			

[1]Dynamic and equilibrium surface tension data
[2]Equilibrium surface tension data
[3]Critical micelle concentration only
[4]Further critical micelle concentrations obtained from Esumi [33] for N_{EO} ranging from 9 to 63.

We introduce a new parameter defined as the molecular mass fraction of the hydrophobic moiety, y_{phob}, such that:

$$y_{phob} = \frac{M_w^{phob}}{M_w^{phob} + M_w^{phil}} \tag{3}$$

where M_w^{phob} is the molar mass of the hydrophobic moiety, i.e. the alkyl carbons, and M_w^{phil} is the molar mass of the hydrophile, i.e. the ethylene glycol groups and terminal hydroxide. For C_iE_j, M_w can be simply defined using the number of alkyl carbons, N_C, and the number of ethylene glycol units, N_{EO}:

$$M_w^{phob} = 14.027\ N_C + 1.008 \tag{4}$$

$$M_w^{phil} = 44.053\ N_{EO} + 17.007 \tag{5}$$

$$y_{phob} = \frac{14.027\ N_C + 1.008}{14.027\ N_C + 44.053\ N_{EO} + 18.015} \tag{6}$$

y_{phob} will be used to determine the appropriate scaling of the Gibbs free energy of adsorption and micellization for the collected data on C_iE_j surfactants.

3.1. Critical Micelle Concentration

The free energy of micellization, defined as the change in free energy required to self-assemble molecules into a micelle, ΔG^{mic}, can be written in terms of the mole fraction of surfactant at the critical micelle concentration, x_{CMC}:

$$f = \Delta G^{mic} \approx RT \ln(x_{CMC}) \approx -RT\alpha \tag{7}$$

where $RT\alpha$ is defined by Israelachvili as a monomer-monomer 'bond' energy in the aggregate relative to the free monomer in solution [4]. Specifically, $RT\alpha \approx \mu_1^0 - \mu_N^0$, where μ_1^0 is the standard state chemical potential of a surfactant monomer in solution, and μ_N^0 is that of a surfactant in a micelle. Note that the approximation above is in the limit of the free monomer concentration approaching $x_{CMC} = e^{-\alpha}$ and thus does not depend on micelle dimensionality [4]. See the supplementary material for the detailed derivation. Two fundamental relationships between x_{CMC} and the size of the hydrophobe/hydrophile have been proposed based on empirical correlations: the Klevens equation [35],

$$f = A + B \cdot N_C \tag{8}$$

and the more general equations proposed by Becher and Ravey and co-workers [37, 38]

$$f = A + B \cdot N_C + C \cdot N_{EO} + D \cdot N_C \cdot N_{EO}, \tag{9}$$

for C_iE_j surfactants. Note that both equations include a term with a linear dependence on N_C.

While these equations, particularly (9) can be empirically fit to correlate x_{CMC}, there are several drawbacks to this model: (i) there are four fitting parameters which cannot be determined *a priori* and (ii) a good fit requires that the fitting parameters depend on N_C and/or N_{EO}. For example, several studies[8, 75, 36] show that the values of A and B in (8) depend nonlinearly on N_{EO}. This fact is demonstrated in Figure S2, where a single Becher-Ravey equation has been fit to all available x_{CMC} data. The equation particularly fails at large N_{EO} and would require additional parameters or coefficients which depend on N_C and/or N_{EO} to quantitatively capture the entire experimental dataset. Furthermore, this model is by definition only good for interpolation and should be fit many times to small ranges of data to ensure a good fit.

Instead, we start from the thermodynamic relationship in (7) and parameterize the free energy based on the chemical structure. We propose a superposition of the contributions from N_C and a power law scaling with y_{phob} such that $f \sim \ln(y_{phob}^n) + k\ N_C$, where k relates to the incremental

contribution of methylene groups added to the hydrophobe. Several studies have empirically determined a value of k, which will be discussed below [8, 75, 58]. In order to determine the coefficients n and k, data is grouped with constant N_C and fit by linear least squares regression. The best fit lines for constant N_C are shown in Figure S3. This approach allows for a power law to be determined without assuming a fixed value for the dependence on N_C. The best fit parameters are $n = -1 \pm 0.35$ and $k = -1.2 \pm 0.01$. Note that the errors represent the standard deviation of the best fit parameters. The average coefficients are plotted along with all datasets in Figure 1a. The model is in excellent agreement with all datasets for $i < 16$. For $i = 16$, the average model parameters under predict the data, which could be due to the technical grade surfactants used in these studies [33]. Figure 1b shows a master curve for all C_iE_j for the average model parameters. The master curve clearly captures the effect of both changing N_C and N_{EO} and shows quantitative agreement for most experimental datasets.

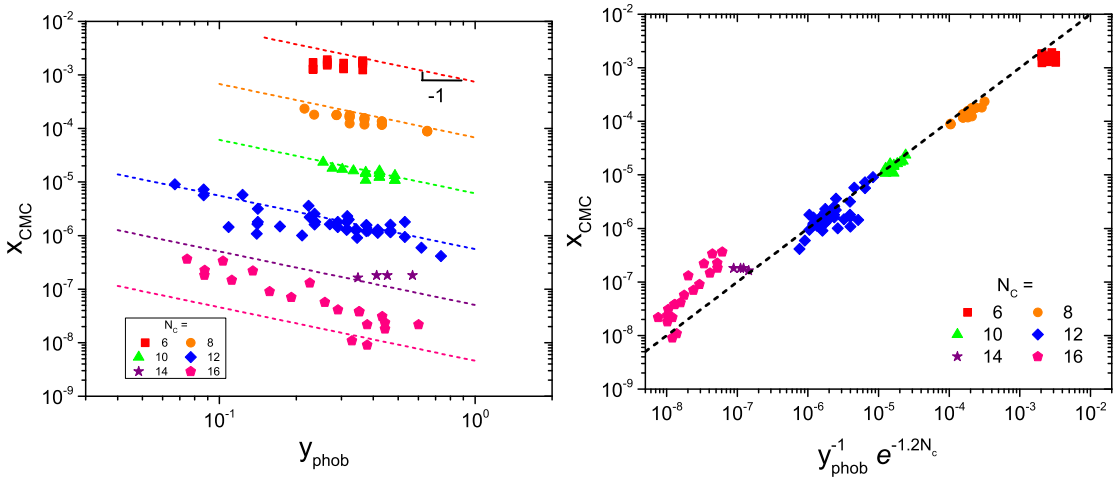

Figure 1: Critical micelle concentration as a function of (a) y_{phob} and (b) the proposed scaling. Lines in (a) represent the determined power law scaling of $n = -1$ and $k = -1.2$ while the line in (b) represents (10). The data are shown in log scale for clarity.

The agreement between the data and scaling suggests a functional form of:

$$x_{CMC} = y_{phob}^{-1} \ \exp\left(-1.2 N_C\right), \tag{10}$$

$$f = \Delta G^{mic} = -RT \ \left(\ln y_{phob} + 1.2 N_C\right) \tag{11}$$

This model incorporates the original arguments that the interaction energy scales with the length of the hydrophobe as well as the suggestions of Israelachvili and others that the interaction energy should scale with the mass (or volume) of the hydrophobe [4], including arguments for the HLB [42, 43]. The value of $k = -1.2$ is in very good agreement with the works of Rosen and Meguro et al., who obtained a hydrophobe contribution to ΔG^{mic} of $-1.12RT$ and $-1.15RT$ per methylene group, respectively [8, 75]. Corkill et al. admit that the value of k is difficult to determine due to experimental error, but that it is on the order of unity [58]. This value is slightly lower than what

is expected of a pure alkane chain, which has a factor of about 1.5 per added $-CH_2-$ [39]. This supports the arguments of Aniansson that the free energy reduction for added $-CH_2-$ is lowered by the proximity of the hydrophile to the micellar core [78, 4].

Equation (11) suggests that the hydrophobe and hydrophile contribute separately to the free energy of micellization, i.e.the hydrophile contributes $-RT \ln y_{phob}$, and the hydrophobe contributes $-1.2RTN_C$. However, it is not possible to change N_C without affecting both the contribution of the alkane chain and the hydrophile. In other words, an increase in N_C by unity corresponds to an increment in α of 1.2. Subsequently for a constant N_C, an increase in α by 1.2 corresponds to a factor of four decrease in N_{EO}. This strongly supports the arguments in the literature that suggested the hydrophile decreases the propensity of the hydrophobe to phase separate [58, 79]. From this it is clear that engineering a surfactant system for a desired x_{CMC} can be easily achieved by varying N_C compared to varying N_{EO}. This is consistent with dominance of hydrophobe interactions in the micellar core [4]. Furthermore, the dependence of x_{CMC} on y_{phob} captures the tendency for the hydrophile to resist micellization and agrees with the volume arguments for the free energy derived by Kumar and Tilton which relates x_{CMC} to the volume fraction of hydrophobe in a micelle, which is analogous to y_{phob} [80].

As discussed above, the Becher-Ravey equation was not able to fit the entire dataset. For comparison, the mean error of the Betcher-Ravey equation for all x_{CMC} data is 280%, while the mean error for (10) is 35%, see supplementary for additional details. This demonstrates a significant improvement in molecular modeling for CMC.

Another important aspect is the effect of temperature on CMC. Figure 2 shows a small dataset for x_{CMC} at various temperatures plotted versus the proposed scaling determined at 25°C. The data span a moderate range in both N_C and N_{EO} as compared to Figure 1b. It is clear from Figure 2 that the model shows good agreement with different x_{CMC} measured at different temperatures. However, there is clearly a systematic deviation with increasing temperature, which suggests that one or more parameters may depend on temperature. The most likely parameter to depend on T is the methylene interaction coefficient k. This is supported by the fact that the hydrophile is known to dehydrate with increasing temperature, which would increase the interaction energy of the hydrophobe towards that of a pure alkane chain, i.e. $k \to -1.5$ with increasing T [32]. In any case, the change would need to be very small. The model is expected to fail at a temperature driven phase change, i.e. cloud point.

3.2. Adsorption Isotherm Parameters

The free energy of adsorption, defined as the change in free energy required for a molecule to adsorb to an interface, is generally written as,

$$g = \Delta G^{ads} = -RT \ \ln K_x \tag{12}$$

K_x represents the dimensionless equilibrium constant in terms of mole fraction, e.g. for a first order kinetic model, i.e. the Langmuir rate equation, K_x becomes, [81, 82]

$$K_x = \frac{\Gamma}{x \cdot (\Gamma_\infty - \Gamma)} \tag{13}$$

where Γ is the surface concentration of surfactant, Γ_∞ is the maximum surface concentration, and x is the solution mole fraction. Note that the measure of K_x is model dependent. For simplicity,

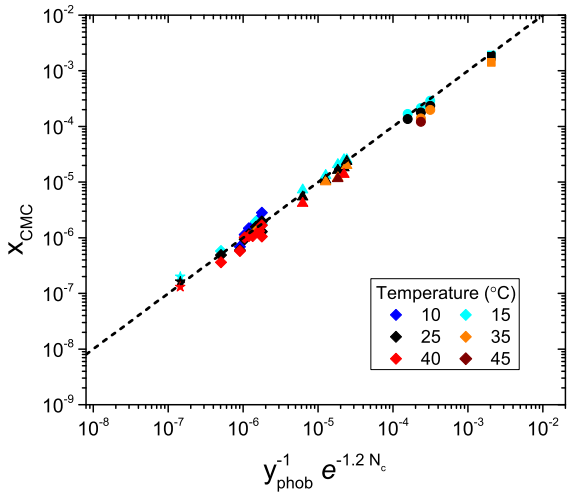

Figure 2: Critical micelle concentration for a select dataset as a function of the proposed scaling at different temperatures. Symbols correspond to different N_C as shown in the legend of Figure 1b. Data were obtained from [13, 70, 58, 74]. The dashed line represents (10).

we determine K_x from experimental data using the Langmuir-von Szyszkowski equation of state (EOS), given by

$$\gamma = \gamma_0 - RT\Gamma_\infty \ln(1 + x \cdot K_x) \tag{14}$$

where x is the bulk surfactant mole fraction, γ_0 is the pure interfacial tension (72.01mN/m for $T = 298.15$ K [83]), and Γ_∞ is the maximum surface concentration (a.k.a. the ideal monolayer concentration). While this EOS does not necessarily capture all the equilibrium adsorption physics of C_iE_j's [50], it fits C_iE_j's adsorption isotherms sufficiently well (see Figure S4). Furthermore, the development of more realistic physical models of interfacial kinetics has occurred over the many years since Langmuir's idealized interface [84]. However, the choice of the Langmuir equation of state is made because of: (i) its common use in describing surfactant phenomena [32, 85], (ii) its efficacy in capturing surface tension over the entire useful concentration range, and (iii) its simplicity. The Langmuir isotherm includes only two parameters, which physically correspond to the physics of adsorption. Although the Langmuir isotherm is often considered restrictive with regards to its assumptions (based on a lattice model), trends in parameters with molecular structure represent a good estimate of relative effects. More advanced isotherms could be evaluated in a similar manner, however additional parameters increase the level of uncertainty of fitting and effect the principle adsorption parameters unpredictably. Furthermore, the functional form of the free energy of adsorption for higher order isotherms depends on multiple equation of state parameters implicitly [86], making determination of ΔG^{ads} from experimental surface tension data convoluted. By contrast, the Langmuir isotherm used in this work allows for a single measured parameter dependence of ΔG^{ads}, i.e. K_x.

One might propose that K_x scales with either N_C or N_{EO}. However, Figure S5 shows very clearly that K_x does not scale with either. Instead, if we follow from Rosen that the free energies of micellization and adsorption should have analogous functional forms [8], then $g \sim \ln(y_{phob}^m) + k'N_C$, i.e. K_x should scale with some power law in y_{phob} and some linear contribution of N_C. The

dependence of ΔG^{ads} on N_C has been determined previously by Rosen to be $k' = -1.035$ per hydrophobe carbon for C_iE_j's [8, 32] and by Kumar and Tilton to be $k' = -1.375$ [80] illustrating that the contributions to the free energies of micellization and adsorption are not significantly different within the uncertainty of surface tension measurements. Note that this value may be dependent on chemistry, for example Rosen suggests a value of $k' = -1.522$ for ionic surfactants [32]. Unfortunately due to the limited concentrations measured in the literature, there are not sufficient data to determine both k' and m. In order to reduce this uncertainty, we set the coefficient in the interaction energy of the hydrophobe equal to that of ΔG^{mic}, i.e. $k' = k$. The fits are shown in Figure S6 with an average power law in y_{phob} of $m = -4.9 \pm 0.5$. Good fits are achieved for both datasets, however due to the restrictive number of points and narrow range of y_{phob}, the best-fit model values may change with a larger dataset.

Fig. 3a shows the model prediction using the average value of m for four datasets of constant N_C. The model sufficiently captures both the effect of N_C and y_{phob} for all datasets. Figure 3b shows a master curve of K_x for a small dataset of C_iE_j's with different N_C and y_{phob}, suggesting the functional form:

$$K_x = y_{phob}^{-4.9} \exp(1.2N_C) \tag{15}$$

$$g = \Delta G^{ads} = -RT(-\ln y_{phob}^{4.9} + 1.2N_C). \tag{16}$$

It has been shown that fitting K_x to limited ranges of γ versus C lead to erroneous values due to the difficulty in assuring unique fits [87, 88]. Therefore, Figure 3 only considers reliably measured values of K_x, i.e. where γ versus $\log C$ was measured to sufficiently low concentrations to confidently fit the value of K_x. More details are discussed in the supplementary material. Figure S9 shows comparison and good agreement of the model to the entire K_x dataset, with some expected outliers. This functional dependence on y_{phob} is in good agreement with the exponential dependence of ΔG^{ads} on the hydrophile suggested by Rosen [32]. However, (15) disagrees with Kumar and Tilton who suggested that K_x is only a function of N_C [80].

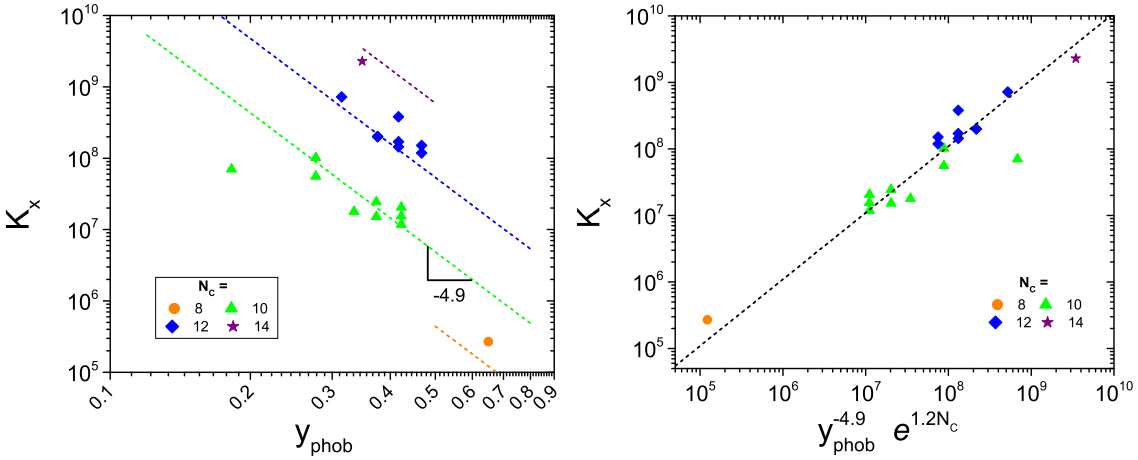

Figure 3: Adsorption equilibrium constant as a function of (a) y_{phob} and (b) the proposed scaling. In (a) lines represent power laws of $m = -4.9$. The dashed line in (b) represents (15).

The models described above allow for physical insight into adsoprtion and self-assembly thermodynamics. Equation (16) indicates that ΔG^{ads} increases with increasing y_{phob}, while ΔG^{mic} decreases with increasing y_{phob}. This implies that the adsorption interaction energy becomes less favorable for larger y_{phob} compared to the micelle interaction energy which becomes more favorable. Furthermore, unexpectedly, the equilibrium constant decreases with increasing y_{phob} and constant N_C, meaning desorption is more favorable for hydrophobes larger than the hydrophile. The dependence on N_C demonstrates a decreasing ΔG^{ads} for increasing N_C. We postulate that this is due to the attractive interactions between adsorbed hydrophobes at the interface. By setting $k' = k$, we are suggesting that the molecular interactions in the micellar core (closely packed) are similar to that of the adsorbed (spread) state [89]. This is due to the hydrophobe's influence on the phase separation of surfactant to the interface, suggesting that the hydrophobe length equally drives the surfactant molecule to either micellize or adsorb, whichever removes the hydrophobe from solution. The hydrophile increases the propensity for adsorption with increasing N_{EO}. In other words, there is a competition between forces: the hydrophobe driving adsorption and the hydrophile remaining in solution. Our results agree with Huston and Larson, who show that in the dilute regime, a decrease in y_{phob} increases the affinity of the surfactant for the interface, i.e. makes the free energy more negative [90]. Huston and Larson suggest that this effect is solely due to increasing N_{EO}. However, Figure S7b clearly shows that both N_C and N_{EO} contribute to this affinity. Ultimately, we find that it is the relative length of N_{EO} to N_C, i.e. y_{phob}, that effectively scales the data. One physical explanation for these observed trends is that the magnitude and sign of the adsorption free energy depends on the hydration of the hydrophobe at the interface, which depends on the both N_{EO} and N_C [91]. More specifically, the smaller the y_{phob}, the more hydrated the hydrophobe remains at the interface, which requires a lower energetic penalty, i.e. smaller ΔG^{ads}. For larger y_{phob}, the hydrophobe is significantly more dehydrated at the interface, which is less energetically favorable since it restricts the entropy of the hydrophile. These thermodynamic arguments are in line with Heusch, who hypothesized that the orientation/penetration of the interface by the surfactant is directly related to Griffin's HLB, i.e. y_{phob} [92]. These arguments would benefit from further molecular dynamic simulations.

The remaining thermodynamic parameter, Γ_∞, has seldom been correlated to molecular parameters. By definition Γ_∞ is denoted by the asymptotic value of the Gibbs EOS, i.e. the slope of $d\gamma/d\ln C$ near the CMC. This value of Γ_∞ is model independent. Note that Γ_∞ determined from nonlinear isotherms with additional parameters does not necessarily equal the Γ_∞ determined from Gibbs EOS, e.g. [50]. The Langmuir isotherm on the other hand does capture the value of Γ_∞ from Gibbs EOS quite well. Γ_∞, as determined by the experimental slope or the Langmuir isotherm, is a function of the molecular area, the orientation of the molecules at the interface, and any interfacial interactions [32]. We are looking for a correlation between these effects on Γ_∞ and molecular structure.

One might correlate Γ_∞ from a simple molecular area argument, similar to the aggregation number in self-assembly [4], or using MD simulations [86]. One particular study, using a limited dataset of C_iE_j chemistries, showed that the change in molecular packing was related to hydrophile coiling, i.e. smaller Γ_∞ for higher N_{EO} [93]. This conformational change of ethylene glycol units is known to occur at $N_{EO} \approx 9$ due to attraction between oxygen atoms [44]. The overall size of these coils, and therefore their effective area $1/\Gamma_\infty$, increases with increasing N_{EO}. Sedev proposes a relationship between Γ_∞ and N_{EO}, considering polymer scaling laws for the radius of gyration of an ethylene oxide chain with length N_{EO}, i.e. $\Gamma_\infty \sim N_{EO}^{-1/2}$ [80, 94]. This dependence only considers the hydrophile and ignores the role of the hydrophobe. However, Sedev showed examples

of the scaling prefactor which was argued to depend on N_C [94]. Figure S7 tests these hypotheses using a large dataset. While Figure S7b shows a clear dependence on N_{EO}, Figure S7a confirms Sedev's arguments of a slight dependence of Γ_∞ on N_C. It is evident that an appropriate model for Γ_∞ must depend on both N_C and N_{EO}.

Instead of using a molecular area argument, we follow the derivation proposed by Rosen [6, 32], whereby the equation of state is evaluated at a concentration which leads to a fixed surface pressure. Here, we evaluate the isotherm at a fixed concentration, x_{CMC}, which leads to a surface pressure, Π_{CMC}, using (14) [8]. For all C_iE_j's reported here, $x_{CMC} \cdot K_x \gg 1$. Therefore, (14) can be rearranged in terms of the free energies:

$$\Gamma_\infty \approx \frac{\Pi_{CMC}}{(f-g)} \approx \frac{\Pi_{CMC}}{RT\ (\ln y_{phob}^{-5.9})} \tag{17}$$

where f and g are given by (11) and (16), respectively (see supplementary material for the detailed derivation). Note that this result strongly depends on the chosen isotherm, e.g. a similar, but different result was found analytically for the Brunauer–Emmett–Teller (BET) isotherm [95]. One important similarity between our result and the BET isotherm is that both result in Γ_∞ being a function of the difference in free energies [95].

Equation (17) depends on the value of Π_{CMC}, which may be a function of molecular parameters. Figure S8 shows the dependence of Π_{CMC}/RT versus y_{phob}. For all C_iE_j's, $\Pi_{CMC}/RT \approx 1.6 \times 10^{-5}$ mol/m^2, and for the purpose of this study Π_{CMC} is assumed to be a constant. Thus, (17) becomes:

$$\frac{10^{-6}}{\Gamma_\infty} \approx -0.369 \ln y_{phob} \tag{18}$$

This implies that $1/\Gamma_\infty$ goes with $\ln y_{phob}$ only. Figure 4 shows a master curve of $1/\Gamma_\infty$ as a function of $\ln y_{phob}$ for all surfactants compared to the prediction of (18). Equation (18) shows very good agreement with experimental trends, validating the assumptions and the free energy models discussed above. Note that if $k' \neq k$, then (18) would have an explicit term for N_C. One test of the assumption that $k' = k$ is to fit the k' values independently to the datasets and use them in the analysis, which would give $k' = -1.5$ and $k = -1.2$. We found that when $k' \neq k$, the model does a significantly poorer job of capturing the Γ_∞ data. Although this is not proof that $k' = k$, we expect that their values are very similar and certainly within the error of the data. One limit to the applicability of the model for Γ_∞ is the assumption that Π_{CMC} is a constant for all chemistries. Relaxing this assumption and using Π_{CMC} as a function of y_{phob} and N_C would likely improve agreement.

Previous molecular models and hypotheses for Γ_∞ have argued for an explicit dependence on N_{EO} [80, 96, 94, 93]. In contrast, our model argues that the hydrophobe contributes to the maximum surface concentration of a given C_iE_j surfactant at the air-water interface. This directly contradicts the arguments of Schick that the absolute size of the hydrophobe does not contribute to the monolayer density [93]. Furthermore, we can directly compare the data presented in Figure 4 to previous models depending only on N_{EO}. Figure S7b compares Γ_∞ as a function of N_{EO} to the model, $\Gamma_\infty = 1/(19N_{EO}^{1/2})$ detailed in Kumar and Tilton [80], which consistently over predicts the experimental data. The better agreement observed with y_{phob} suggests that the hydrophobe influences the packing density at the interface and thus a simple molecular area argument is not sufficient to capture the data. Instead, Γ_∞ more generally depends on the molecular cross-section, interactions between adsorbed molecules, and the configuration of the adsorbed molecule. For the

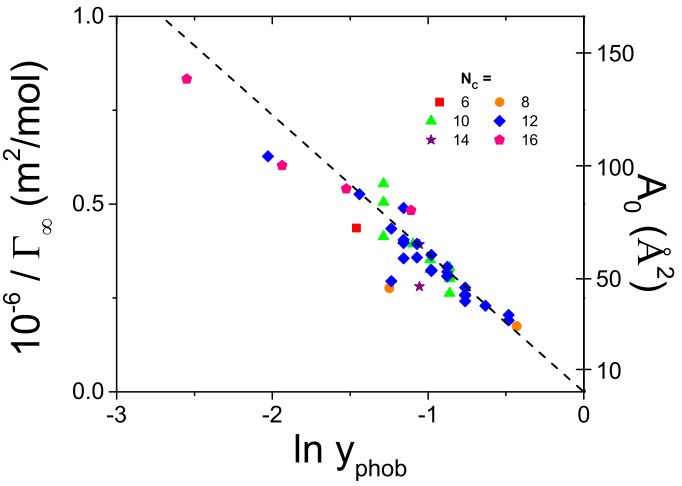

Figure 4: Maximum surface concentration as a function of $\ln y_{phob}$. A_0 represents the effective interfacial area occupied by one surfactant molecule, i.e. $A_0 = 1/(N_A\ \Gamma_\infty)$ where N_A is Avogadro's number. The dashed line represents (18).

case of C_iE_j's, these effects are all accounted for by $\ln y_{phob}$. Physically, this translates to more hydrophobic molecules packing more tightly at the interface.

4. Conclusions

The field of interfacial thermodynamics has always relied on empirical relationships and trial and error correlations. The literature has long proposed that the free energies of micellization and adsorption should be a function of N_C or HLB. Many attempts have been made to generate a model that can capture experimental data. In this paper, we propose models that combine HLB, via y_{phob}, and N_C to capture the effect of surfactant chemistry on adsorption and micellization thermodynamic parameters. We demonstrate that the models for x_{CMC} and K_x are capable of collapsing all surfactant data onto master curves. Furthermore, the resulting models for ΔG^{mic} and ΔG^{ads} are validated by their ability to predict the dependence of Γ_∞ on y_{phob}.

There are several advantages of the proposed models over existing empirical models. For example, the leading empirical equation for x_{CMC}, i.e. Becher-Ravey correlation, was not able to fit the entire dataset. Furthermore, the model presented here is capable of both interpolation and extrapolation to previously unmeasured surfactant chemistries. This allows for the prediction of the CMC of novel C_iE_j molecules, particularly larger N_{EO} surfactants. This is a great improvement over previous empirical models, group contribution models [24], and molecular dynamics [29] approaches, especially considering the significant reduction in parameters and computational expense.

Another advantage to the proposed models is that many hypotheses are quantitatively explained as a function of surfactant chemistry. For example, it has long been argued that the interaction of surfactants in a micelle is strongly dominated by the hydrophobe [32], however others have argued that the hydophile contributes opposition to micellization [80]. Our model confirms the linear dependence of ΔG^{mic} on N_C as well as the importance of the length of the hydrophile, via y_{phob}. More specifically, the model combines the contributions of the hydrophile and hydrophobe to the CMC.

The choice of surfactant for targeted x_{CMC} is controlled mostly by N_C. The model holds at various temperatures and suggests a very small temperature dependence of the interaction parameter of alkane chains, i.e. the N_C prefactor. With regards to adsorption physics, several studies propose that both the hydrophobe and hydrophile drive adsorption, which is not readily obvious [90]. Our model confirms that ΔG^{ads} explicitly depends linearly with N_C and is also a strong function of N_{EO}, via y_{phob}. As hypothesized, the contributions of the hydrophile and hydrophobe both increase the rate of adsorption and/or decrease the rate of desorption of the molecule, i.e. larger equilibrium constant. Lastly, previous theories have suggested that the maximum packing at the interface is only determined by the cross-sectional area contributed by the hydrophile [94]. Our model shows that Γ_∞ is a function of only y_{phob}, and thus the length of the hydrophile and hydrophobe affect the area occupied by the molecule at the interface in a non-trivial way.

This paper summarizes years of effort toward structure-property relationships in nonionic surfactants, particularly highlighting a large collection of data and previous theoretical and empirical models for C_iE_j's. We demonstrate that interfacial thermodynamics is capable of properties by chemical design. We have shown that the targeting of surfactant properties can be achieved by changes in both N_C and y_{phob}. The proposed model allows us to screen values of x_{CMC}, K_x, and Γ_∞ based simply on chemistry, meaning the entire range of surface tensions can be predicted from molecular structure alone. This also allows for targeted selection of surfactants for desirable transport performance. One example is that experiments can be designed with different surfactants where the thermodynamics are kept constant, but the diffusion coefficient is very different. Therefore, different surfactants with the same thermodynamics can be tested in a range of applications to determine the importance of transport timescales on process efficacy [97, 98].

Our model introduces a formalism that can be easily applied to other surfactant systems, broadening the community's ability to correlate structures with properties. For example, we have already shown that for nonionic polyglycol surfactants the differences in free energy also depend on y_{phob} and N_C [99, 100]. However, it must be stated that these models are based on certain assumptions that might restrict their generality. For example, we expect that the difference in free energy of adsorption and micellization will depend on other aspects of surfactant chemistry, e.g. ionization states for charged surfactants [33]. Future studies will examine whether these simple models can be applied to surfactants with strong surface interactions and complex architecture.

Acknowledgement

This material is based upon work supported by the National Science Foundation under Grant No. 1847140.

Appendix A: Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:

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