Methodological Approach To Selecting State Equations And Adsorption Isotherms

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The selection of the state equation and adsorption isotherm is based on the fit between the theoretical and experimental values of surface tension. From this, properties such as surface concentration (Γ) are calculated, which is necessary for determining the surfactant concentration needed to cover a given surface area. An incorrect calculation of the property above could lead to a mischaracterization of a formulation and possibly to the detriment of the surfactant's performance due to a possible underestimation of ϵ_0. Consequently, many of the conclusions that could be drawn from a study may need to improve the analysis of results due to the value of the surface concentration which is not closest to the real one. A necessary condition that a state equation and an adsorption isotherm must meet is the prediction of surface tension values. However, this is not a sufficient condition, which is obtained by comparing the values of elasticity at infinity with those predicted by the state equation and adsorption isotherm. How the state equation and the adsorption isotherm are chosen is essential in analyzing interfacial phenomena. This work presents the methodology to select the state equation and adsorption isotherm based on predicting surface tension values and elasticity at infinite frequency, ϵ_0.

Keywords: surface tension; state equation; adsorption isotherm; elasticity at infinite frequency

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1. Introduction

The theoretical description of surfactant adsorption at an interface is accomplished through an adsorption isotherm, which relates the equilibrium surfactant concentration (c) to the amount of surfactant adsorbed on the surface (Γ). This is coupled with a state equation that relates the surface pressure (Π) to the adsorbed amount (Γ). This combination is crucial for describing the relaxation processes of adsorbed surfactants at interfaces and for the theoretical prediction of dilatational elasticity, ε_0. The use of these equations is necessary to determine the limit of elasticity at high frequency, ε_0, and the characteristic angular frequency of diffusion (ω_0), which has been considered a proper parameter in the selection of the surfactant system to be used through the calculation of viscoelastic models [1, 2], ε_d and η_d, and their dependence on frequency and concentration with models such as the Lucassen van den Temple model [3].

A condition that a state equation and an adsorption isotherm must meet is the prediction of surface tension values. However, this is not a sufficient condition. The sufficiency is achieved by comparing the elasticity values at infinity, ε_0, with the values predicted by the state equation and adsorption isotherm. This demonstrates that these equations represent the high-frequency surface phenomena at the interface. ε_0 is the limit of elasticity at high frequency [4–6], also known as the limit value for an insoluble monolayer [7]. It should be noted that ε_0 is sensitive to relaxation processes within the interface, which are generally high-frequency processes. The theoretical prediction of dilatational elasticity requires using adsorption isotherms and state equations to determine the limit of elasticity at high frequency, ε_0, which is given by:

$$\varepsilon_0 = \Gamma \frac{d\Pi}{d\Gamma} = \frac{d\Pi}{d\ln\Gamma} = -\frac{d\gamma}{d\ln\Gamma} \tag{1}$$

2. Guidelines for the selection of state equations and adsorption isotherms

The conditions that both the state equation and the adsorption isotherm must meet are:

- Adjust the experimental values of surface tension, γ.
- Predict the values of ε_0.

In order to validate the appropriateness of the calculated parameters of the adsorption isotherm and state equation, various models such as Langmuir, Frumkin, Compressibility models (from I to IV), Aggregation, and Reorientation are utilized. The parameters of each model are fitted [8], based on the experimental surface tension values at different surfactant concentrations, and these are compared with the values predicted by each model. Subsequently, the elastic modulus at infinite frequency (ε_0), calculated from each model at different surfactant concentrations, is compared with experimental results. In this way, the adsorption isotherm and state equation that align with the surface tension and elastic modulus at infinite values may yield reliable derivative properties. The surface tension data reported in Stubenrauch and Miller [5] for n-dodecyl-β-D-Maltoside were used, and the values of the elastic modulus at infinite frequency (ε_0) reported in Grigoriev and Stubenrauch [9] and Boos et al. [10] were selected. This type of surfactant was chosen for its numerous advantages [11]. In each model, the calculated parameters for n-dodecyl-β-D-Maltoside are shown to observe the differences in the parameters according to the model.

2.1. Langmuir and Frumkin Models

The Langmuir model [12–14] is the simplest; it does not consider the interaction between surfactant molecules. The Frumkin model [12–16] considers this interaction through the interaction parameter a. The adsorption isotherm Eq. (2) and the state Eq. (3) for the Frumkin model are:

$$bc = \frac{\Gamma\varpi}{1-\Gamma\varpi} \exp(-2a\Gamma\varpi) \tag{2}$$

$$\Pi = -\frac{RT}{\varpi}\left[\ln(1-\Gamma\varpi) + a(\Gamma\varpi)^2\right] \tag{3}$$

Where, b: adsorption constant (*l/mmol*). Γ : the amount of surfactant adsorbed on the surface $\left(\mathrm{mol/m^2}\right)$.ϖ : molar area $\left(\mathrm{m^2/mol}\right)$ on a surface with compact packing. a : interaction parameter between the molecules. In the case where a equals zero (no interaction), the equations become those of the Langmuir model. The parameters of the Langmuir and Frumkin models for n-dodecyl- β-D-Maltoside are shown in Table 1.

2.2. Compressibility Models

The most well-known adsorption isotherms and state equations do not consider that the molar area, ϖ, of the surfactants at the interface may depend on the surface pressure, implying that certain compressibility is not considered, as shown in Gehlert and Vollhardt [17] and Fainerman et al. [18]. Compressibility models assume that the molar area of water, and surfactant are equal for $\Pi = 0$. In contrast, the molar area of the surfactant changes, and the molar area of the solvent remains constant. From here, ϖ_0 is the molar area determined by extrapolating the surface pressure to zero. Different models are obtained considering different forms of the variation of the molar area with the surface pressure, ranging from considering non-ideality in enthalpy and entropy to only considering non-ideality in entropy. Compressibility models I-III consider the presence of solvent and surfactant in the surface layer.

2.2.1. *Model I*

In this model [19, 20], non-ideality in entropy is assumed, which results from the difference between the molar area of the surfactant and water. Non-ideality in enthalpy results from intermolecular interaction (a), the adsorption isotherm Eq. (4), state Eq. (5), and molar area of surfactant Eq. (6) are given by:

$$bc = \frac{\Gamma\varpi}{n(1-\Gamma\varpi)^n} \exp(-2an\Gamma\varpi) \tag{4}$$

$$\Pi = -\frac{RT}{\varpi_0}\left[\ln(1-\Gamma\varpi) + (1-1/n)\Gamma\varpi + a(\Gamma\varpi)^2\right] \tag{5}$$

$$\varpi = \varpi_0(1-\xi\Pi) \tag{6}$$

Where, ϖ_0 : molar area of water determined by extrapolation at zero surface pressure $\left(\mathrm{m^2/mol}\right)$,ϖ : molar area of surfactant $\left(\mathrm{m^2/mol}\right)$, n : parameter that considers the non-ideality in entropy through the ratio between the molar area of the surfactant and water (ϖ/ϖ_0), ξ : compressibility coefficient.

2.2.2. *Model II*

In this model, the molar area of the surfactant and water are approximately equivalent, thus having an ideal mixing entropy, provided that $\xi\Pi \ll 1$. The molar area (ϖ) of the surfactant at the interface depends on the surface pressure (Π) according to Eq. (6). Although only at $\Pi = 0$, the molar area of the water and the surfactant are assumed to be equal. Additionally, being a state equation obtained from a

Table 1. Parameters of the Langmuir and Frumkin Models for n-dodecyl- β-D-Maltoside

Model	*b (l/mmol)*	ϖ (m^2/mol)	*a*
Langmuir	$2.0684 \cdot 10^2$	$2.200 \cdot 10^5$	-
Langmuir in Stubenrauch and Miller [5]	$2.1786 \cdot 10^2$	$2.247 \cdot 10^5$	-
Langmuir in Santini et al. [6]	$3.5971 \cdot 10^2$	$2.000 \cdot 10^5$	-
Frumkin	$2.1367 \cdot 10^2$	$2.260 \cdot 10^5$	$4.010 \cdot 10^{-2}$

generalized Butler equation, in which the molar area of the water is fixed, it is understood that even at $\Pi \neq 0$, the mixing entropy is non-ideal. It is an excellent approximation to disregard this contribution if $\xi\Pi \ll 1$, thus having an ideal entropy $(n \approx 1)$. This model's isotherm and state equation differ from Model I when considering the ideal entropy.

2.2.3. *Model III*

When considering the water molecule's and the surfactant's geometry, assuming that the condition $\varpi = \varpi_0$ should be at $\Pi_{\max} = \Pi_{CMC}$ is more appropriate. As the surfactant concentration increases, the area per surfactant molecule decreases, reaching the smallest area at the CMC values, which intuitively leads to this condition. In this case, for $\Pi = 0$ and for $\Pi < \Pi_{\max}$, the value of w is larger than ϖ_0 [20]. The division of the surface in Model III is located 0.1nm deeper into the solution than in Model I. Thus, Models I and III differ in the choice of the molar area of water. For the same value of the surfactant's molar area, the value of ϖ_0 for Model III is approximately half that of Model I. This difference is compensated by the factor n, which is larger for Model III. Hence, the surface pressure values for the two models are approximately equal [20]. The adsorption isotherm and the state equation for this model are given by Eqs. (4) and (5). This model assumes that the molar area Eq. (7) and the parameter n Eq. (8) are given by:

$$\varpi = \varpi_0(1 - \xi\Pi)/(1 - \xi\Pi_{\max}) \quad (7)$$

$$n = (1 - \xi\Pi)/(1 - \xi\Pi_{\max}) \quad (8)$$

2.2.4. *Model IV*

This model considers the concept of Gibbs surface division, in which the solvent adsorption is assumed to be zero. In this way, ϖ_0 should be considered as the molar area of the surfactant at $\Pi = 0$ [20]. The Eq. (4) gives the adsorption isotherm with the value of $n = 1$. The state equation is given by:

$$\Pi = -\frac{RT}{\varpi_0(1 - \xi\Pi/2)}\left[\ln(1 - \Gamma\varpi) + a(\Gamma\varpi)^2\right] \quad (9)$$

The parameters of the Compressibility I-IV model for n-dodecyl- β-D-Maltoside are given in Table 2.

2.3. Aggregation Model

There may be instances where adsorbed molecules aggregate at the interface. Like the formation of micelles within a surfactant solution, critical adsorption at which aggregation begins, Γ_c, is defined [21]. The Eq. (10) relates the concentration of aggregates and monomers on the surface [22, 23]:

$$\Gamma_n = \Gamma_1 \left(\Gamma_1/\Gamma_c\right)^{n-1} \quad (10)$$

The previous equation shows that if $\Gamma_c \leq 10^{-9}$ mol/m^2, the adsorption layer is almost entirely composed of aggregates. Conversely, for $\Gamma_c \geq 10^{-4}$ mol/m^2, the aggregates on the surface can be neglected [23]. Assuming that the aggregates are composed of n molecules, the equations of the model are given by:

$$bc = \frac{\Gamma_1\varpi}{\left(1 - \Gamma_1\varpi\left[1 + (\Gamma_1/\Gamma_c)^{n-1}\right]\right)^{\varpi_1/\varpi}} \quad (11)$$

$$\Pi = -\frac{RT}{\varpi}\ln\left(1 - \Gamma_1\varpi\left[1 + (\Gamma_1/\Gamma_c)^{n-1}\right]\right) \quad (12)$$

$$\frac{\varpi}{\varpi_1} = \frac{1 + n\,(\Gamma_1/\Gamma_c)^{n-1}}{1 + (\Gamma_1/\Gamma_c)^{n-1}} \quad (13)$$

Where, Γ_1: monomers surface concentration (*mol/m*^{2}). ϖ_1: partial molar area of monomers (*m*^{2}*/mol*). Γ_c: critical surface concentration (*mol/m*^{2}). ϖ: average molar area of monomers and aggregates (*m*^{2}*/mol*). The parameters of the aggregation model for n-dodecyl- β-D-Maltoside are given in Table 3.

2.4. Reorientation Model

This model assumes that when molecules are adsorbed at the interface, they can acquire two orientations to the interface. One possible orientation is when the tail is inclined at the interface, while the other orientation occurs when the tail is perpendicular to it. If the inclined orientation is more energetically favorable than the vertical (upright) position of the tail, then the inclined orientation will be preferred at a small interface concentration (where it is not very dense). With the gradual increase in concentration, more molecules will be forced to assume a vertical position. The model assumes that different molar area values characterize the two states of the molecules at the interface,

Table 2. Parameters of the Compressibility Models I-IV for n-dodecyl- β-D-Maltoside

Model	*b (l/mmol)*	ϖ_0 (m^2/mol)	a	$\xi(m/mN)$	$\Pi_{max}(mN/m)$
I	$2.3601{\cdot}10^2$	$2.890{\cdot}10^5$	$4.200{\cdot}10^{-1}$	$3.50{\cdot}10^{-3}$	-
II	$2.1665{\cdot}10^2$	$2.255{\cdot}10^5$	$1.700{\cdot}10^{-2}$	$8.10{\cdot}10^{-3}$	-
III	$1.2987{\cdot}10^2$	$2.320{\cdot}10^5$	$9.004{\cdot}10^{-1}$	$4.60{\cdot}10^{-3}$	$5.240{\cdot}10^1$
IV	$2.4769{\cdot}10^2$	$2.775{\cdot}10^5$	$2.510{\cdot}10^{-1}$	$5.60{\cdot}10^{-3}$	-

Table 3. Parameters of the Aggregation Model for n-dodecyl- β-D-Maltoside

Model	*b (l/mmol)*	ϖ_1 (m^2/mol)	Γ_c (mol/m^2)	n
Aggregation	$2.1847{\cdot}10^2$	$2.250{\cdot}10^5$	$2.6000{\cdot}10^{-1}$	4.30

that is ϖ_1 and ϖ_2 for the inclined and vertical (upright) orientation, respectively ($\varpi_1 > \varpi_2$). It is also assumed that the adsorption mechanism governed by diffusion is what regulates the adsorption process, so the flow from the bulk of the liquid to the interface leads to the formation of a mixture of two molecular subsystems on the surface, each characterized by a surface concentration Γ_1 and Γ_2, ϖ is no longer a parameter, but now depends on the concentration in the bulk of the liquid [14, 20, 24, 25].

2.4.1. *Reorientation R*

This model considers the ideal enthalpy and mixing entropy at the surface [13, 14, 23, 26, 27]. The equations for this model are given by:

$$bc = \frac{\Gamma_2 \varpi}{(1-\Gamma\varpi)^{\varpi_2/\varpi}} \tag{14}$$

$$\Pi = -\frac{RT}{\varpi}\ln(1-\Gamma\varpi) \tag{15}$$

$$\Gamma = \Gamma_1 + \Gamma_2 \tag{16}$$

$$\varpi\Gamma = \varpi_1\Gamma_1 + \varpi_2\Gamma_2 \tag{17}$$

$$\frac{\Gamma_1}{\Gamma_2} = \exp\left[\frac{\varpi_1-\varpi_2}{\varpi}\right]\left[\frac{\varpi_1}{\varpi_2}\right]^{\alpha}\exp\left[-\frac{\Pi(\varpi_1-\varpi_2)}{RT}\right] \tag{18}$$

The adsorption constant, b, indicates the favorability of a surfactant's adsorption process. It signifies the propensity of surfactant molecules to occupy the interface rather than remain dissolved in the water. In this model, $b = b_2$, where b_1 and b_2 represent the adsorption constants for states 1 and 2, respectively. (α) is introduced as a factor to account for the difference between these two adsorption constants. If $\alpha = 0$, it is assumed that there is no difference between b_1 and b_2, implying that the tendency of surfactant molecules to adsorb at the interface is the same regardless of their orientation. Conversely, if $\alpha \neq 0$, this suggests that b_1 may be greater than b_2, indicating a preference for state 1. The state with a larger area is more favored regarding adsorption. The Eqs. (16) and (17) determine the surface concentration for each orientation and the total. The Eq. (18) describes the dependency of the surface concentration ratio for both orientations on the surface pressure.

2.4.2. *Reorientation RC*

In this model, ϖ_2 takes into account the compressibility at the interface, denoted as ξ. The Eqs. (16) to (18) remain the same for this model. ϖ_2 is given by:

$$\varpi_2 = \varpi_{20}(1-\xi\Pi) \tag{19}$$

ϖ_{20} is the molar area of the surfactant in state 2 at $\Pi = 0$.

2.4.3. *Reorientation R0*

This model assumes the non-ideality of both enthalpy and entropy. The Eqs. (16) to (18) remain the same for this model [28]. The equations for this model are:

$$\begin{aligned} bc &= \frac{\Gamma_1\varpi_{20}}{(\varpi_1/\varpi_2)^{\alpha}(1-\Gamma\varpi)^{\varpi_1/\varpi_{20}}}\exp\left[-\frac{\varpi_1}{\varpi_{20}}(2a\Gamma\varpi)\right] \\ &= \frac{\Gamma_2\varpi_{20}}{(1-\Gamma\varpi)^{\varpi_2/\varpi_{20}}}\exp\left[-\frac{\varpi_2}{\varpi_{20}}(2a\Gamma\varpi)\right] \end{aligned} \tag{20}$$

$$\Pi = -\frac{RT}{\varpi_{20}}\left[\ln(1-\Gamma\varpi) + \Gamma\varpi\left(1-\frac{\varpi_{20}}{\varpi}\right) + a(\Gamma\varpi)^2\right] \tag{21}$$

$$\frac{\Gamma_2}{\Gamma_1} = \frac{(\varpi_2/\varpi_1)^{\alpha}}{(1-\Gamma\varpi)^{(\varpi_1-\varpi_2)/\varpi_{20}}}\exp\left[-\frac{(\varpi_1-\varpi_2)}{\varpi_{20}}(2a\Gamma\varpi)\right] \tag{22}$$

$$\varpi_2 = \varpi_{20}(1-\xi\Pi(\Gamma\varpi)) \tag{23}$$

3. Results

To evaluate the best state equation and adsorption isotherm model representing n-dodecyl- β-D-Maltoside, both tension and elasticity at infinite frequency were calculated for each model. These values were then compared with experimental values to select the most suitable model, as suggested in this work, Fig. 1. In comparison, different models represent surface tension values; not all predict elasticity at infinite frequency. It is observed that the best adsorption

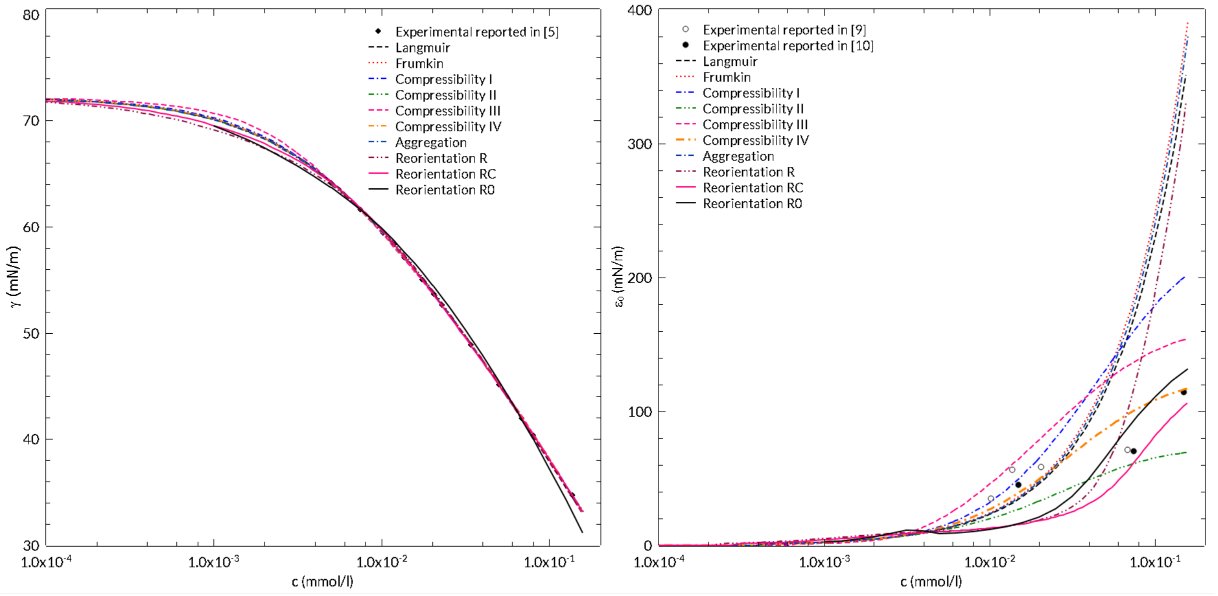

Fig. 1. (left) Experimental surface tension (♦) and (right) experimental elastic modulus at infinity frequency (0, •) for n-dodecyl- β-D-maltoside vs. concentration reported in Grigoriev and Stubenrauch [9] and Boos et al. [10]. Prediction from each model respectively

Table 4. Parameters of the Reorientation Model for n-dodecyl- β-D-Maltoside

Model	*b (l/mmol)*	ϖ_1 (m^2/mol)	$\varpi_2$0 (m^2/mol)	α	a	$\xi(m/mN)$
R	$2.0630{\cdot}10^2$	$1.130{\cdot}10^6$	$2.200{\cdot}10^5$	$8.350{\cdot}10^{-1}$	-	-
RC	$1.9973{\cdot}10^2$	$1.100{\cdot}10^6$	$2.200{\cdot}10^5$	$6.008{\cdot}10^{-1}$	-	$6.60{\cdot}10^{-3}$
R0	$2.0010{\cdot}10^2$	$1.050{\cdot}10^6$	$2.700{\cdot}10^5$	$6.800{\cdot}10^{-1}$	$3.000{\cdot}10^{-1}$	$4.50{\cdot}10^{-3}$

isotherm and state equation model is the Compressibility IV model, which most accurately predicts the experimental values of γ and ε_0. This is followed by the Reorientation R0 and RC models and Compressibility II. The remaining models, which do not adjust the ε_0 values, could underestimate or overestimate the surface concentration values (Γ). The surface concentration was also calculated with each model and using the Gibbs equation [4, 9, 29], Fig. 2. The Γ values of the Compressibility IV model were observed to agree with those obtained with the Gibbs equation. Under this result, in cases where experimental values of ε_0 are not obtained, the values predicted by the Gibbs isotherm can be used as data to select an adsorption isotherm and state equation. These are necessary for surfactant mixture systems where one wishes to predict their performance. However, it is suggested that experiments be conducted where Γ can be measured, and these values be compared with those predicted by the model that best adjusts both the surface tension and the infinite frequency elastic modulus (ε_0) to confirm the results of our calculations [30].

4. Conclusions

This work evaluated various state equations and adsorption isotherm models for n-dodecyl- β-D-maltoside. The comparison between calculated tension and elasticity at infinite frequency with those experimental values suggests that the Compressibility IV model is the most accurate to represent this surfactant. The agreement between the surface concentration values (Γ) from the models and those obtained via the Gibbs equation reinforces the Compressibility IV model as the most accurate model. When ε_0 data are unavailable, the Gibbs isotherm could predict values as reliable data for selecting an adsorption isotherm and state equation. It is recommended, however, that empirical validation through measurement of (Γ) values be pursued to corroborate the theoretical predictions. Drawing upon the results, when selecting an appropriate adsorption isotherm and state equation, the dual ability to fit both the surface tension curve and the elastic modulus at infinite frequency against surfactant concentration is vital, ensuring the results' reliability [31]. As experimental elasticity values at in-

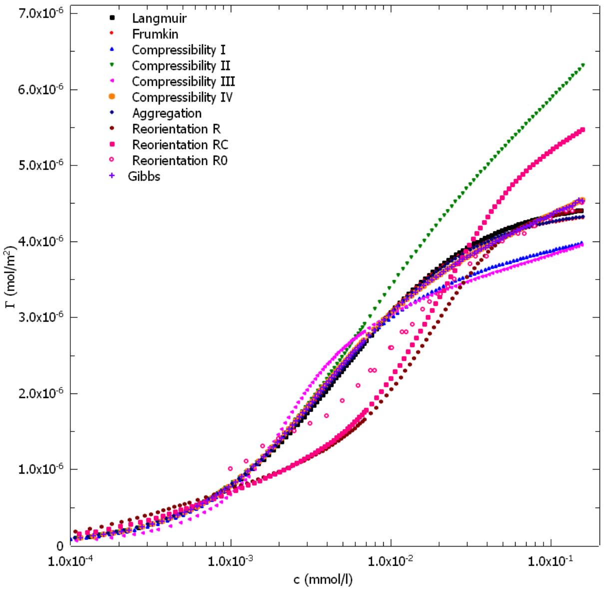

Fig. 2. Calculate surface concentration (Γ) for n-dodecyl-β-D-maltoside vs. concentration. Predictions from each model and Gibbs equation

finite frequency are employed, close attention must be paid to obtaining measurements with the minimum possible experimental errors [1, 10, 32–35]. Inaccurate predictions of ε_0 values by specific models could result in substantial discrepancies in surface concentration.

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