

Design of Surfactant Solutions with Optimal Macroscopic Properties

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ABSTRACT

This paper addresses the design of surfactant solutions with optimal values of macroscopic properties for a particular application. A theoretically rigorous treatment is adopted to link structural parameters such as surfactant head group size, tail length, and polarity with intermediate fundamental solution properties determining the size, shape and surfactant concentration at which micelles form. Correlations, using fundamental solution properties as descriptors, are then employed to bridge the remaining gap to macroscopic properties of interest such as the HLB, emulsivity, detergency and foaming stability. An inner optimization stage minimizes the Gibbs free energy of solution to identify the fundamental solution properties while an outer optimization stage determines the surfactant molecular structure that optimizes the suitability of a surfactant for a particular application expressed in terms of macroscopic variables. The proposed theoretical, algorithmic and computational framework is illustrated with a simple example.

INTRODUCTION

The design of surfactant solutions with specified properties is an important problem in many industries. Surfactants are extensively utilized in many diverse applications such as detergents, emulsifiers and (de)foamers or to ensure film coating, waterproofing, and encapsulation of pharmaceutical substances. The large amount of time and resources required to perform iterative experiments to find the best surfactant for a particular application can be significantly alleviated with the use of optimization techniques coupled with predictive models. Two different models are employed in this work. First, rigorous models relate surfactant structure to fundamental solution properties describing the solution thermodynamics of micelles. These fundamental solution properties are then related through local regression models to the macroscopic surfactant properties of interest. These macroscopic properties may include detergency, viscosity, solubilization, foam stability, emulsivity, etc. characterizing the suitability of a surfactant for a particular application. Given a surfactant architecture, we define the forward problem as the task of estimating its macroscopic properties through the cascade of rigorous modeling followed by local regression. The inverse problem addresses

the task of identifying the surfactant architecture which matches a number of macroscopic property targets. An optimization framework which embeds the forward problem is proposed for the latter. Figure 1 pictorially illustrates the proposed framework for surfactant selection through two-stage modeling and optimization.

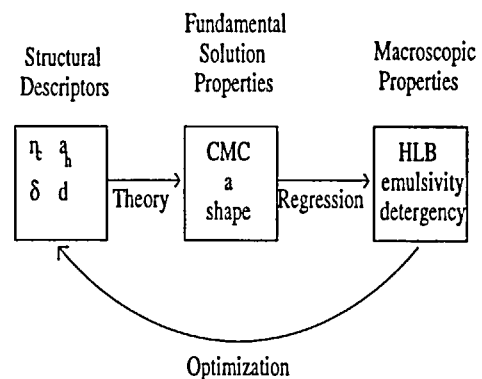


Figure 1: Diagram of forward and inverse problems for surfactant design

The structural descriptors include the number of carbon atoms in the surfactant tail n_c , the cross-sectional area of the head a_h , the charge separation for an ionic

head group δ , and the dipole separation for dipolar surfactants d . These descriptors provide a concise description of the surfactant molecular topology and polarity. They are theoretically related to fundamental solution properties which include the equilibrium area per molecule in a micelle a , the micellar shape, and the concentration at which micelles form (known as the critical micellar concentration or CMC). These properties are related through local regression models to macroscopic surfactant properties characterizing the suitability and effectiveness of the surfactant for a particular application (e.g., hydrophilic-lipophilic balance number (HLB)).

Extensive work has been devoted to the forward problem, namely the prediction of macroscopic solution properties based on a known surfactant molecular architecture. Nagarajan and Ruckenstein (1991), and Nagarajan (1997) proposed a procedure, employed in this paper, for rigorously calculating fundamental solution properties of micelles having as input the structural descriptors of the surfactant molecule. Other efforts include the work of Zoeller and Blankschtein (1995), who developed a computer program that predicts surfactant solution properties for both single and mixed surfactant systems. However, no research work has so far been devoted to the inverse problem of finding the structural descriptors of a surfactant molecule that involves optimal levels of macroscopic properties.

PROBLEM DESCRIPTION

The problem of identifying the molecular structure of a surfactant with optimal values for the desired macroscopic properties can be posed as a two-stage optimization problem. The inner stage identifies the the CMC and other micellar properties by minimizing the free energy μ_g , while the outer stage optimizes over the surfactant structural descriptors. A conceptual optimization formulation of the problem is as follows:

$$\begin{aligned} & \max / \min && f(\text{macroscopic properties}) \\ & \text{subject to} && \\ & \text{macroscopic properties} = && \\ & && g(\text{fundamental properties}) \\ & \min \mu_g(\text{structural descriptors}) \rightarrow && \\ & && \text{fundamental properties} \\ & && \text{bounds on structural descriptors} \end{aligned}$$

Here f is the objective function, which we typically define as the sum of the scaled squared errors between the

macroscopic properties and their target values, and g is a local regression model which relates macroscopic properties to the fundamental properties of a surfactant solution.

The evaluation of the fundamental solution parameters (CMC and area a of a surfactant molecule within a micelle) follows the analysis of Nagarajan (1997). The starting point is the aggregate size distribution equation

$$X_g = X_1^g \exp(-g\mu_g)$$

where X_g is the concentration of aggregates containing g surfactant molecules, X_1 is the concentration of free surfactant molecules, and μ_g is the free energy difference between a free surfactant molecule in water and a surfactant molecule in a micelle of aggregation number g . The free energy μ_g can be written as a function of the surfactant structural descriptors and solution conditions such as temperature and concentration of any added salt. The aggregate size distribution equation allows the calculation of the size distribution of micelles in solution.

The CMC is estimated as the surfactant concentration at which the concentration of the unassociated surfactant molecules is equal to the concentration of the aggregated ones, that is, when $X_1 = \sum g X_g$. One of the aggregation numbers typically dominates the micellar size distribution, and thus we can simplify the CMC constraint to become $X_1 = (g X_g)_{max}$. The CMC can then be calculated by considering the following stepwise procedure.

Step 1: Initialize X_1 .

Step 2: Compute X_g by minimizing μ_g .

Step 3: Test whether CMC constraint $X_1 = \sum g X_g$ is satisfied. If the constraint is satisfied within tolerance, end. Otherwise, compute a new value for X_1 using fixed point iteration and return to Step 2.

At each iteration, the free energy of micellization must be minimized with respect to a . For a non-ionic surfactant, the free energy of micellization can be written as (Nagarajan, 1997):

$$\mu_g = \mu_{tr} + \mu_{def} + \mu_{int} + \mu_{ster}$$

where μ_{tr} is the free energy required to transfer the surfactant tail from the bulk aqueous solution into the micelle, μ_{def} is the free energy required to deform the surfactant tail in order to pack the tail into the micelle, μ_{int} is the free energy required to form the core-water interface

of the surfactant, and μ_{ster} is the steric repulsion between the head groups of the surfactant molecules in a micelle.

The free energy required to transfer the tail from the bulk into a micelle is a function of only the temperature T and n_c :

$$\mu_{tr} = (n_c - 1)(5.85 \ln(T) + \frac{896}{T} - 36.15 - 0.0056T) + (3.38 \ln(T) + \frac{4064}{T} - 44.13 + 0.02595T)$$

where T is in degrees (K) and μ_{tr} is in kT units (k is the Boltzmann constant). In contrast, the free energy of deformation of the surfactant tail is a complex function of the micellar area per molecule:

$$\mu_{def} = \frac{9P\pi^2 R_s^2}{80NL^2}$$

where P is the packing factor, which depends on the micellar geometry, R_s is the radius of the micelle, N is the number of segments in the surfactant tail, and L is the length of a tail segment. During the free energy minimization process, the free energy must be evaluated for a sequence of values for a . For each one of these values, a corresponding geometry exists (spherical, ellipsoidal, cylindrical, etc.). Knowing this geometry allows the proper choice of equation for P and R_s .

The free energy required to create the core-water interface of the micelle is written as

$$\mu_{int} = \sigma_{agg}(a - a_0)$$

where σ_{agg} is the aggregate core-water interfacial tension (in units of kT), and is computed as a function of the surface tensions of the surfactant tail and that of water, and a_0 is the surface area per molecule shielded from contact with water, which is a function of the cross-sectional area of the head a_h . Finally, the free energy needed to overcome steric interactions between the surfactant head groups is given as

$$\mu_{ster} = -\ln\left(1 - \frac{a_h}{a}\right)$$

For ionic and dipolar surfactants, further terms are required to account for head group ionic or dipolar interactions. All of the free energy contributions are then summed, and the value of a which minimizes μ_g is determined using the truncated-Newton optimization algorithm (Nash, 1984). With equations in place defining the free energy required to transfer a surfactant molecule from

the bulk to a micelle, CMC and a can be computed given the molecular descriptors. Next, a simple example illustrates the proposed optimization procedure.

ILLUSTRATIVE EXAMPLE

In this example, the identification of a nonionic surfactant molecule is sought whose hydrophilic-lipophilic balance (HLB) is equal to 13.8. Note that HLB is a widely used measure of the emulsifying ability of a surfactant. A high value for HLB implies high water solubility and suitability as a detergent or an emulsifier.

A local regression model is constructed which relates HLB to CMC as follows:

$$\ln HLB = 2.76 + 0.04 \ln CMC$$

$$r = 0.9889, N = 23$$

Here r is the correlation coefficient and N is the number of surfactants employed in the correlation set. This equation is then imported to the optimization framework, and the inverse problem of identifying the cross sectional area of the head a_h and the number of carbons in the tail n_c of a surfactant whose HLB is as close to 13.8 as possible is solved. To simplify the example, we have chosen to design only non-ionic surfactants with single straight chains.

The truncated-Newton algorithm was started from a number of initial starting points, and in each case, the algorithm converged to the same optimal solution involving a head cross-sectional area of 0.54977 nm² and 5.997 carbons in a straight-chain tail. The CMC for this surfactant was found to be 0.034 mM. A search over tabulated surfactant properties reveals that a surfactant molecule with a dimethyl phosphine oxide head group and a six-carbon tail is compatible with those structural descriptors. Convergence required between 15 and 30 iterations of the outer loop of the algorithm, depending on the initial starting point, and the CPU time for these runs was 5 to 10 seconds on an IBM RS/6000 397 workstation. While this example only involved finding a surfactant molecule which matched one property value, the proposed formulation allows a number of property targets to be matched simultaneously.

SUMMARY

In this work, we have described an optimization methodology for the design of surfactant molecules with optimal

levels of macroscopic properties. A hybrid modeling approach is adopted utilizing a cascade of rigorous modeling followed by local regression models. Current efforts are aimed at developing an extensive surfactant property database to be utilized for developing regression models for many important macroscopic properties.

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