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Pattern search methods for pendant drops: Algorithms for rapid determination of surface tension and surfactant transport parameters

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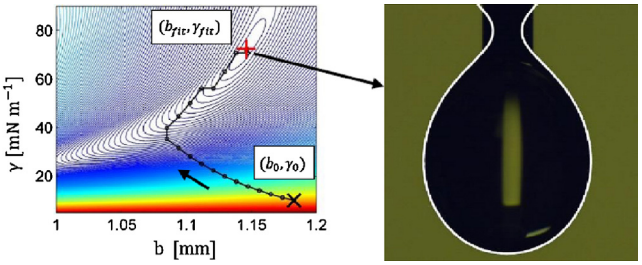
HIGHLIGHTS

- Algorithms for measuring surface tension/sorption kinetics proposed.
- Equilibrium surface tension measured with axisymmetric drop shape analysis (ADSA).
- Surfactant transport parameters measured using Frumkin isotherm.
- Minimizations of objective functions are shown.
- Data from the literature are used as examples with good agreement.

GRAPHICAL ABSTRACT



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ABSTRACT

In this manuscript we introduce algorithms based on the pattern search method that are used to estimate equilibrium surface tension and surfactant transport parameters from pendant drops. The pattern search method is an efficient minimization technique for estimating multiple unknown parameters. To introduce and validate the method for measuring surface tension and transport parameters we use axisymmetric drop shape analysis (ADSA) for pendant drops of aqueous sodium oleate (SO) and aqueous sodium dodecyl sulfate (SDS) in mineral oil, along with several other classical data sets from the literature. The data show good agreement with other studies suggesting that the pattern search method may be a robust alternative to gradient based search methods.

1. Introduction

In this manuscript we outline a process to apply pattern search methods to estimate equilibrium surface tension and surfactant transport parameters from pendant drops. The technique may be extended to other systems where robust minimization or search methods are required to estimate multiple unknown parameters. There are unique advantages with utilizing this technique to estimate properties of surfactant systems where minimization occurs between a known (experimental drop shapes or surface tension data) and unknown (Young–Laplace solution or isotherms) set of data, of which pendant drop analysis is an example. The main advantage stems from the fact that estimates for the unknown properties are produced by minimizing the common ℓ^2-norm between the known and unknown data sets which can be used to formulate an objective function used for minimization. To validate the technique for measuring surface tension we consider pendant drops of aqueous sodium oleate (SO) and aqueous sodium dodecyl sulfate (SDS) in mineral oil, along with several other classical data sets from the literature. This will be followed by implementation of the pattern search method to fit the equilibrium surface tension data to the Frumkin isotherm which requires the simultaneous

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minimization of three unknown parameters used to quantify surfactant transport.

The analysis begins with estimates of surface tension data. To generate surface tension data an axisymmetric drop shape analysis (ADSA) for pendant drops will be considered. This generally consists of fitting drop shapes prescribed by the Young–Laplace equation to experimentally measured drop shapes. There are two unknown parameters in the ADSA process: the surface tension and the curvature. Constructing the objective function is the most robust method for determining the best fit using ADSA. But it is also the most costly since the numerically generated solution to the Young–Laplace equation requires solving differential equations in multiple dimensions. Furthermore, the range of surface tension and curvature values must be bounded in order to determine the region where the minimum exists along with choosing an appropriate size for incrementing the independent variables.

Within the past few decades gradient-based solvers have been developed to perform the ADSA minimization process. The most common example of such a method is through implementation of the well-known Newton–Raphson scheme [1]. To perform the analysis the objective function is expanded in a Taylor series about the unknown parameters. Unfortunately gradient-based solvers too are computationally intensive, requiring the additional calculation of gradients to update the unknown in the iterative process. Additionally gradient-based solvers are not guaranteed to converge and tend to diverge if the initial guess is not sufficiently close to the best fit.

Instead we apply a pattern search method for determining best fits of the Young–Laplace equation. The pattern search method is an example of a direct search method which is more commonly used for performing modern error minimization. Direct search methods are less computational expensive than gradient based methods because they typically do not require any additional mathematical manipulation of an objective function. Drawbacks in utilizing these methods exist because they are not necessarily robust in terms of convergence to a local minimum. An example of a direct method is the Nelder–Mead simplex method [2,3], generally recognized as the first non-gradient based search method. With this method, minimization is achieved by reaching the local minimum in a region usually defined by some $p+1$ points where p is the number of unknowns, or dimensions. Points are updated by determining minima at points reflected through the line formed at the other p points. This method has been used in [4] where the MATLAB function *fminsearch* was used to perform the implementation with good results. Although the Nelder–Mead simplex method is capable of producing good results there are no guarantees that it converges to a local minimum.

On the other hand, the pattern search method has been shown through robust mathematical analysis to consistently converge to a local minimum the details of which were described in [5,6]. A brief analysis of why the pattern search method converges is as follows: an objective function based on the ℓ^2-norm in multiple dimensions can possess a local minimum because the distance measured between the computational and experimental data d_i is squared. For example, in one dimension let the distance between a point generated numerically by the Young–Laplace equation and one measured experimentally be a function of only the surface tension and be denoted $d_i(\gamma_n)$. Now bound $d_i(\gamma_n)$ above and below by adding and subtracting some small-equidistant amount δ, respectively, from the unknown quantity γ_n. Then the error at step n is bounded by $\gamma_n \pm \delta$, i.e. $\sqrt{d_i(\gamma_n)^2} < \sqrt{d_i(\gamma_n \pm \delta)^2}$. This condition forms the basis for the pattern search algorithm. We will explore how to implement this method, and discuss situations where the condition may break down in regards to determining equilibrium surface tension and surfactant transport parameters, in the following sections.

2. Pattern search algorithm

2.1. General pattern search algorithm

We begin a discussion of the general pattern search algorithm that may be used to generate simultaneous estimates for multiple unknown parameters. The pattern search technique relies on the existence of a local minimum in an objective function for a set of unknown quantities. We will show that objective function estimates using an ℓ^2-norm are sufficient to satisfy this criteria for determining equilibrium surface tension and surfactant transport parameters under certain conditions. The ℓ^2-norm has been a standard for automated calculation of surface tension [1] and errors estimated using the ℓ^2-norm can be generalized to any type of curve fitting method. The ℓ^2-norm is simply defined by the Euclidean distance

$$\psi(c_{1,n}, c_{2,n}, \ldots, c_{p,n}) = \sqrt{\sum_{i=1}^{I} d_i(c_{1,n}, c_{2,n}, \ldots, c_{p,n})^2}, \tag{1}$$

where $\psi(c_{1,n}, c_{2,n}, \ldots, c_{p,n})$ is the objective function of p unknowns $c_{1,n}, c_{2,n}, \ldots, c_{p,n}$ which also serve to denote coordinates $(c_{1,n}, c_{2,n}, \ldots, c_{p,n})$. The variable d_i is used to denote the distance measured between I points of some numerically generated and experimentally generated data sets at specific positions i along an axis of the independent variable at minimization step n.

The general algorithm goes as follows: starting with initial guesses for the coordinates $(c_{1,0}, c_{2,0}, \ldots, c_{p,0})$, we update these points to find a trajectory that leads to the local error minimum. For the pattern search algorithm this is achieved without the use of calculating gradients by determining the minimum in the set,

$$\begin{aligned} A = \quad & \{\psi(c_{1,n} + L_1\Delta c_{1,n}, c_{2,n} + L_1\Delta c_{2,n}, \ldots, c_{p,n} + L_1\Delta c_{p,n}), \\ & \psi(c_{1,n} + L_2\Delta c_{1,n}, c_{2,n} + L_1\Delta c_{2,n}, \ldots, c_{p,n} + L_1\Delta c_{p,n}), \\ & \ldots \\ & \psi(c_{1,n} + L_3\Delta c_{1,n}, c_{2,n} + L_3\Delta c_{2,n}, \ldots, c_{p,n} + L_3\Delta c_{p,n})\}, \end{aligned} \tag{2}$$

where $[L_1, L_2, L_3] = [-1, 0, 1]$. There are 3^p elements in set A if one includes the initial coordinates at each minimization step $(c_{1,n}, c_{2,n}, \ldots, c_{p,n})$. Let $\beta_1, \beta_2, \ldots, \beta_p = 1, 2$ or 3 be used to denote the indices $L_{\beta_1}, L_{\beta_2}, \ldots, L_{\beta_p}$ corresponding to the objective function minimum at step n in set A located at coordinates $(c_{1,n} + L_{\beta_1}\Delta c_{1,n}, c_{2,n} + L_{\beta_2}\Delta c_{2,n}, \ldots, c_{p,n} + L_{\beta_p}\Delta c_{p,n})$. If the elements of the vector $\mathbf{M} = (M_1, M_2, \ldots, M_p) = (L_{\beta_1}, L_{\beta_2}, \ldots, L_{\beta_p})$ contain these values then new guesses at step $n+1$ for the unknowns can be written as

$$\begin{bmatrix} c_{1,n+1} \\ c_{2,n+1} \\ \ldots \\ c_{p,n+1} \end{bmatrix} = \begin{bmatrix} c_{1,n} \\ c_{2,n} \\ \ldots \\ c_{p,n} \end{bmatrix} + \begin{bmatrix} M_1\Delta c_{1,n+1} \\ M_2\Delta c_{2,n+1} \\ \ldots \\ M_p\Delta c_{p,n+1} \end{bmatrix}. \tag{3}$$

The step sizes $\Delta c_{1,n+1}, \Delta c_{2,n+1}, \ldots, \Delta c_{p,n+1}$ remain constant until the minimum of set A produces the zero vector, i.e. $\beta_1 = \beta_2 = \cdots = \beta_p = 2$ such that $\mathbf{M} = \mathbf{0}$. If this occurs then the step size is uniformly reduced by ϕ, i.e. $\Delta c_{1,n+1}, \Delta c_{2,n+1}, \ldots, \Delta c_{p,n+1} = \phi\Delta c_{1,n+1}, \phi\Delta c_{2,n+1}, \ldots, \phi\Delta c_{p,n+1}$ with $0 < \phi < 1$ and the procedure continues. The iterative process is completed when one or several of the unknowns meet a user defined minimum error requirement between two consecutive steps $|c_{1,n+1} - c_{1,n}|$ or $|c_{2,n+1} - c_{2,n}|$ or … or $|c_{p,n+1} - c_{p,n}| \ll 1$.