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On the predictions and limitations of the Becker–Döring model for reaction kinetics in micellar surfactant solutions

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ABSTRACT

We investigate the breakdown of a system of micellar aggregates in a surfactant solution following an order-one dilution. We derive a mathematical model based on the Becker–Döring system of equations, using realistic expressions for the reaction constants fit to results from Molecular Dynamics simulations. We exploit the largeness of typical aggregation numbers to derive a continuum model, substituting a large system of ordinary differential equations for a partial differential equation in two independent variables: time and aggregate size. Numerical solutions demonstrate that re-equilibration occurs in two distinct stages over well-separated timescales, in agreement with experiment and with previous theories. We conclude by exposing a limitation in the Becker–Döring theory for re-equilibration of surfactant solutions.

1. Introduction

When surfactant exceeds a particular bulk concentration in solution, termed the *critical micelle concentration* (CMC), it becomes favourable for aggregates or *micelles* to form. The micelles can have various sizes and shapes but for many simple surfactants with a single hydrocarbon chain the aggregates are approximately spherical and contain of the order of 100 monomers [1]. The distribution of aggregate sizes is localized around this optimum value with a half-width of the order of the square root of the aggregation number. Aggregates that are much smaller than the mean aggregation number are energetically highly unfavourable and consequently appear in much lower concentrations [2–5].

The re-equilibration and subsequent restructuring of a micellar surfactant solution upon a disturbance from equilibrium is of great importance for the adsorption kinetics of micellar solutions. Such a process is generally assumed to occur via stepwise monomer loss or gain [2–4], which leads to the Becker–Döring description [6], a special case of Smoluchowski coagulation theory which, more generally, allows all aggregates sizes to combine and dissociate [7]. Coagulation theory has been used to model aggregation in numerous situations (for a review see [8] and references therein). The original Becker–Döring formulation describes a system in which the monomer concentration is held constant. This can be interpreted as a phase transition in which a supersaturated gas condenses to form liquid drops at constant pressure. Penrose and Lebowitz [9] extend this theory to account for systems which conserve mass. Billingham and Coveney [10] consider the formation of micelles in a system out of thermodynamic equilibrium, and a reduced description of this system which preserves all the properties of the infinite-dimensional Becker–Döring equations is presented by Coveney and Wattis [11]. Coagulation theory has also been analysed in more complex situations, such as within a flowing fluid, with particular application to biological systems. For example, Band et al. [12] combine the Becker–Döring theory with an advection-diffusion model to describe crystal aggregation in the lower urinary tract, while Guy et al. [13] model the formation of a blood clot in a shearing flow.

Aniansson and Wall [2] consider the small dilution of a surfactant with a realistic aggregation distribution, comprised predominantly of either monomers or aggregates localized around the large optimum aggregation number, with aggregates in between occurring at much lower concentrations, and demonstrate re-equilibration on two distinct timescales, termed the τ_1 and τ_2 processes [14]. The first, more rapid, timescale corresponds to the replenishment of monomer via release of individual monomers from aggregates. However, to return the monomer to its equilibrium value requires some aggregates to break down entirely. Some of the monomers released replenish the monomer concentration to its critical value, while the remainder join those aggregates which have not broken down. The associated relaxation times differ by at least three orders of magnitude, with monomer loss occurring on the μs–ms timescale and complete micelle breakdown on the ms–min timescale [1]. Recently, Rusanov et al. [15–19] provided a mathematical analysis of the micellization process, based on

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the Aniansson and Wall kinetic model, that outlines nine characteristic kinetic times of micellization in non-ionic surfactant solutions, although they propose no method of probing these experimentally.

While some temperature-jump and pressure-jump experiments do indeed satisfy the limit of small dilutions examined in [2], there are many physically important situations for which this is not the case. While large-deviation re-equilibration has been well studied in scenarios where there are a finite number of aggregates, all of which occur in equal concentrations at equilibrium (for example [8,12]), the re-equilibration of a surfactant with a realistic aggregate distribution following an order-one dilution has not been analysed in detail. As a consequence, the Aniansson and Wall model has been applied to many situations where the deviations from equilibrium are much too large for the linearized theory to be applicable.

In this paper we use the full Becker–Döring model to investigate the relaxation upon an order-one dilution (which leaves the system above the CMC) of a micellar surfactant solution with a realistic equilibrium aggregate distribution. In this case, the monomer concentration must be replenished to its equilibrium value via the breakdown of some of the aggregates, while a proportion of surfactant will still reside in aggregate form. We describe the mechanism by which this is achieved and the restructuring process of aggregates that ensues, demonstrating that the two-timescale behaviour predicted by Aniansson and Wall for small deviations from equilibrium is still a prominent feature.

Richardson et al. [20] exploit the large number of monomers that typically comprise an aggregate to derive a continuum model for the formation of lipid/protein microdomain structures within plasma membranes which interact via Smoluchowski coagulation theory. Tracking the evolution of a continuous function rather than the concentration of all individual species vastly simplifies the problem, and we employ a similar strategy in this paper.

We first validate our continuum model by comparing its predictions with simulations of the discrete Becker–Döring system. We then use this representation to elucidate the two-timescale behaviour and to analyse the two stages of re-equilibration. We show that the relative concentration of smaller aggregates to the micelle concentration is a key parameter, setting the relative timescales at which the two processes occur. The predictions of our models are compared with experimental data obtained from stopped-flow experiments [1].

We conclude by discussing surfactant systems for which our description fails. In such circumstances the assumptions made by the Becker–Döring theory must be relaxed, and a new mechanism for micelle breakdown must exist, which we analyse in a follow-up to this paper.

2. A discrete model

2.1. The Becker–Döring equations

As discussed in Section 1, the self-assembly and dissociation of aggregates is assumed to occur via stepwise monomer loss and gain [2–4], in the following reaction scheme:

$$\text{monomer} + n\text{-mer} \underset{\kappa_n^-}{\overset{\kappa_n^+}{\rightleftharpoons}} (n+1)\text{-mer}. \tag{1}$$

Here, we use the term n-mer to denote an aggregate containing n monomers, and $\kappa_n^{\pm}$ are the association and dissociation rate coefficients. The reaction kinetics for this system are described by the *Becker–Döring* equations [6]

$$\frac{\mathrm{d}\mathcal{X}_n}{\mathrm{d}\mathcal{T}} = \kappa_{n-1}^+\mathcal{X}_1\mathcal{X}_{n-1} - \kappa_{n-1}^-\mathcal{X}_n - \kappa_n^+\mathcal{X}_1\mathcal{X}_n + \kappa_n^-\mathcal{X}_{n+1}, \tag{2}$$

for $n \geqslant 2$, where $\mathcal{X}_n = \mathcal{X}_n(\mathcal{T})$ denotes the (molar) concentration of an aggregate containing n monomers at time $\mathcal{T}$.

The net bulk concentration of monomer contained in all aggregates is given by

$$\mathcal{C}_b = \sum_{n=1}^{\infty} n\mathcal{X}_n. \tag{3}$$

Under the assumption that $\mathcal{C}_b$ is conserved for all time, the free monomer concentration is determined by

$$\mathcal{X}_1(t) = \mathcal{C}_b - \sum_{n=2}^{\infty} n\mathcal{X}_n(t) = \mathcal{X}_1(0) - \sum_{n=2}^{\infty} n(\mathcal{X}_n(t) - \mathcal{X}_n(0)). \tag{4}$$

Along with (2), this gives us an infinite-dimensional system of ODEs for $\mathcal{X}_2(t),\ \mathcal{X}_3(t), \ldots$. The solution of this system requires us to specify all the initial concentrations $\mathcal{X}_1(0),\ \mathcal{X}_2(0), \ldots$.

For mathematical simplicity, it is customary to truncate the system at some large finite value $n = N$ and to assume that all the reaction rates are equal (see, for example, [21]). This is equivalent to setting

$$\kappa_n^{\pm} = \begin{cases} \kappa^{\pm} & 1 \leqslant n \leqslant N-1, \\ 0 & n \geqslant N. \end{cases} \tag{5}$$

As we will see below, this approximation fails to capture the correct physics for many real-life systems, and we will focus on analysing the system (2) with reaction rates consistent with real surfactants.

2.2. The equilibrium distribution

Determination of the aggregate size distribution for different surfactants and different micelle shapes is a subject of extensive debate. Since concentrations in the intermediate aggregate region are orders of magnitude smaller than those close to the optimum aggregation number, there are no direct experimental methods available for their measurement. It is, however, possible to calculate an equilibrium aggregate size distribution from knowledge of the chemical potential differences between monomers in different sized aggregates. This may be done via Molecular Dynamics (MD) simulations [22–24] or by Molecular Thermodynamics (MT) [5,25,26]. Either method predicts a distribution characterized by the following key features. Almost all surfactant material is contained within either a region of *pre-micellar aggregates* (monomer, dimers, trimers etc.) or a region of *proper micelles* close to the peak aggregation number. These are connected by an *intermediate region* containing a very low concentration of aggregates; see Fig. 1. (The change in slope at $n = 90$ arises from a change in the model from a sphere to a rod with spherical end-caps. In reality, micelles will pass through an ellipsoidal shape between spheres and rods that smooths out the distribution.) These predictions are in agreement with experimental techniques such as light-scattering methods or small-angle neutron scattering (SANS) experiments which may be used to determine the optimum aggregation number, and stopped-flow experiments to determine the CMC [1].

In modelling terms, an equilibrium distribution corresponds to a steady solution of the Becker–Döring system. Substitution of $\mathcal{X}_n = \mathcal{X}_n^* =$ constant into (2) yields a system of algebraic equations to determine $\mathcal{X}_n^*$, in terms of the reaction coefficients $\kappa_n^{\pm}$ and the net surfactant concentration $\mathcal{C}_b$. At equilibrium, the principle of microscopic reversibility requires that each mechanistic step in a reversible reaction must itself be in equilibrium, and so Eq. (2) implies that

$$\kappa_n^+\mathcal{X}_1^*\mathcal{X}_n^* - \kappa_n^-\mathcal{X}_{n+1}^* \equiv \kappa_i^+\mathcal{X}_1^*\mathcal{X}_i^* - \kappa_i^-\mathcal{X}_{i+1}^*, \tag{6}$$

for all $n, i \geqslant 1$. To ensure that the system contains a finite amount of surfactant, we must have $\mathcal{X}_i^* \to 0$ as $i \to \infty$, and hence