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Kinetic models of micelles formation

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ABSTRACT

Four possible aggregation models in surfactant solutions are considered. It is shown that only the model taking into account interactions between clusters of sub-micellar size shows a transition to the micelles formation at a concentration above the CMC.

1. Introduction

Surfactants are widespread in nature, industry and everyday life [1–5]. They play an important role in many technological applications, such as dispersion stabilization, enhanced oil recovery, and lubrication. It may be argued that surfactants are the most widely spread chemicals in the world.

Surfactant molecules are diphilic, with a hydrophilic head and a hydrophobic tail. That is why they preferably adsorb on interfaces. They are soluble both in oil and aqueous phase with solubility depending on their hydrophile–lipophile balance (HLB) [6]. At low concentrations surfactant molecules are believed to exist in the solution mainly as single molecules. If the concentration increases and reaches some critical value, CMC, the surfactant molecules form new objects referred to as micelles [6–13]. In aqueous solutions hydrophobic tails are collected inside the micelle and only hydrophilic heads are exposed to the aqueous phase.

The detailed picture of the micellization kinetics and routes of micelles formation is still under consideration in spite of the clear understanding of thermodynamic background of the micelles formation [7,14,15]. Theoretical models have been suggested, which allow evaluation of the relaxation times associated with micellar solutions. A two-state model [16,17] considers a monomeric state and an associated state consisting of all species larger than the monomer unit. This model describes only the fast process (temperature-jump, pressure-jump, stopped flow) and makes the assumption that the rate constant for association and dissociation of the monomer from the micelle is independent of the size of micelles. A theory of relaxation applicable for both slow and fast processes has been developed [18–20] using a quasi-chemical approach [13]. The approach is based on the application to surfactant solutions the theory of aggregation (coagulation) of colloids proposed by Smoluchowsky [21] and further developed in [22], where disaggregation processes were taken into account.

According to [18–20] the most probable way of relaxation in micellar solutions is the exchange by single molecules between micelles and solution. The latter mechanism is the consequence of the bimodal size distribution: small aggregates, mainly singlets, and proper micelles. This model is supported by thermodynamic studies [23,24] as well as experimental data [25]. Further development of conception of micelles formation was performed in [26–34] including consideration of micellization starting from initial monomolecular state [25,30,32]. Approach developed in [32–34] allows calculation of equilibrium concentrations singlets and micelles as well as the relaxation times if the values of maximum and minimum work on aggregates formation are known, for example, from thermodynamic estimations [23,24]. It was shown in [26–31] that under certain conditions (for ionic surfactants, block copolymers, etc.) the fusion/fission of aggregates could be important route of micelles formation. Note that in the studies discussed above only symmetrical processes aggregation/disaggregation have been considered with rate constants, which depend on the thermodynamic characteristics of aggregates (work on aggregate formation).

Below different kinetic models of micelle formation including asymmetric ones are considered to establish the aggregation model, which predicts the formation of clusters (doublets, triplets and so on) in non-ionic aqueous surfactant solutions below the CMC and

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micelles formation above the CMC. The quasi-chemical approach is used.

In this part we briefly summarize the known theoretical results relevant to the quasi-chemical approach of the micelles formation [13,22,35]. The terminology used in [22,35] is adjusted below for the consideration of surfactant solutions.

Let $n_i(t)$, $i = 1, 2, 3, \ldots$ be the number concentration of clusters with 1, 2, 3, ... initial molecules at the moment t. The rate of aggregation of two clusters of sizes i and j in one bigger cluster of size $i+j$ is $a_{i,j}n_in_j$, where $a_{i,j}$, $i, j = 1, 2, 3, \ldots$ are corresponding aggregation rates. The rate of disaggregation of the cluster of size $i+j$ into two smaller clusters of sizes i and j, respectively, is $b_{i,j}n_{i+j}$, where $b_{i,j}$, $i, j = 1, 2, 3, \ldots$ are disaggregation rates. Aggregation/disaggregation rates satisfy the following symmetry conditions: $a_{i,j} = a_{j,i}$, $i, j = 1, 2, 3, \ldots$, $b_{i,j} = b_{j,i}$, $i, j = 1, 2, 3, \ldots$.

Using the above notations development over time of cluster concentrations can be written as [22,35]:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1}\Psi_{i,k-i} - \sum_{i=1}^{\infty}\Psi_{k,i}, \quad k = 1, 2, 3, \ldots, \tag{1}$$

where $\Psi_{ij} = a_{i,j}n_in_j - b_{i,j}n_{i+j}$.

The first sum in the right hand side of Eq. (1) represents all aggregation/disaggregation events with cluster those sizes range from 1 to $k-1$ (the total flux to the state k from all possible states $i < k$), while the second sum in the right hand side represents all aggregation/disaggregation events with clusters those sizes range from k to ∞ (the total flux from the state k to all states $i > k$).

System of differential equations (1) can be rewritten in a more conventional form as

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1}^{k-1}a_{i,k-i}n_in_{k-i} - \frac{n_k}{2}\sum_{i=1}^{k-1}b_{i,k-i} - n_k\sum_{i=1}^{\infty}a_{k,i}n_i + \sum_{i=1}^{\infty}b_{k,i}n_{k+i}, \quad k = 1, 2, 3, \ldots. \tag{2}$$

It is possible to show that the latter system of differential equations satisfies the condition of conservation of the total number of surfactant molecules in the system under consideration at any aggregation/disaggregation rates $a_{i,j}$, $i, j = 1, 2, 3, \ldots$, $b_{i,j}$, $i, j = 1, 2, 3, \ldots$, which satisfy the symmetry conditions:

$$\sum_{k=1}^{\infty}kn_k = N, \tag{3}$$

where N is the initial number concentration of single surfactant molecules.

Let $n = \sum_{k=1}^{\infty}n_k$ be the total number of aggregates. Using Eq. (2) it is possible to conclude that

$$\frac{dn}{dt} = -\frac{1}{2}\sum_{i,j=1}^{\infty}(a_{i,j}n_in_j - b_{i,j}n_{i+j}). \tag{4}$$

Let us consider the steady state solution of the system of Eq. (2), that is,

$$0 = \frac{1}{2}\sum_{i=1}^{k-1}a_{i,k-i}n_in_{k-i} - \frac{n_k}{2}\sum_{i=1}^{k-1}b_{i,k-i} - n_k\sum_{i=1}^{\infty}a_{k,i}n_i + \sum_{i=1}^{\infty}b_{k,i}n_{k+i}, \quad k = 1, 2, 3, \ldots \tag{5}$$

The important conclusion obtained in [13,35] is as follows: the steady state solution of the system (5) corresponds to the minimum of the free energy of the system under consideration.

2. Models of aggregation/disaggregation

Below we distinguish between clusters (doublets, triplets, and so on, with number of surfactant molecules smaller than in micelles) and micelles itself. Four different aggregation/disaggregation models are considered below. It is shown that only one of these models, *Model C*, results in a transition from low sized cluster formation to the micelles formation at and above some critical concentration of surfactant molecules. All other models show a continuous increase in averaged cluster size with the increase of the surfactant concentration.

Model A (Fig. 1(A1 and A2)): aggregation/disaggregation of surfactant molecules according to this model occurs via exchange by one molecule at the time between clusters/micelles as shown in Fig. 1(A1 and A2) there only single molecules can be connected/disconnected to/from any cluster (including micelles if any). This model corresponds to that proposed in [18–20] and generally accepted now.

According to *Model B* (Fig. 1(B1 and B2)), aggregation/disaggregation of clusters of any size can take place.

Connection/disconnection of clusters/individual surfactant molecules go in a symmetrical way according to *Models A* and *B*.

With *Model C* aggregation/disaggregation of clusters (or micelles if any) occurs asymmetrically: clusters of any size can aggregate but only single molecules can leave clusters or micelles. Fig. 1(C1 and C2) shows that clusters of different sizes can be connected into a new bigger cluster/micelle but only single molecules can disconnect from the cluster/micelle.

Usually *Models B* and *C* are excluded from the consideration arguing that there is a strong bimodal distribution (single molecules and equilibrium micelles) in surfactant solutions above the CMC, concentration of submicellar clusters is small and therefore contribution of cluster/cluster interaction could be neglected. It is true for many solutions close to equilibrium at concentrations far above the CMC. However, we consider the equilibration process, which started from the solution, where only monomers are present. Therefore, presence of small clusters is inevitable and should be taken into account. Moreover, even in the solutions close to equilibrium at concentrations close to CMC and above it the contribution from the clusters in the relaxation processes is sometimes very important as it is shown in Refs. [26–31,36,37].

With *Model D* aggregation/disaggregation of clusters (or micelles if any) occurs also asymmetrically: only single molecules can join clusters but clusters of any size can disaggregate. Fig. 1(D1 and D2) presents this situation.

Analytical solutions and numerical simulations below show that in the case of *Models A*, *B*, and *D* equilibrium distribution of doublets, triplets and so on develops continuously with concentration and does not undergo a transition to the micelles formation at any concentration.

Situation is completely different (see below) in the case of the *Model C* (Fig. 1(C1 and C2)): equilibrium distribution of low sized clusters (doublets, triplets, and so on) is possible only at concentrations below some critical. Above this critical concentration the system undergoes a transition to the micelles formation which results in the formation of a new very distinct bimodal distribution. The latter means that this critical concentration is the CMC.

In the case of pure Brownian aggregation $a_{i,j}$, $i, j = 1, 2, 3, \ldots$ are determined by Smoluchowsky [21,38] as

$$a_{i,j} = \frac{2kT}{3\mu}\left(\frac{1}{a_i} + \frac{1}{a_j}\right)(a_i + a_j), \tag{6}$$