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.

Key words: surfactant solution, cluster, micelle formation.

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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.

In spite of the clear understanding of thermodynamic background of the micelles formation [7,14], there is no kinetic theory at present, which can predict both cluster formation (doublets, triplets and so on) below CMC and transition to the micelle formation above the CMC in surfactant solutions based on their aggregation/disaggregation rates.

Aggregation and disaggregation of single molecules and clusters of surfactant molecules is a complex phenomenon, which is still to be understood. The theory of aggregation (coagulation) of colloids was proposed by Smoluchowsky [15] and further developed in [16], where disaggregation of colloids was introduced. Application of such approach to surfactant solutions is referred to as a quasi-chemical approach [13].

Theoretical models have been suggested, which allow evaluation of the relaxation times associated with micellar solutions. A two-state model [17-18] 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 [19-21] using a quasi-chemical approach. However, transition process from monomolecular to micellar state in surfactant solutions was not considered in these publications: it was taken for granted that the micelles formation already took

place. It was a reason why the value of CMC has not been determined in [19-21] based on the aggregation/disaggregation model adopted in [19-21].

The aim of this paper is 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 micelles formation above the CMC. The quasi-chemical approach is used below.

In this part we briefly summarize the known theoretical results relevant to the quasi-chemical approach of the micelles formation [13], [16], [22]. The terminology used in [16], [22] is adjusted below for the consideration of surfactant solutions.

Let $n_i(t)$, $i=1,2,3,...$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 $a_{i,j}n_i n_j$, where $a_{i,j}$, $i, j = 1,2,3,...$ 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 $b_{i,j}$, $i, j = 1,2,3,...$are disaggregation rates. Aggregation/disaggregation rates satisfy the following symmetry conditions: $a_{i,j}=a_{j,i}$, $i, j = 1,2,3,...$, $b_{i,j}=b_{j,i}$, $i, j = 1,2,3,....$

Using the above notations development over time of cluster concentrations can be written as [16], [22]:

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

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

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

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

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:

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

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

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

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

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

The important conclusion obtained in [13], [22] is as follows: the steady state solution of the system (5) corresponds to the minimum of the free energy of the system under consideration.

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 [19-21] 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 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 the contribution from the small clusters in the relaxation processes is sometimes very important [23,24].

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.

Being aware that the probability of realization either *Model B* or *D* is rather small, because in this case several intermolecular bonds should be broken simultaneously, we still consider these *Models* for the sake of completeness.

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,...*are determined by Smoluchowsky [15,25] as

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

where k is the Boltzmann constant, T is the absolute temperature, μ is the dynamic viscosity of dispersion medium or solvent in the case of surfactant solutions. Following Smoluchowsky [15,25] it is assumed further that in *Models B* and *C* collisions occurs mainly between particles of close sizes and therefore for these models $a_{i,j}=a_{B,C}=8kT/3\mu$. Obviously for *Models A* and *D* collision occurs mainly between particles of different size. It was assumed that in this case $a_{i,j}=const=a_A>a_{BC}$.

Disaggregation rates $b_{i,j}$, *i,j=1,2,3,...*depend solely on the interaction energy between clusters and these coefficients are also assumed independent of the cluster size. That is, in all four models below aggregation/disaggregation rates are assumed to be constant, a_I and b_I, respectively, independently of the cluster size.

Model A.

According to this model only single molecules can connect/disconnect to/from clusters.

All possible events with a cluster of size *k, k=1,2,3,4,...* are as follows:

- connection of one molecule to a cluster of *k-1* size, which results in an increase of n_k value; the reaction rate of this process is a_A. However, at *k=2* the reaction rate is $2a_A$;
- disconnection of one molecule from a cluster of size *k+1*, which results in an increase of n_k value; the reaction rate of this process is b_A or $2b_A$ at *k=1;*
- disconnection of one molecule from a cluster of size *k,* which results in a decrease of n_k value; the reaction rate of this process is b_A;
- connection of one molecule to a cluster of size *k,* which results in a decrease of n_k value; the reaction rate of this process is a_A or $2a_A$ at *k=1.*

Taking all these events into consideration the following system of equations can be deduced from the general system (2)

$$\frac{dn_1}{dt} = -a_A n_1 n - a_A n_1^2 + b_A (n - n_1) + b_A n_2$$
$$\frac{dn_k}{dt} = a_A n_{k-1} n_1 + b_A n_{k+1} - b_A n_k - a_A n_k n_1, \quad k = 2,3,4,... \tag{7}$$

with conservation condition of conservation of the total number of particles (3).

Under steady state conditions the left hand sides of Eqs. (7) should be set to zero. Let $f_k=n_k/N$, $k=1,2,3,$ ... be the fraction of clusters of size k, and $\alpha=a_A N/b_A$ be the dimensionless concentration. Using these notations system of Eqs. (7, 3) under steady state conditions takes the following form

$$0 = \alpha f_{k-1} f_1 + f_{k+1} - f_k - \alpha f_k f_1, \; k=2,3,... \tag{8}$$

$$\sum_{k=1}^{\infty} k f_k = 1 \tag{9}$$

Solution to system of Eqs. (8), (9) is deduced in Appendix 1 (Eqs. (A1.10)-(A1.11)):

$$f_1 = \frac{1}{\alpha + 0.5 + \sqrt{\alpha + 0.25}} \tag{10}$$

$$f_k = \frac{\alpha^{k-1}}{[\alpha + 0.5 + \sqrt{\alpha + 0.25}]^k}, \; k=2,3,... \tag{11}$$

It is possible to conclude using Eq. (11) that $f_k(\alpha), \quad k = 2,3,4,...$ dependencies go from zero at $\alpha=0$ to zero at $\alpha \to \infty$ via the maximum value (see Appendix 1 for details) at

$$\alpha_{k,\max} = \frac{k^2 - 1}{4}, \quad k = 2,3,4,... \tag{12}$$

and that maximum value is equal to

$$f_{k,\max} = 4\frac{(k-1)^{k-1}}{(i+1)^{k+1}}, \quad k = 2,3,4,... \tag{13}$$

Dependencies $f_k(\alpha)$, $k=1, 2, 3, ...$ according to Eqs. (10, 11) are shown in Fig. 2. Note, α is the dimensionless concentration. Fig. 2 shows that there is no restriction on concentration in *the Model A*. Let us introduce $F(\alpha) = \sum_{k=1}^{\infty} f_k$. It is easy to see that the average cluster size, $<k>=1/F(\alpha)$. Using Eqs. (8)-(9) we can conclude that the averaged cluster size in the case under consideration is $< k >= 0.5 + \sqrt{\alpha + 0.25}$. That

is, <*k*> is an increasing, **convex** function of the dimensionless concentration, α, and this dependency does not have any inflection point.

That is, there is no CMC and there is no transition to the micelles formation in *the Model A*.

Model B.

All possible events with a cluster of size *k* are as follows (Fig. 1, B1 and B2):

- connection of one cluster of size *i* to a cluster of *k-i* size (*i=1,2,...k-1*), which results in an increase of n_k value; the reaction rate of this process is a_B;
- disconnection of a cluster of size *k* from a higher cluster, *k+i*, *i=1,2,...,* which results in an increasing of n_k value; the reaction rate of this process is b_B. If *i=k* then this reaction results in a formation of 2 clusters of *k* size, this means this reaction rate is $2b_B$ in this case;
- disconnection of cluster of any size from the cluster *k* size, *i=1,2,.., k-1*; reaction rate is b_B. However, at *i=k/2* the reaction rate is $2b_B$. Hence, the cases of even and odd *k* should be considered separately;
- connection of clusters of size *k* and *i* and *i=1,2,...* reaction rate is *a*. If clusters are of the same size *k*, then reaction rate is $2a_B$.

Eq. (2) now can be rewritten as

$$\begin{cases} \dfrac{dn_1}{dt} = -n_1 a_B \sum_{i=1}^{\infty} n_i - a_B n_1^{\,2} + b_B \sum_{i=1}^{\infty} n_i - b_B n_1 + b_B n_2 \\ \dfrac{dn_{2k}}{dt} = \dfrac{a_B}{2} \sum_{i=1}^{2k-1} n_i n_{2k-i} + \dfrac{a_B}{2} n_k^{\,2} - k b_B n_{2k} - a_B n_{2k} \sum_{i=1}^{\infty} n_i - a_B n_{2k}^{\,2} + b_B \sum_{i=1}^{\infty} n_i - b_B \sum_{i=1}^{2k} n_i + b_B n_{4k} \\ \dfrac{dn_{2k+1}}{dt} = \dfrac{a_B}{2} \sum_{i=1}^{2k} n_i n_{2k+1-i} - k b_B n_{2k+1} - a_B n_{2k+1} \sum_{i=1}^{\infty} n_i - a_B n_{2k+1}^{\,2} + b_B \sum_{i=1}^{\infty} n_i - b_B \sum_{i=1}^{2k+1} n_i + b_B n_{4k+2} \end{cases}$$

k=1,2,3,… (14)

with the conservation condition of the total number of particles (3) satisfied.

Under steady state conditions and using fraction of clusters of size *k*, $f_k=n_k/N$, *k=1,2,3,* ... and the dimensionless concentration, $\alpha=a_B N/b_B$, as in the *Model A,* the latter system becomes:

$$\begin{cases} 0 = -\alpha f_1 f - \alpha f_1^{\,2} + f - f_1 + f_2 \\ 0 = \dfrac{\alpha}{2}\sum_{i=1}^{2k-1} f_i f_{2k-i} + \dfrac{\alpha}{2} f_k^{\,2} - k f_{2k} - \alpha f_{2k} f - \alpha f_{2k}^{\,2} + f - \sum_{i=1}^{2k} f_i + f_{4k} \\ 0 = \dfrac{\alpha}{2}\sum_{i=1}^{2k} f_i f_{2k+1-i} - k f_{2k+1} - \alpha f_{2k+1} f - \alpha f_{2k+1}^{\,2} + f - \sum_{i=1}^{2k+1} f_i + f_{4k+2} \end{cases}$$

k=1,2,3,… (15)

with the conservation law (9).

The system of Eqs. (15), (9) has exactly the same solution as the *Model A*, which is given by Eqs. (10), (11). The latter can be checked by the direct substitution of Eqs. (10), (11) into system of Eqs. (15), (9).

The latter means that there is no restriction on concentration in *Model B*. **That is, there is no CMC and there is no micelles formation according to both *Model B* and *Model A*.**

Model C.

According to this model any two clusters of different sizes can be connected in a new bigger cluster but only single molecules can leave clusters (Fig. 1, C1 and C2).

All possible events with a cluster of size *k, k=1,2,...* are as follows:

- connection of one cluster of size *k-i* to a cluster of *i* size (*i=1,2,..., k-1*), which results in an increase of n_k value; the reaction rate of this process is $a_C=a_B$;
- disconnection of one molecule from a cluster of size *k+1*, which results in an increase of n_k value; the reaction rate of this process is $b_C=b_A$. Disconnection of one molecule from any doublet results in a creation of 2 single molecules, this means, the reaction rate of this process is $2b_C$;
- connection of a cluster of size *k* to any other cluster of *i* size (*i=1,2,3,...*), which results in a decrease of n_k value; the reaction rate of this process is a_C. If *i=k* then the reaction rate is $2a_C$;
- disconnection of one molecule from a cluster of size *k*, which results in a decrease of n_k value; the reaction rate of this process is b_C.

System (2) in this case transforms into

$$\begin{cases} \dfrac{dn_1}{dt} = -a_C n_1 \sum_{i=1}^{\infty} n_i - a_C n_1^2 + b_C \sum_{i=2}^{\infty} n_i + b_C n_2, \\ \dfrac{dn_k}{dt} = \dfrac{1}{2} a_C \sum_{i=1}^{k-1} n_i n_{k-i} + a_C \dfrac{1+(-1)^k}{4} n_k^2 - b_C n_k - a_C n_k \sum_{i=1}^{\infty} n_i - a_C n_k^2 + b_C n_{k+1}, \quad k > 1 \end{cases} \tag{16}$$

Under steady state condition system (14) can be rewritten as

$$\begin{cases} 0 = -a_C n_1 \sum_{i=1}^{\infty} n_i - a_C n_1^2 + b_C (n - n_1) + b_C n_2, \\ 0 = \dfrac{1}{2} a_C \sum_{i=1}^{k-1} n_i n_{k-i} - b_C n_k - a_C n_k n - \dfrac{3-(-1)^k}{4} a_C n_k^2 + b_C n_{k+1}, \quad k > 1 \end{cases}, \tag{16'}$$

where $n = \sum_{i=1}^{\infty} n_i$ is the total number of clusters including single molecules (clusters of size *1*). Using dimensionless concentrations introduced as $z_k = N n_k a_C / 2 b_C = f_k \alpha / 2, \quad k = 1,2,3,...$ the latter system of equations and the conservation law (3) can be rewritten as:

$$\begin{cases} 0 = -2 z_1 z - 2 z_1^2 + (z - z_1) + z_2 \\ 0 = \sum_{i=1}^{k-1} z_i z_{k-i} - z_k - 2 z_k z - \dfrac{3-(-1)^k}{2} z_k^2 + z_{k+1}, \quad k > 1 \\ \sum_{i=1}^{\infty} i z_i = \dfrac{\alpha}{2} \end{cases}, \tag{17}$$

where $z = \sum_{i=1}^{\infty} z_i$.

Below system of algebraic Eqs. (17) is simplified as follows: it is ignored that the aggregation of two equal sized clusters results in a twice higher reaction rate, that is, terms $2 z_1^2$, $\dfrac{3-(-1)^k}{2} z_k^2$ are omitted in first and second equations of the system of Eqs. (17), respectively. This is done to make it possible to get an analytical solution of Eqs. (17). Using direct numerical simulation of the system of Eqs. (16) we show (see below) that our conclusions based on a simplified the system of Eqs. (16') remain valid.

Using these simplifications the system of Eqs. (17) becomes:

$$\begin{cases} 0 = -2z_1 z + (z - z_1) + z_2 \\ 0 = \sum_{i=1}^{k-1} z_i z_{k-i} - z_k - 2z_k z + z_{k+1}, \quad k > 1 \\ \sum_{i=1}^{\infty} i z_i = \dfrac{\alpha}{2} \end{cases} \tag{18}$$

Note, both systems of Eqs. (17) and (18) independently satisfy the conservation condition of the total number of particles.

Second equations of the system of Eqs. (18) can be summarized over *k* from 2 to infinity, which results in

$$\begin{aligned} &0 = \sum_{k=2}^{\infty} \left(\sum_{i=1}^{k-1} z_i z_{k-i} - z_k - 2z_k z + z_{k+1} \right) = \\ &z^2 - (z - z_1) - 2z(z - z_1) + (z - z_1 - z_2) = -z^2 + 2zz_1 - z_2 \end{aligned} \tag{19}$$

Using Eq. (19) the system of Eqs. (18) can be rewritten as

$$\begin{cases} z_1 = z - z^2 \\ z_2 = 2zz_1 - (z - z_1) \\ z_{k+1} = z_k + 2z_k z - \sum_{i=1}^{k-1} z_i z_{k-i}, \quad k > 1 \\ \sum_{i=1}^{\infty} i z_i = \dfrac{\alpha}{2} \end{cases} \tag{20}$$

Let us try to find the solution of the system of Eqs. (20) in the following form

$$z_k = -S_{k+1} z^{k+1} + S_k z^k, \quad k = 1,2,3,..., \tag{21}$$

where S_k, $k = 1,2,3,...$ are unknown coefficients. Substitution of expressions (21) into first three equations of the system of Eqs. (20) shows, that (a) solution in the suggested form (21) really exists and (b) unknown coefficients should satisfy the following relation

$$S_k = \sum_{i=1}^{k-1} S_i S_{k-i}, \quad k = 2,3,4,... \tag{22}$$

with the initial condition:

$$S_1 = 1, \tag{23}$$

which follows from the first Eq. (20) (see Appendix 2 for details).

Let us multiply both sides of Eq. (22) by z^k, $k=1,2,3,..$. After summation over k from 1 to infinity this gives:

$$Y(z)=\sum_{k=1}^{\infty} S_k z^k = \sum_{k=1}^{\infty}\sum_{i=1}^{k-1}\left(S_i z^i\right)\left(S_{k-i} z^{k-i}\right)= Y^2(z)+z\,.$$

where $Y(z)=\sum_{k=1}^{\infty} S_k z^k$. The latter equation can be rewritten as

$$Y(z)=Y^2(z)+z \qquad (24)$$

If we take into account condition $Y(0)=0$, which follows from the definition of $Y(z)$, then the solution of Eq. (24) is

$$Y(z)=\frac{1}{2}-\sqrt{\frac{1}{4}-z} \qquad (25)$$

This solution is defined only if

$$z \le 0.25\,. \qquad (26)$$

Let us substitute solution in the form (21) into the last equation of the system (20), which gives after some transformations (see Appendix 2): $Y(z)=\frac{\alpha}{2}$, or, using Eq. (25),

$$\sqrt{1-4z}=1-\alpha \qquad (27)$$

It is easy to see from the latter equation that solution exists only if $\alpha \le 1$, or

$$N \le \frac{b_C}{a_C}$$

If $N>b_C/a_C$ then the equilibrium solution does not exist and formation of clusters of an infinite size starts. That means,

$$\frac{b_C}{a_C}=CMC \qquad (28)$$

in this model.

That is, ***the Model C*** **results in the existence of CMC**, which is determined by Eq. (28). Below CMC equilibrium clusters form: doublets, triplets and so on and

cluster size distribution is similar to that in the *Models A* and *B*. Above CMC system under consideration can not be any more in equilibrium and formation of micelles starts.

Distribution of fraction of clusters below CMC calculated according to Eqs. (A2.6) is given in Fig. 3. The average cluster size, <k>, is as follows: $< k >= \frac{\alpha}{2z} = \frac{1}{1-\alpha/2}$. The latter dependency is an increasing but **concave** function at concentrations below CMC. As soon as concentration reaches CMC, cluster size changes from *2* to infinity. That is, CMC can be considered as an "inflection point" and this gives an important hint for the subsequent consideration.

According to the consideration above the formation of micelles of an infinite size starts above CMC. In our computer simulation below we introduce an equilibrium number of individual surfactant molecules in a micelle, $\aleph$, which is used as a parameter in our calculations below.

***Model C*: computer simulations.**

Computer simulations are carried out to solve the kinetic Eqs. (2) in the case of the *Model C*:

$$\frac{df_k}{d\tau} = \frac{\alpha}{2}\sum_{i=1}^{k-1} A_{i,k-i} f_i f_{k-i} - \frac{f_k}{2}\sum_{i=1}^{k-1} B_{i,k-i} - \alpha f_k \sum_{i=1}^{\infty} A_{k,i} f_i + \sum_{i=1}^{\infty} B_{k,i} f_{k+i}, \quad k = 1,2,3,.. \tag{29}$$

where $\tau = tb$ is the dimensionless time, with initial conditions

$$f_1(0) = 1, \; f_i(0) = 0, \; i = 2,3,4,... \tag{30}$$

Coefficients A_{ij} and B_{ij} are selected as follows:

$$A_{ij} = \begin{cases} 1, & if \;\; i < \aleph, \quad j < \aleph, \quad and \quad i \neq j, \\ 2, & if \quad i = j, \; and \quad i < \aleph, \\ 0, & if \quad i \geq \aleph, \quad or \quad j \geq \aleph, \end{cases} \tag{31}$$

and

$$B_{ij} = \begin{cases} 1, & if \quad i = 1, \quad or \quad j = 1, \quad and \quad i \neq j, \\ 2, & if \quad i = 1, \quad and \quad j = 1, \\ 0, & if \quad i > 1, \quad and \quad j > 1. \end{cases}, \tag{32}$$

where ℵ is the equilibrium number of individual surfactant molecules in a micelle. The latter choice of coefficients means that any two clusters of size below ℵ can aggregate, however, if the resulting cluster includes more than ℵ surfactant molecules then this cluster is not equilibrium one and surfactant molecules can only leave this cluster one at the time until the equilibrium number of molecules in the cluster, ℵ, is reached.

Transient behavior and equilibrium solution (at $t\to\infty$) of Eqs. (29)-(32) are discussed below. Solutions depend on both the dimensionless concentration of surfactant molecules, α, and the equilibrium number of molecules in micelles, ℵ.

Transient behavior of dimensionless concentration of clusters is presented in Fig. 4, calculated according to Eqs. (29)-(32) at the dimensionless concentration α=15 and the equilibrium number of individual molecules in micelles, ℵ=200. Concentration α=15 according to our previous consideration should be well above the CMC.

Fig. 4 shows the time evolution of cluster sizes according to *Model C*. After initial lag time a bi-modal size distribution forms, which develops in time.

In Fig. 5 the equilibrium distribution of dimensionless concentration of clusters on dimensionless concentration of surfactant molecules is presented calculated according to Eqs. (29)-(32) at ℵ=200. Calculations are carried out at α=1.5 (close to the dimensionless CMC), α=15 (the same as in Fig. 4), α=150. Concentrations of micelles progressively increases with concentration, while the distribution of low sized clusters remains almost unchanged.

In Figs. 6 and 7 dependences of averaged cluster size on dimensionless concentration are presented for two cases ℵ=200 (Fig. 6) and ℵ=50 (Fig. 7). In both figures these dependences have an inflection point between 1 and 1.5, which corresponds to the CMC in dimensionless units.

Model D.

All possible events with a cluster of size *k* are as follows:

- connection of one molecule to a cluster of *k-1* size, which results in an increase of n_k value; the reaction rate of this process is $a_D=a_A$;

- disconnection of a cluster of size k from a higher cluster, $k+i$, $i=1,2,...,$ which results in an increasing of n_k value; the reaction rate of this process is $b_D=b_B$. If $i=k$ then this reaction rate is $2b_D$;
- disconnection of cluster of any size from the cluster k size; reaction rate is b_D;
- connection of one molecule to a cluster of size k, which results in a decrease of n_k value; the reaction rate of this process is a_D.

Eq. (2) now can be written as

$$\begin{cases} \dfrac{dn_1}{dt} = -a_D n_1^2 - a_D n_1 n - b_D n_1 + b_D n_2 + b_D n \\ \dfrac{dn_{2k}}{dt} = a_D n_1 n_{2k-1} - k b_D n_{2k} - a_D n_{2k} n_1 + b_D n - b_D \sum_{i=1}^{2k} n_i + b_D n_{4k} \qquad \text{k=1,2,3,…(33)} \\ \dfrac{dn_{2k+1}}{dt} = a_D n_1 n_{2k} - k b_D n_{2k+1} - a_D n_{2k+1} n_1 + b_D n - b_D \sum_{i=1}^{2k+1} n_i + b_D n_{4k+2} \end{cases}$$

with the conservation condition of the total number of particles (3).

Using fraction of clusters of size k, $f_k=n_k/N$, $k=1,2,3,$ ..., dimensionless concentration, $\alpha=a_D N/b_D$ and the dimensionless time $\tau = tb$ the latter system becomes:

$$\begin{cases} \dfrac{df_1}{d\tau} = -\alpha f_1^2 - \alpha f_1 f + f - f_1 + f_2, \quad f_1(0) = 1 \\ \dfrac{df_{2k}}{d\tau} = \alpha f_1 f_{2k-1} - k f_{2k} - \alpha f_{2k} f_1 + f - \sum_{i=1}^{2k} f_i + f_{4k}, \quad f_{2k}(0) = 0 \\ \dfrac{df_{2k+1}}{d\tau} = \alpha f_1 f_{2k} - k f_{2k+1} - \alpha f_{2k+1} f_1 + f - \sum_{i=1}^{2k+1} f_i + f_{4k+2}, \quad f_{2k+1}(0) = 0 \end{cases} \qquad (34)$$

$k = 1,2,3,...$

with the conservation law (9).

Direct numerical solution of this system of differential equations was undertaken. Only equilibrium solution of the latter system (that is solution at $\tau \to \infty$) are discussed below.

Figs. 8 and 9 show results of our calculations. In Fig. 8 dimensionless concentration of clusters is presented. This figure shows that according to the *Model D* the concentration of clusters goes via its maximum value at $n=2$ (doublets),

concentration of doublets increases and the distribution becomes wider with concentration. However, there is no transition to micelle formation at any concentration.

In Fig. 9 dependence of the averaged cluster size on concentration is presented. This dependence is the convex function and does not have any inflection point in the whole range of concentrations. The latter observation confirms that there is no transition to micelle formation according to the *Model D*.

Conclusions

Four possible models of cluster formation in surfactant solutions are considered. It is shown that only one of these models shows a transition to the micelles formation at concentration above some critical, which corresponds to CMC. Three other models show a continuous increase in an averaged cluster size with concentration and do not show transition to micelles formation.

Model A (Fig. 1, A1 and A2*):* aggregation/disaggregation of surfactant molecules occurs via exchange by one molecule at the time between clusters/micelles.

*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*. The equilibrium cluster concentrations are identical in the case of these two models and do not show transition to the micelles formation at any concentration.

With *Model C* (Fig. 1, C1 and C2) 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.

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

Solutions and numerical simulation 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 do not undergo transition to the micelles formation at any concentration.

Situation is completely different 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, CMC, the system undergoes a transition to the micelles formation. If the surfactant concentration is above the CMC then the system does not have an equilibrium solution and shows a transient behavior, which results in the formation of a new very distinct bimodal distribution: low sized clusters (single molecules, doublets, triplets and so on) and micelles.

Acknowledgement

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Appendix 1

Model A. *Solution of system of Eqs. (6,7).*

Let us determine

$$f = \sum_{k=1}^{\infty} f_k \qquad \text{(A1.1)}$$

Taking definition (A1.1) into account and

$$\sum_{k=2}^{\infty} f_k = f - f_1, \quad \sum_{k=2}^{\infty} f_{k+1} = f - f_1 - f_2, \quad \sum_{k=2}^{\infty} f_{k-1} = f$$

after summation of all Eqs. (6) over k from 2 to infinity the following equation is obtained

$$f_2 = \alpha f_1^2 \qquad \text{(A1.2)}$$

From Eqs. (6) at $k=2$ one can conclude using Eq. (A1.2)

$$f_3 = \alpha^{\,2} f_1^3 \qquad \text{(A1.3)}$$

From Eqs. (6) at $k=3$ one can conclude using Eq. (A1.3)

$$f_4 = \alpha^{\,3} f_1^4 \qquad \text{(A1.4)}$$

From Eqs. (A1.2)-(A1.4) using Eqs. (6) it is possible to conclude that for any $k=2,3,4,$ ...

$$f_k = \alpha^{\,k-1} f_1^k, \quad k = 2,3... \qquad \text{(A1.5)}$$

and the only unknown value is f_1 , which should be found using Eqs. (7) and (A1.5). Combination of these equations results in

$$\sum_{k=1}^{\infty} k\alpha^{k-1} f_1^k = 1 \qquad \text{(A1.6)}$$

Differentiation of Eq. (A1.6) with respect to α shows that $f_1'(\alpha)<0$ that is $f_1(\alpha)$ is a decreasing function of dimensionless concentration α. It is easy to see that $f_1(0)=1$ should be satisfied.

Solution of Eq. (A1.6). In order to solve Eq. (A1.6) the following function Ω(x) is introduced $\Omega(x) = \sum_{k=1}^{\infty} x^{k} = \frac{x}{1-x}, \quad \Omega' = \sum_{k=1}^{\infty} k x^{k-1}$

Using αf_1 as x results in

$$\Omega(\alpha f_1) = \sum_{k=1}^{\infty} (\alpha f_1)^k = \frac{\alpha f_1}{1-\alpha f_1} \tag{A1.7}$$

and

$$\Omega' = \sum_{k=1}^{\infty} k(\alpha f_1)^{k-1} = \frac{1}{f_1} \sum_{k=1}^{\infty} k\alpha^{k-1} f_1^{k} = \frac{1}{f_1}, \tag{A1.8}$$

where at the last step Eq. (A1.6) is used.

It is easy to calculate the first derivative using Eq. (A1.7) in a different way as

$$\Omega' = \frac{1}{(1-\alpha f_1)^2} \tag{A1.9}$$

Comparing Eqs. (A1.8) and (A1.9) results in the following equation for f_1 determination

$$\frac{1}{f_1} = \frac{1}{(1-\alpha f_1)^2}$$

Solution to the latter equation, taking into account that $f_1=1$ at $\alpha=0$ results in

$$f_1 = \frac{1}{\alpha + 0.5 + \sqrt{\alpha + 0.25}} \tag{A1.10}$$

Now from Eqs. (A1.5) and (A1.10)

$$f_k = \frac{\alpha^{k-1}}{[\alpha + 0.5 + \sqrt{\alpha + 0.25}]^k}, \quad k = 2,3,4,... \tag{A1.11}$$

The total number of particles and the averaged number of particles in clusters are $\frac{N}{0.5 + \sqrt{\alpha + 0.25}}$ and $< k >= 0.5 + \sqrt{\alpha + 0.25}$, respectively.

From Eq.(A1.11) we conclude, that f_k, $k=2,3,$ ...dependencies on α go from zero at $\alpha=0$ via maximum value to zero at $\alpha \to \infty$. Maximum values are reached at

$$\alpha_{k,\max} = \frac{k^2 - 1}{4}, \quad k = 2,3,... \tag{A1.12}$$

and that maximum value is equal to

$$\max f_k(\alpha) = f_k(\alpha_{k,\max}) = 4\frac{(k-1)^{k-1}}{(k+1)^{k+1}}, \quad k = 2,3,... \tag{A1.13}$$

Appendix 2

Model C. *Solution of the system of Eqs. (18).*

In this section we show that expressions (19)-(21) give the solution of the system of Eqs. (18).

Let us compare

$$z_k = -S_{k+1} z^{k+1} + S_k z^k, \quad k = 1,2,3,... \tag{A2.1}$$

at *k=1* with the first equation of the system (18)

$$z_1 = z - z^2 \tag{A2.2}$$

Comparison gives $S_1 = 1$ and $S_2 = \sum_{i=1}^{1} S_i S_i = 1$. Hence, expression (A2.1) and

$$S_k = \sum_{i=1}^{k-1} S_i S_{k-i}, \quad k = 2,3,4,... \tag{A2.3}$$

is valid at k=1 and the first equation of system (18) is satisfied.

Substitution of the Eq. (A2.1) into the second equation of system (18)

$$z_{k+1} = z_k + 2z z_k - \sum_{i=1}^{k-1} z_i z_{k-i} \tag{A2.4}$$

gives

$$-S_{k+2} z^{k+2} + S_{k+1} z^{k+1} = -S_{k+1} z^{k+1} + S_k z^k - 2S_{k+1} z^{k+2} + 2S_k z^{k+1} -$$
$$\sum_{i=1}^{k-1} S_{i+1} S_{k-i+1} z^{k+2} + \sum_{i=1}^{k-1} S_{i+1} S_{k-i} z^{k+1} + \sum_{i=1}^{k-1} S_i S_{k-i+1} z^{k+1} - \sum_{i=1}^{k-1} S_i S_{k-i} z^k.$$

or

$$z^2 \left[-S_{k+2} + 2S_{k+1} + \sum_{i=1}^{k-1} S_{i+1} S_{k-i+1} \right] + z \left[2S_{k+1} - 2S_k - \sum_{i=1}^{k-1} S_{i+1} S_{k-i} - \sum_{i=1}^{k-1} S_i S_{k-i+1} \right] +$$
$$+ \left[S_k - \sum_{i=1}^{k-1} S_i S_{k-i} \right] = 0 \tag{A2.5}$$

The latter equation should be zero at any z, this means that all three expressions in square brackets should be equal to zero. Expression in the third square brackets is equal to zero according to the definition Eq. (A2.1).

The expression in the first square bracket of Eq. (A2.5) can be rewritten as:

$$-S_{k+2}+2S_{k+1}+\sum_{i=1}^{k-1}S_{i+1}S_{k-i+1}=-S_{k+2}+2S_{k+1}+\sum_{j=2}^{k}S_jS_{k-j+2}=$$

$$=-S_{k+2}+2S_{k+1}+\sum_{j=1}^{k+1}S_jS_{k-j+2}-2S_{k+1}=-S_{k+2}+2S_{k+1}+S_{k+2}-2S_{k+1}=0$$

The expression in the second square bracket of Eq. (A2.5) can be rewritten as

$$2S_{k+1}-2S_k-\sum_{i=1}^{k-1}S_{i+1}S_{k-i}-\sum_{i=1}^{k-1}S_iS_{k-i+1}=2S_{k+1}-2S_k-\sum_{j=2}^{k}S_jS_{k-j+1}-\sum_{i=1}^{k-1}S_iS_{k-i+1}=$$

$$=2S_{k+1}-2S_k-\sum_{j=1}^{k}S_jS_{k-j+1}+S_k-\sum_{i=1}^{k}S_iS_{k-i+1}+S_k=2S_{k+1}-2\sum_{j=1}^{k}S_jS_{k-j+1}=0$$

according to Eq. (A2.3). This means that solution of system (18) is really given by Eqs. (19)-(21).

Substitution of relations (A2.1) into the left hand side of the third equation of system (18) gives

$$\sum_{k=1}^{\infty}kz_k=\sum_{k=1}^{\infty}k\left(-S_{k+1}z^{k+1}+S_kz^k\right)=-\sum_{k=1}^{\infty}k\left(S_{k+1}z^{k+1}\right)+\sum_{k=1}^{\infty}k\left(S_kz^k\right)=$$

$$=-\sum_{k=2}^{\infty}(k-1)\left(S_kz^k\right)+\sum_{k=1}^{\infty}k\left(S_kz^k\right)=-\sum_{k=2}^{\infty}k\left(S_kz^k\right)+\sum_{k=2}^{\infty}\left(S_kz^k\right)+\sum_{k=1}^{\infty}k\left(S_kz^k\right)=$$

$$=S_1z+\sum_{k=2}^{\infty}\left(S_kz^k\right)=\sum_{k=1}^{\infty}\left(S_kz^k\right)=F(z)$$

From system (18) we can now find

$$z_1=z-z^2,\quad z_2=z^2-2z^3,\quad z_3=2z^3-5z^4$$

or

$$f_1=2(z-z^2)/\alpha,\quad f_2=2(z^2-2z^3)/\alpha,\quad f_3=2(2z^3-5z^4)/\alpha \qquad \text{(A2.6)}$$

where $z=\dfrac{2\alpha-\alpha^2}{4}$.

Distribution of volume fraction of clusters below CMC is given in Fig. 3.

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FIGURE LEGENDS

Fig. 1

Disaggregation/aggregation kinetics according to *Models A* (A1 and A2), *B* (B1 and B2), *C* (C1 and C2) and *D* (D1 and D2).

Model A

A1: disaggregation $A_{n+1} \rightarrow A_n + A_1$, n=2,3,4…

A2: aggregation $A_n + A_1 \rightarrow A_{n+1}$, n=1,2,3,4…

Model B

B1: disaggregation $A_{i+j} \rightarrow A_i + A_j$, i,j=1,2,3,4…

B2: aggregation $A_i + A_j \rightarrow A_{i+j}$, i,j=1,2,3,4…

Model C

C1: disaggregation $A_{n+1} \rightarrow A_n + A_1$, n=2,3,4…

C2: aggregation $A_i + A_j \rightarrow A_{i+j}$, i,j=1,2,3,4…

Model D

D1: disaggregation $A_{i+j} \rightarrow A_i + A_j$, i,j=1,2,3,4…

D2: aggregation $A_n + A_1 \rightarrow A_{n+1}$, n=1,2,3,4…

Fig.2

Models A and *B*. Fractions of clusters f_k, $k = 1,2,3,4$ according to Eqs. (8)-(9) as function of dimensionless concentration, α, under equilibrium conditions. No restriction on concentration.

1 f_1, single molecules,

2 f_2, doublets,

3 f_3, triplets,

4 f_4, quadruplets.

Fig.3

Model C. Fractions of clusters f_k, $k = 1,2,3$ according to Eqs. (A2.6) as functions of dimensionless concentration, α, under equilibrium conditions at concentrations below CMC (CMC=1 in dimensionless units).

1 f_1, single molecules,

2 f_2, doublets,

3 f_3, triplets,

Concentration in the range $0<\alpha<1$.

Fig. 4

Model C. Transient behavior of dimensionless concentration of clusters, αf_n, at different moments of dimensionless time, τ. Dimensionless concentration α=15 and the equilibrium number of molecules in micelles $\aleph$=200.

1 $\tau=1$
2 $\tau=10$
3 $\tau=18$
4 $\tau=26$
5 $\tau=38$
6 $\tau=57.5$

Fig. 5

Model C. Equilibrium distribution of concentration of clusters on dimensionless concentration of surfactant molecules,α, at $\aleph$=200

1 $\alpha=1.5$ (close to the dimensionless CMC)

2 $\alpha=15$ (the same as in Fig 4)

3 $\alpha=150$

Fig. 6

Model C. Averaged cluster size on dimensionless concentration. Inflection point is close to 1.5 and corresponds to the dimensionless CMC. $\aleph$=200

Fig. 7

Model C. Averaged cluster size on dimensionless concentration. Inflection point is close to 1.3 and corresponds to the dimensionless CMC. $\aleph$=50

Fig. 8

Model D. Dimensionless concentration of clusters on the dimensionless concentration, α.

1 α=1

2 α=10

3 α=100

4 α=1000

Fig. 9

*Model D. D*ependence of averaged cluster size on concentration, α.

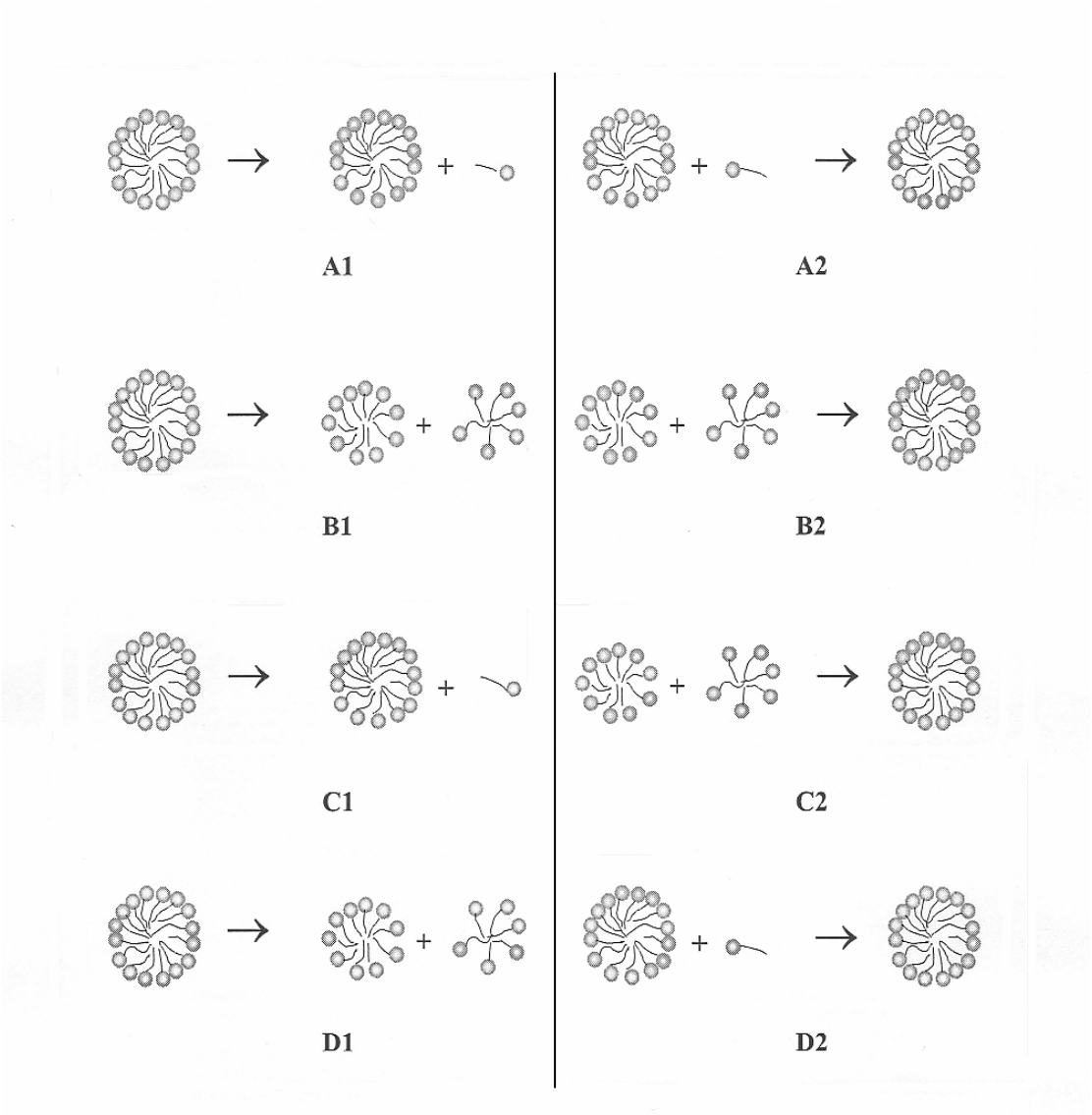
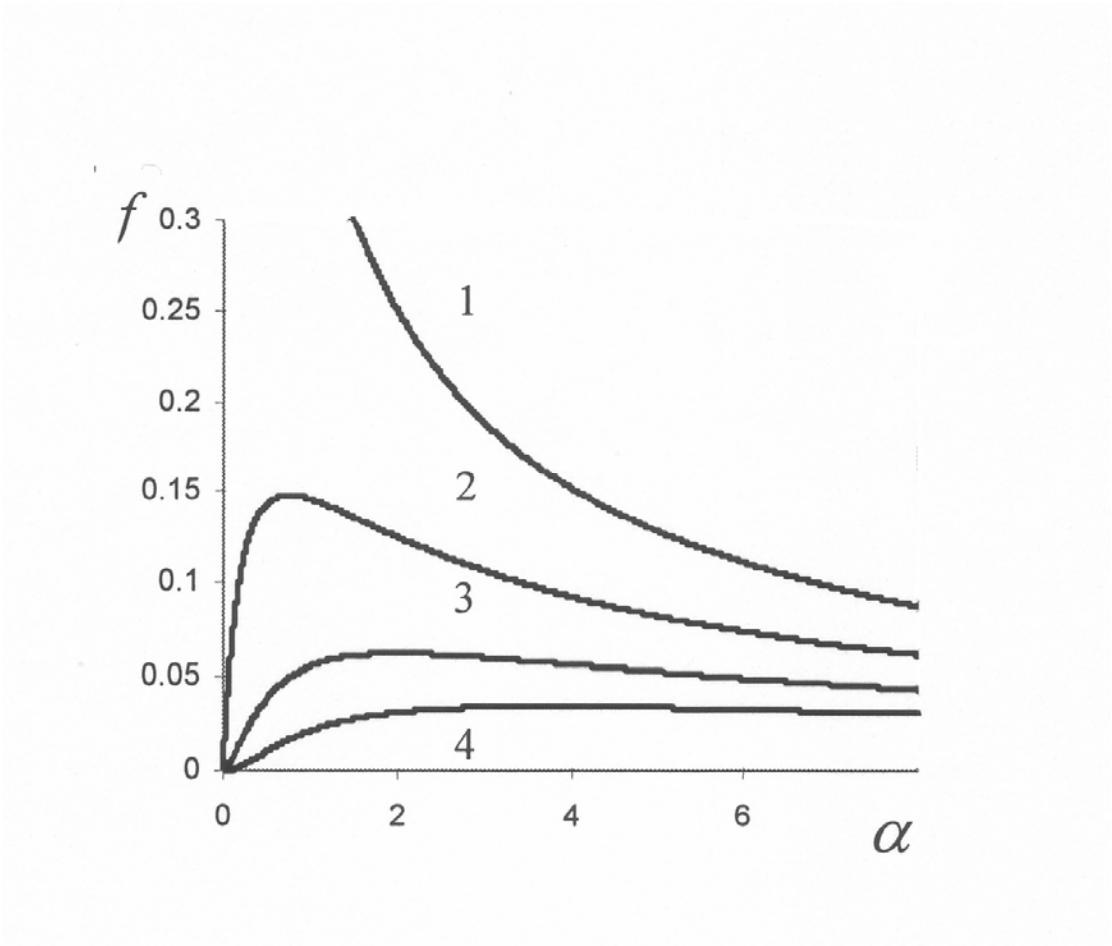


Fig. 1



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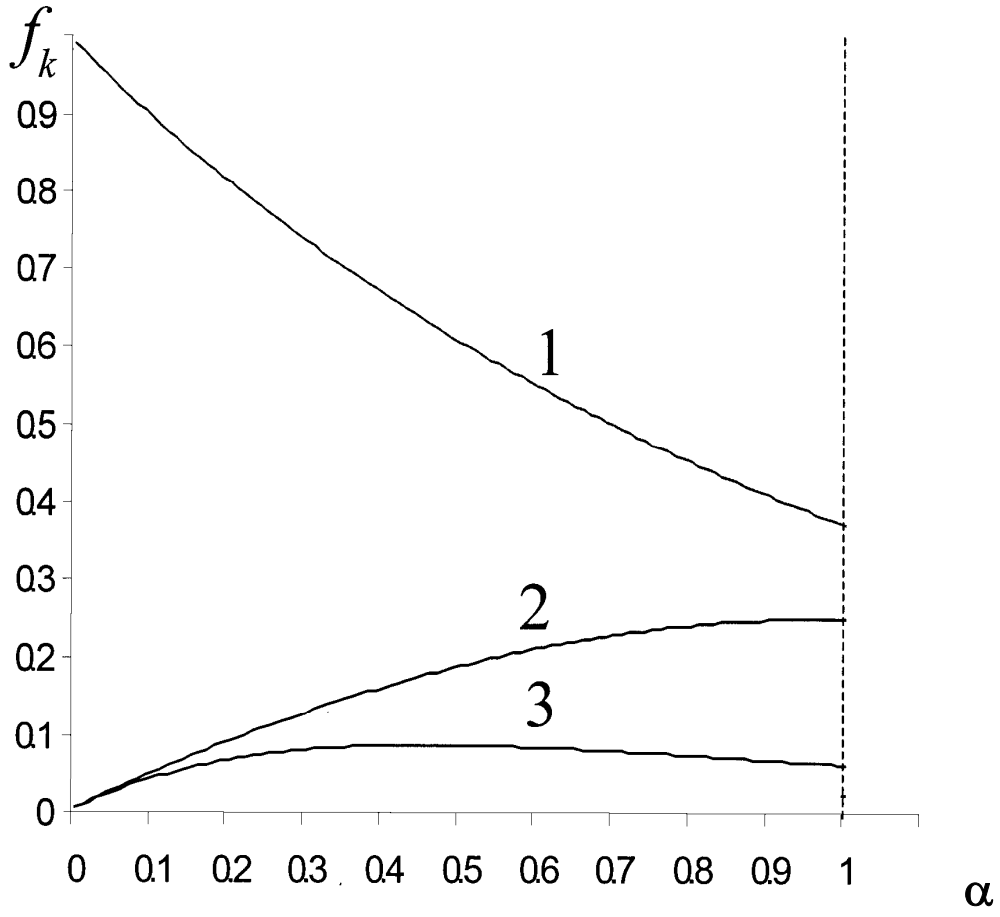
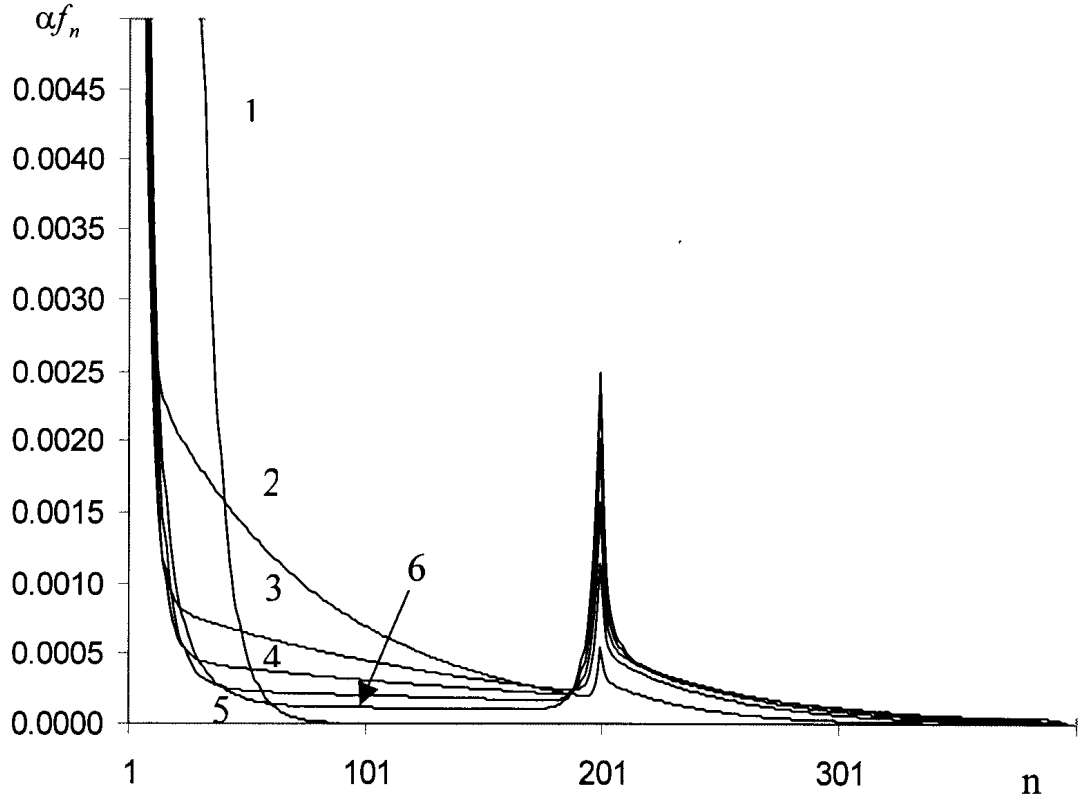


Fig. 3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5
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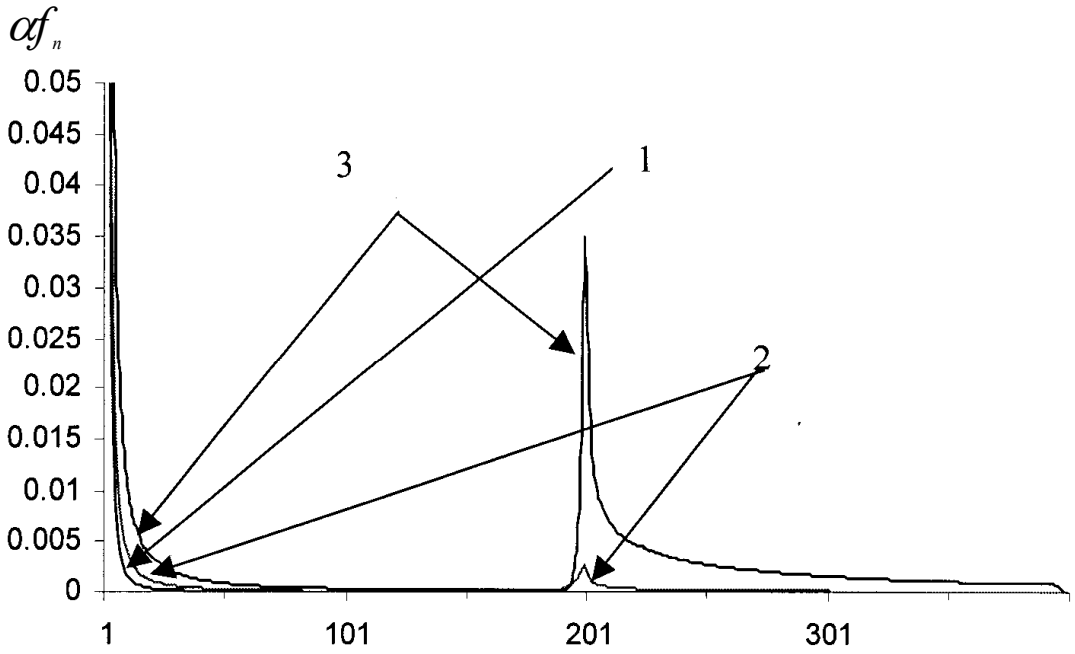
301
n

Fig. 4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3
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Fig. 5

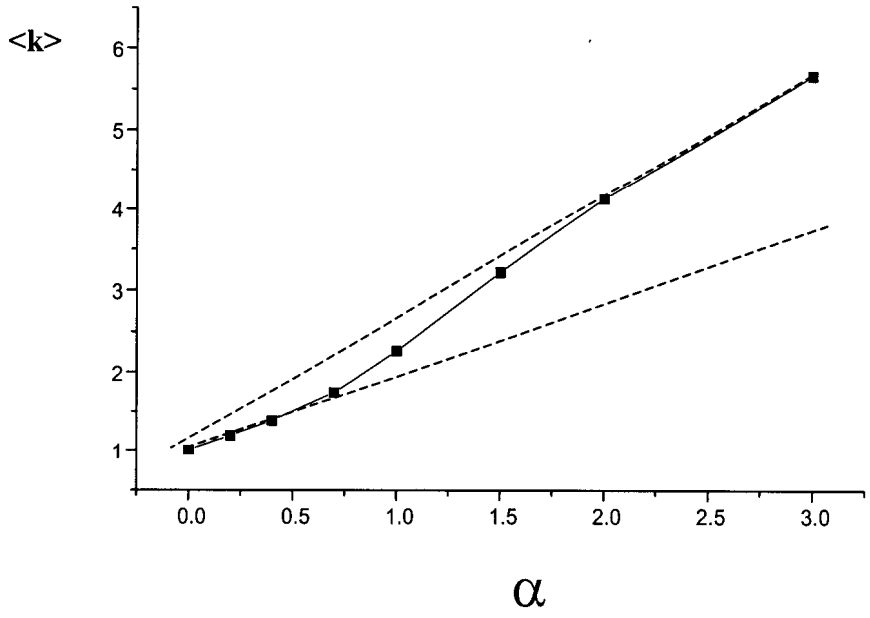

Fig. 6

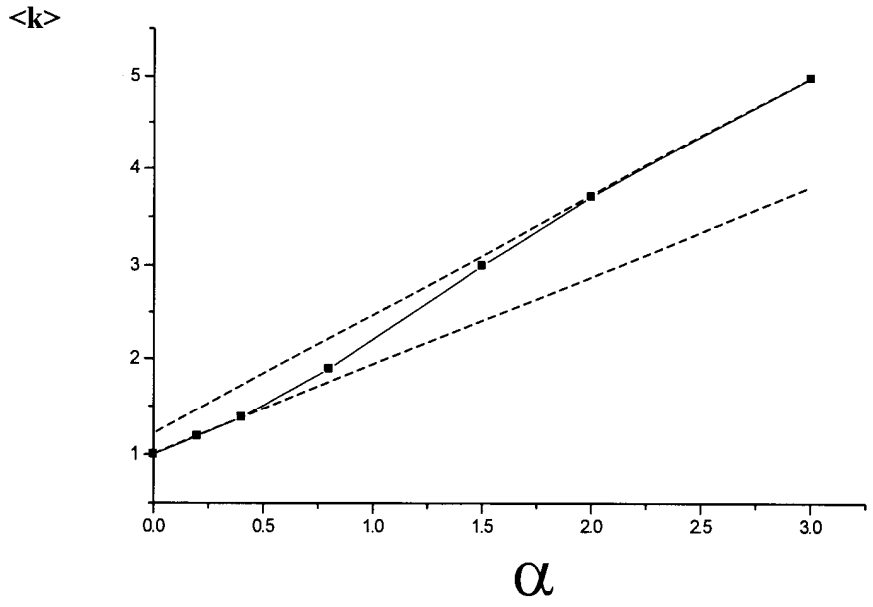

Fig. 7

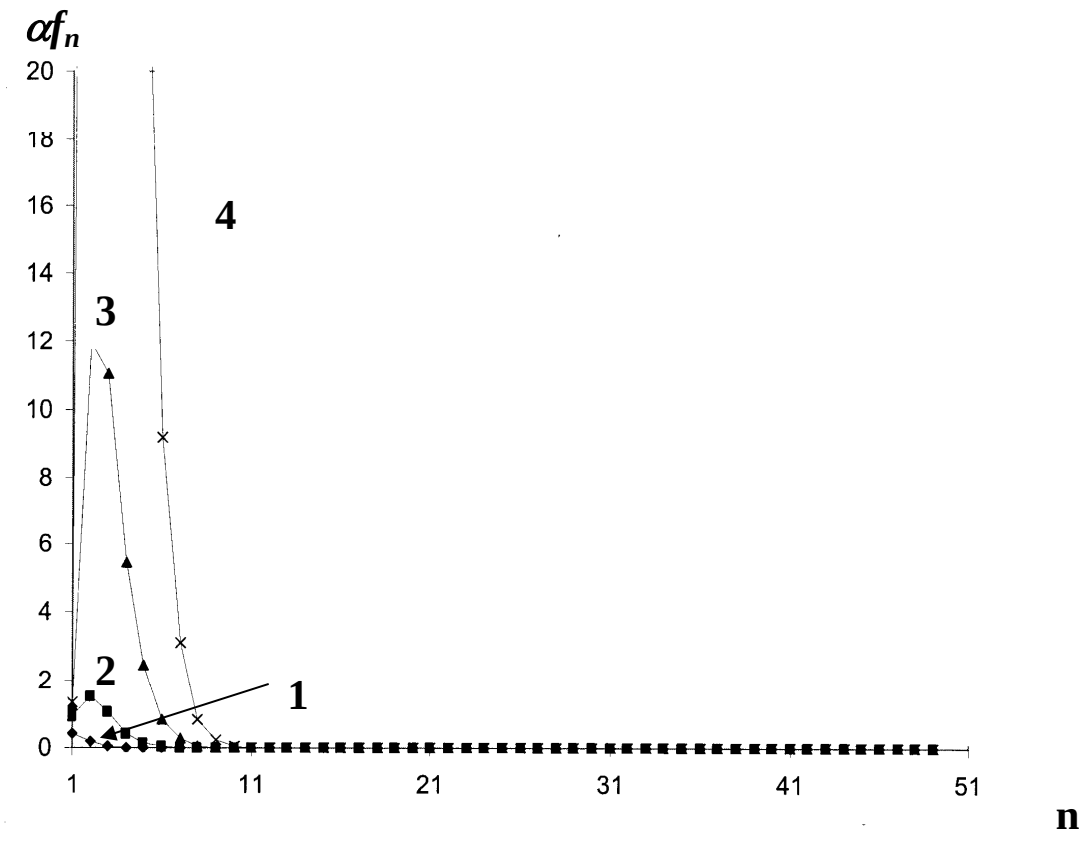

Fig. 8

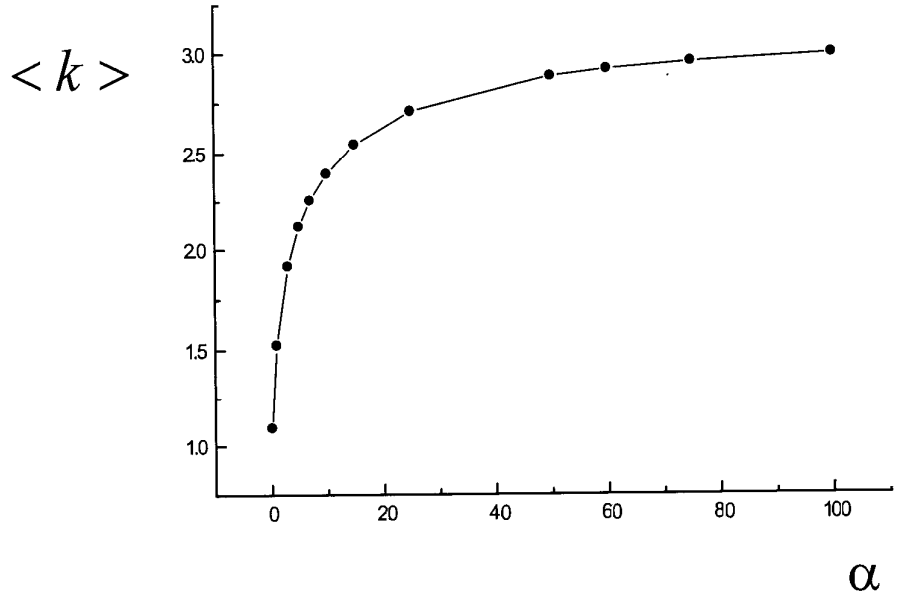

Fig. 9