nanoparticles, micelles,
colloid-polymer interactions

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COMPLEXATION OF NANOSIZED OBJECTS WITH LONG POLYMER CHAINS - A COMPARISON OF NANOPARTICLES AND MICELLES

The process of formation of complexes composed of a number of colloidal objects (nanoparticles or micelles) attached to a single macromolecule has been studied. The distribution of nanoobjects between polymer molecules was described by a modified Poisson probability distribution. It has been found that due to different mechanisms of complex formation the distribution of micelles between macromolecules can be more uniform, at the same nanoobject-to-macromolecule number concentration ratio, than the distribution of nanoparticles. Relation between the statistical nanoobject distribution and the shape of polymer adsorption isotherms is discussed.

The process of binding small colloidal objects to large polymer molecules is of interest in many fields. Interactions between very fine particles and very large polymers are important in water and wastewater purification and paper manufacture [1]. The interactions between supersized polymers and small colloidal objects are also relevant to a number of biological problems, most notably to the packaging of chromosomal DNA by histones to form chromatin fibers [2]. Another field of interactions of large macromolecules with nanosized objects is the formation of polymer-micelle complexes [3] (including protein-micelle complexes [4]). Studies concerning the association of nanocolloids with end-grafted long polymer chains are relevant to nanotechnology (*e.g.* the formation of gradient nanoparticle structures on surfaces that are of potential importance in catalysis or in detection and capturing of harmful viruses and toxins [5]) and to the material science (*e.g.* the production of non-fouling surfaces [6]).

When colloidal particles/micelles are much smaller than macromolecules, a single polymer molecule can accommodate a number of such nanoobjects. If the net colloid-polymer interaction is attractive and the number concentration of nanoobjects exceeds that of macromolecules, multiplets composed of a number of particles/micelles attached to a single macromolecule can be formed [3,7-9]. However, the mechanism

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of multiplet formation is different for nanoparticles and micelles. In the first case the process is due to the adsorption of polymer segments on the particle surfaces [7-8], whereas in the second case the micelles are formed directly on polymer chains as a result of the reversible association of surfactant molecules [9].

In this study we have investigated the dependence of the statistical distribution of nanoobjects between macromolecules on the mechanistic details of multiplet formation, in particular, on the way by which colloidal species are divided between polymer molecules. The implications of these differences on the nanoparticle and micelle distributions for the polymer adsorption have been also examined.

1. MODEL

Two systems containing monodisperse long polymer chains dissolved in a good solvent and monodisperse nanoobjects are considered. In one of the systems the nanoobjects are represented by monodisperse nanoparticles, whereas in another - by micelles being in the equilibrium with free surfactant molecules. It is assumed that in both systems there are conditions favorable for multiplet formation. It is also assumed that each macromolecule can accommodate only a certain maximum number of nanoobjects, N_{max}. The polymer-particle multiplets arise from the random distribution of particles between macromolecules; the complexation takes place when a particle collides with an empty (free) macromolecule or a multiplet which is not filled to capacity yet. On the other hand, the polymer-micelle multiplets are formed as a result of accumulation onto polymer chains of surfactant molecules that are grouped into nanosized objects, each composed of K surfactant molecules (K stands for the aggregation number and it is assumed to be independent on the surfactant concentration and the number of micelles attached to the polymer chain). For the number of polymer accommodated micelles to be the same as that of particles, the number of surfactant molecules accumulated onto the polymer should be K times larger. Thus, the polymer-micelle multiplets arise from the distribution between macromolecules of larger number of species than the corresponding polymer-particle multiplets.

It is assumed that the equilibrium of polymer-nanoobject complexation is shifted towards the multiplet formation. The polymer concentration is low enough for the macromolecules to be treated as individuals moving independently and for the formation of complexes containing two or more polymer molecules to be unlikely. For the sake of simplicity we have neglected mutual interactions between nanoobjects incorporated into multiplets. Thus, the number of particles/micelles per a single macromolecule is a random quantity, which can be described by the probability $P(i)$ given by a binomial distribution. We have assumed that this distribution can be approximated by the Poisson distribution with the mean value X, equal to the nanoobject-to-macromolecule number concentration ratio [10]. The distribution is cut-off at $i = N_{max}$. Thus, the probability distribution of nanoobjects between multiplets

is given by:

$$P(i)=\begin{cases} A\sum_{j=iK}^{(i+1)K}(KX)^j(j!)^{-1} & \text{for} \quad jK \le N_{\max} \\ 0 & \text{for} \quad jK > N_{\max} \end{cases} \tag{1}$$

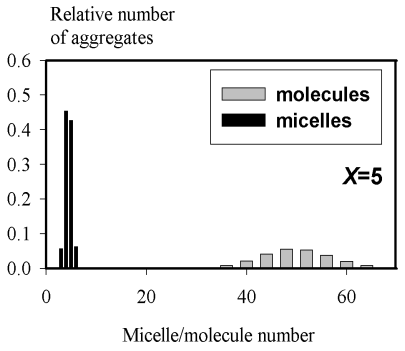

Fig. 1. The distribution of surfactant molecules between macromolecules and the equivalent distribution of micelles (N_{max}=10, K=10).

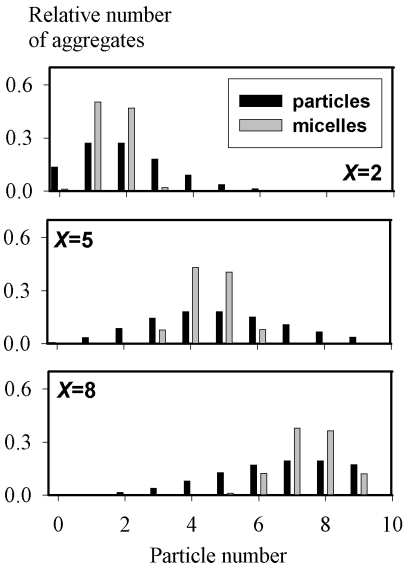

Fig. 2. The distributions of particles and micelles between macromolecules calculated at different nanoobject-to-macromolecule number concentration ratios, X (N_{max}=10).

where A denotes the normalization constant and KX is the mean distribution (when K=1 one deals with nanoparticles).

On the basis of distribution (1) the number of adsorbed macromolecules can be calculated from the following equation:

$$m_C = (1 - P(0))m_0 = (1 - A)m_0 \tag{2}$$

where m_0 is the total number of macromolecules in the system.

2. RESULTS AND DISCUSSION

Fig. 1 shows distributions of surfactant molecules and micelles between macromolecules. Both distributions are calculated for the same average number of surfactant molecules, KX=50. Thus, the average micelle number is equal to KX/K=5. Since N_{max} significantly exceeds the value of X, the standard deviation of the micelle distribution can be calculated in the same way as the standard deviation of non-modified Poisson distribution:

$$\sigma_M = \sqrt{KX}/K \tag{3}$$

whereas the standard deviation of the particle distribution simply reads:

$$\sigma_P = \sqrt{X} \tag{4}$$

The ratio σ_M/σ_P calculated for the same parameters of the distribution (X=5 and N_{max}=10) is equal to 0.316, which indicates that at the same nanoobject concentrations the distribution of particles is broader than that of micelles or, in other words, that micelles are distributed more uniformly.

The distributions calculated for different X values are collected in Fig. 2, in which the influence of the boundary conditions

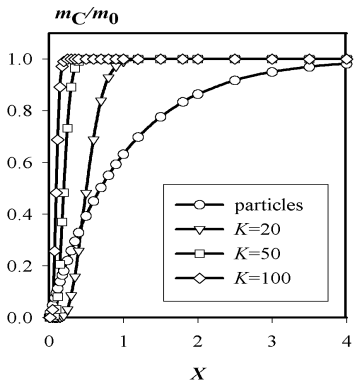

Fig. 3. The dependence of the relative amount of polymer adsorbed on the relative total concentration of nanoobjects (N_{max}=10).

$\langle 0, N_{max} \rangle$ on the distribution shape is shown. One can notice that if X is low, a relatively large number of free (non-adsorbed) macromolecules (~$P(0)$) can be found in the system with nanoparticles, which is not a case in the system with micelles.

Fig. 3 presents the dependencies between the total amount of the polymer adsorbed and the relative particle concentration in the system (X), calculated for different K values. When K=1 (the polymer is adsorbed on nanoparticles) the "low-affinity" isotherm is obtained, whereas in the systems with micelles (K>1) the situation corresponding to the achievement of isotherm plateau (all macromolecules contain at least one micelle) occurs already at very low nanoobject concentrations. This is due to the uniform distribution of micelles between macromolecules; the higher the aggregation number K, the steeper is the initial slope of the curve.

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TWORZENIE KOMPLEKSÓW POMIĘDZY NANOOBIEKTAMI I DŁUGIMI ŁAŃCUCHAMI POLIMEROWYMI - PORÓWNANIE NANOCZĄSTEK Z MICELAMI

Przedmiotem badań był proces powstawania kompleksów zbudowanych z pojedynczej makrocząsteczki i kilku nanoobiektów (nanocząstek lub micel). Rozkład nanoobiektów pomiędzy makrocząsteczki opisano zmodyfikowanym statystycznym rozkładem Poissona. Stwierdzono, że ze względu na różnice w mechanizmach tworzenia się kompleksów, rozkład micel pomiędzy cząsteczki polimeru jest bardziej jednorodny, przy takich samych wartościach stosunku liczbowych stężeń nanoobiektów i makrocząsteczek, niż rozkład nanocząstek. Pokazano też, że różnice w statystycznym rozkładzie nanocząstek i micel pomiędzy makrocząsteczki mają wpływ na kształt izoterm adsorpcji polimeru na tych nanoobiektach.