

Role of Adsorption in Formation of Inorganic Nanoparticles: Kinetic Model

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Abstract—A simple kinetic model is proposed for the formation of inorganic nanoparticles in the presence of additives of readily adsorbing organic compounds. Additives and monomers may occupy the same sites on the surface of a growing particle. The maximum sizes and size distribution of formed particles are estimated under the assumption that the surface curvature of a growing particle has equivalent effects on the rate constants of the growth and adsorption. Equations are derived that relate the polydispersity indices for particle mass and radius distributions to the variances of particle radius distribution. The conditions are determined for the formation of virtually monodisperse nanoparticles.

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INTRODUCTION

Inorganic nanoparticles formed from metals, metalloids, oxides, sulfides, selenides, etc. are frequently synthesized through liquid-phase processes in aqueous and nonaqueous solutions containing organic compounds readily adsorbed on nanoparticles (OCRAs). Synthetic and natural polymers, as well as low- and high-molecular ionic and nonionic surfactants, are commonly used as OCRAs [1–6]. Sometimes, organic solvents or special additives of low-molecular compounds, which have a structure different from that typical of surfactants but intensely interact with nanoparticles, play the role of OCRAs [7]. Their adsorption may be both physical and chemical, with the latter occurring via the formation of strong covalent bonds between adsorbates and adsorbents.

In even the earliest studies [1–7], it was reported that long-lived sols with high aggregation stability cannot be obtained in the absence of OCRAs. The adsorption of OCRAs on nanoparticles gives rise to the formation of organic shells on inorganic nuclei to drastically (by more than an order of magnitude) decrease the interfacial tension; stabilize formed nanoparticles; and dramatically enhance their resistance to external actions, e.g., to the oxidation of metal nanoparticles with atmospheric oxygen.

Depending on the chemical nature of an adsorbate, inorganic nanoparticles with adsorbed OCRA molecules can form stable sols both in water and in polar and nonpolar organic solvents. This fact makes it possible to easily combine inorganic nanoparticles with polymer matrices of diverse chemical natures and to prepare

polymeric nanocomposites containing finely dispersed nanoparticles.

It should be stressed that the synthesis of inorganic nanoparticles in the presence of OCRAs commonly yields nanoparticles with markedly lower average sizes and narrower size distributions [1–8], thus enabling one to obtain inorganic nanocrystals capable of the spontaneous formation of periodic perfectly organized plane and spatial structures. The latter circumstance is of great importance for some nanotechnologies [6–8].

At the same time, the theories of the homo- and heterophase nucleation and growth of particles of new phases developed to date [7–11] actually disregard the possible effect of OCRA adsorption on the sizes and size distribution functions of formed nanoparticles. The explosive rise that has recently taken place in the study of the synthesis processes and physical properties of inorganic nanoparticles produced in the presence of OCRAs, and the above-presented brief list of the peculiarities of these processes unambiguously indicate that the observed regularities need to be theoretically substantiated.

Obviously, the presence of OCRA molecules in a reaction system, which actively block the surface of growing nanoparticles, is the factor that governs the average sizes of formed particles and the pattern of their size distribution.

Note that the reducing influence of OCRA on the interfacial tension during the synthesis of inorganic nanoparticles was realized and successfully applied in experimental studies. The first effort to quantitatively describe the role of polymeric OCRAs in the control of the sizes of formed inorganic nanoparticles was made by Litmanovich and Papisov [12]. However, their

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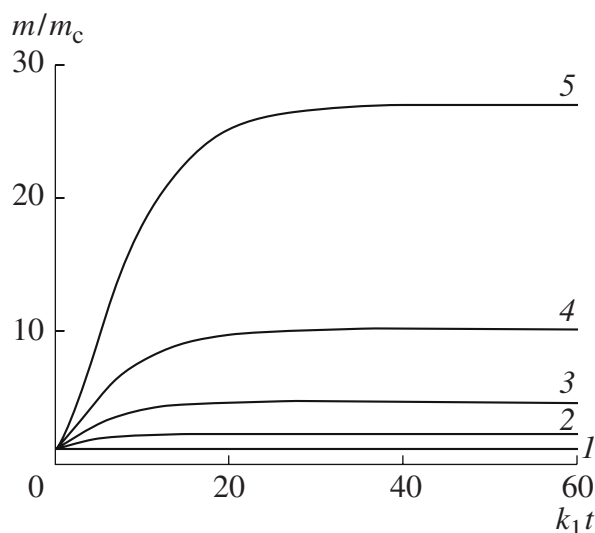


Fig. 1. Kinetic curves for the particle growth at different monomer concentrations: $x = (1) 0.1$, $(2) 0.3$, $(3) 0.5$, $(4) 0.7$, and $(5) 1.0$; $k_2 y / k_1 = 0.5$.

model based on the analogy with template polymerization is, in our opinion, not quite correct.

In this work, we propose a simple kinetic model that enables us to obviously clarify the role of OCRA in the formation of inorganic nanoparticles.

MAXIMUM NANOPARTICLE SIZE

In order to reveal the peculiarities of the formation of inorganic nanoparticles accompanied by OCRA adsorption on them, we consider the growth of a single particle. Within the framework of the proposed model, we shall not take into account the process of new phase nucleation and focus our attention to the competition of soluble monomer and OCRA molecules for a place on the surface of a growing nanoparticle. We shall assume that both of the processes (particle growth and OCRA adsorption) are irreversible.

As the particle grows, its free surface increases with a rise in its volume and decreases as a result of OCRA adsorption. The particle grows while the free surface exists. The maximum size of the particle is predetermined by the time of its growth or, in other words, by the time required for the disappearance of the free surface.

If s is the free surface of a particle with mass m , where m is the number of monomers composing the nanoparticle, the process of the nanoparticle growth is described by the following set of equations:

$$\begin{aligned} \frac{ds}{dt} &= s\delta_1 \frac{dm}{dt} - s\delta_2 k_2 y, \\ \frac{dm}{dt} &= sk_1 x. \end{aligned} \quad (1)$$

Here, k_1 and k_2 are the kinetic constants for the attachment of monomer and adsorbate molecules to the particle, respectively; δ_1 and δ_2 are changes in the free surface area of the particle caused by the attachment of the monomer and OCRA, respectively; and x and y are the concentrations of the monomer and the adsorbate in a solution, respectively. It is assumed that $y \gg x$; hence, the monomer consumption during the particle growth may be ignored.

As the free surface of a spherical particle with an m th size is $s_{\max} = s_0 m^{2/3}$, where s_0 is the area occupied by a monomer molecule on the surface of the growing particle, then $\delta_1 \equiv \frac{\partial s}{\partial m} = \frac{2}{3} s_0 m^{-1/3}$.

Thus, set (1) acquires the following form:

$$\begin{aligned} \frac{ds}{k_1 dt} &= \frac{2s_0}{3} s x m^{-1/3} - s \delta_2 \frac{k_2}{k_1} y, \\ \frac{dm}{k_1 dt} &= s x. \end{aligned} \quad (2)$$

Let us select product $k_1 t$ as the time coordinate. This approach allows us to ignore the dependence of the kinetic constants on the particle surface curvature, which varies in the course of the growth, because the right-hand part of the former equation comprises ratio k_2/k_1 . Indeed, in the general case, the kinetic constants depend on the particles size due to variations in the surface curvature. Without going into a discussion of the character of the effect of the surface curvature, it should only be noted that the rate constants of monomer and OCRA addition to the growing particle decrease to the same extent with an increase in the particle radius. Therefore, it is assumed that this factor does not influence the ratio between these rate constants.

The following model is the simplest from a mathematical point of view, though it is not quite justified in the physical sense. A particle with a critical size is nucleated at an arbitrary time moment at any conversion with respect to x ; its growth proceeds for quite a short time; hence, the value of x may be considered to be unchanged during this time period. System (2) will be integrated under this assumption. The model under consideration is, in essence, an analog of the model of free-radical polymerization.

Figures 1 and 2 exemplify the kinetic curves for the particle growth and variations in the free surface area as depending on concentration x at a fixed concentration of OCRA. It is seen that the kinetic curves of the growth rather soon reach a limit, the value of which rises with concentration x (Fig. 1). As follows from Fig. 2, this phenomenon is explained by the coverage of the growing particle surface with OCRA molecules. The curves of variations in s obviously demonstrate the factor of the competition between the growth and adsorption. Indeed, at relatively low x values, the surface area diminishes from the very beginning (curves 1–3), while

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