NOTE

Adsorption of Colloid Particles at Partially Covered Surfaces

The adsorption kinetics of negatively charged polystyrene latex at mica surface precovered with smaller sized (submicrometer) latex particles was investigated experimentally. The direct microscope observation method combined with the impinging jet technique was used in this study. Experimental results were presented concerning the initial flux and adsorption kinetics of larger particles at surfaces partially covered with smaller sized latex particles. The experimental results were interpreted in terms of the Monte Carlo simulations performed using the random sequential adsorption (RSA) model. Limiting analytical solutions for predicting the initial flux and adsorption kinetics were also formulated. It was found that the experimental results were in good agreement with theoretical predictions (derived for hard particle interaction potential). This confirmed the hypothesis that small colloid particles present in low concentration at surfaces considerably diminish adsorption rates of larger particles. © 1997 Academic Press

Key Words: adsorption of colloids; covered surfaces; polystyrene latex adsorption.

INTRODUCTION

Adsorption of colloid and bioparticles is of a large practical significance for polymer and colloid science, biophysics, and medicine enabling a better control of colloid, protein, and cell separation processes, e.g., by filtration, chromatography, enzyme immobilization, thrombosis, and biofouling of transplants and artificial organs. Often in these processes, especially in filtration, polydisperse suspensions or mixtures are occurring, e.g., colloid/polymer, colloid/macroscopic particle, or protein/surfactant. Due to their higher diffusivity and concentration the smaller sized particles will first adsorb at the interface forming a layer that may exert a significant influence on consecutive adsorption of larger particles. Similar problems appear in model experiments concerning particle or protein adsorption studies when the usual cleaning procedure may produce a layer of contamination at the substrate surface difficult to detect. This is expected to affect adsorption kinetics of the proper experiments. Hence, the subject of particle adsorption at partially covered surfaces seems attractive from practical viewpoint. Because the number of works devoted to this problem is rather limited (1–3) we initiated a series of systematic studies on particle adsorption at precovered (heterogeneous) surfaces. In this note we report some preliminary experiments obtained for monodisperse latex particle adsorption on surfaces partially covered with smaller sized latex colloid.

EXPERIMENTAL PROCEDURE

The experimental setup described in detail in our previous works (4–6) was based on the circular impinging-jet principle and direct *in situ* observations of particles at an arbitrarily chosen surface element. Since the size of

the particle was close to micrometer we were able to determine in real time the surface concentration (number of particles adsorbed over a given surface) of both smaller and larger particles. As the substrate we used the freshly cleaved mica sheets whose surface charge was converted to a positive one due to irreversible adsorption of Al^{3+} salts in a procedure similar to that previously described (4, 5). The latex suspensions were produced in a surfactant-free polymerization procedure with the persulfate initiator (7). In this study we used two monodisperse latex samples: (i) characterized by the averaged size (determine by the Coulter-Counter) $2a_1 = 1.48 \pm 0.1$ μm (hereafter referred to as larger particles) and (ii) $2a_s = 0.68 \pm 0.05$ μm (referred to as smaller particles). Their size ratio a_1/a_s was, therefore, equal 2.2. The ionic strength in these experiments was kept at 10^{-4} M (by addition of recrystallized KCl solution) and the pH was equal to 5.8.

The experimental procedure was the following: first the smaller particles were adsorbed at modified mica surface until a given coverage $\theta_s = \pi a_s^2 N_s$ was attained (where N_s is the surface concentration of small particles determined directly by microscope counting). In our experiments θ_s varied between 0 (uncovered surface) and 30%. Then the small particle suspension was replaced *in situ* by the larger particle suspension characterized by a bulk number concentration n_b. A short transition time (on the order of one minute) was allowed before the proper adsorption experiments of larger particles were recorded.

THEORETICAL SIMULATIONS

The experimental kinetic runs were interpreted in terms of the Monte Carlo computer simulations carried out according to the RSA model (8, 9) extended to polydisperse mixtures in (10). The basic assumptions of the model are:

(i) the interface at which particles adsorb is homogeneous on a microscopic scale;

(ii) if the adsorbing particle overlaps with any preadsorbed particle it is rejected with unit probability;

(iii) otherwise the particle will be adsorbed at a given point over the target with the probability calculated from the Boltzmann distribution; once the particle becomes adsorbed its position does not change (localized adsorption).

Usually, for obtaining a sufficient accuracy (about 3%) of the theoretical kinetic runs, about 10,000 smaller and 10^3 larger particles were simulated for each curve.

RESULTS AND DISCUSSION

It was found by performing extensive statistical analysis according to the method described in (6) that the distribution of smaller and larger particles was statistically uniform within the region near the stagnation point for the entire range of θ_s and θ_1 values (0–30%) in accordance with theoretical simulations. No tendency was observed to aggregate formation or uneven adsorption of larger particles which justified the validity of the surface concentration evaluation via the particle counting technique.

The kinetics of large particle adsorption determined by the counting procedure is shown in Fig. 1 for various surface coverages of smaller particles, i.e., 0, 5.8, 10, 15, 20.5, and 27%. As one can see, the increase in θ_s resulted in a considerable decrease in adsorption rate of larger particles so the surface coverages θ_1 attained after a long time in the presence of preadsorbed smaller particles became much lower than for uncovered surfaces.

The experimental kinetic runs were compared with the RSA simulations performed according to the procedure described above (solid lines in Fig. 1). As one can see, for $\theta_s = 0$ (uncovered surface) the experimental results are very well accounted for by the RSA model with the electrostatic interactions taken into account. On the other hand, for partially covered surfaces, especially for $\theta_s > 5\%$, the RSA model with electrostatic interactions neglected (hard particle limit) reflected better experimental results. This is rather unexpected since the electrostatic interactions, as predicted theoretically from the RSA simulations, should also exert a measurable effect on adsorption at partially covered surfaces. The explanation of this discrepancy can probably be sought in the charge migration effect deduced previously from the interaction energy profiles of colloid particles at mica surface (11). Due to the large field gradient between the negatively charged latex sphere and the positively charged mica surface the charged groups from the latex can, to a considerable degree, be transferred to the mica surface. Also a reverse process of migration of the positive groups from mica to the latex can be plausible. The net effect of these processes would be a mutual charge compensation increasing with time which is expected to be particularly effective for smaller sized particles characterized by low zeta potentials as was the case for our latex spheres. Thus, due to this charge reduction process the small particles behave effectively after a long time (i.e., for higher coverages) as hard spheres. This hypothesis is in accordance with experimental results showing that the best agreement of the hard particle RSA model is observed for higher θ_s values. Systematic studies on this subject are planed in our future works.

It is interesting to compare the experimental results and the RSA simulations with the theoretical predications derived for hard particle mixtures using the scaled particle theory (12) with the modification discussed elsewhere (13). The blocking parameter of larger particles valid for arbitrary surface coverage of small and large particles assumes the form

$$B(\theta_1, \theta_s) = (1 - \theta_1 - \theta_s)e^{-3\theta_1 + (\gamma^2 + 2\gamma)\theta_s/1 - \theta_1 - \theta_s - (\theta_1 + \gamma\theta_s/1 - \theta_1 - \theta_s)^2}, \quad [1]$$

where $\gamma = 2\sqrt{a_1/a_s} - 1$. When $\theta_1 \to 0$ one can derive from Eq. [1] the following expression for the initial flux j_0' of larger particles at partially covered surfaces,

$$\frac{j_0'(\theta_s)}{j_0} = B(0, \theta_s) = B_0(\theta_s) = (1 - \theta_s)e^{-(\gamma^2 + 2\gamma)\theta_s/1 - \theta_s - (\gamma\theta_s/1 - \theta_s)^2}, \quad [2]$$

where j_0 is the initial flux of large particles at uncovered surfaces.

Knowing B one can describe adsorption kinetics of larger particles using the general expression (6)

$$\int_0^{\theta_1} \frac{d\theta}{B(\theta_1, \theta_s)} = \pi a_1^2 j_0 t. \quad [3]$$

However, Eq. [3] can only be integrated analytically in the case for small θ_1 when $B(\theta_1, \theta_s)$ can be linearized to the Langmuir-like form

$$B(\theta_1, \theta_s) = B_0(\theta_s)(1 - C_1'\theta_1) + 0(\theta_1^2), \quad [4]$$

where

$$C_1' = \left[4 + (\gamma^2 + 4\gamma - 4)\theta_s + 2\gamma^2 \frac{\theta_s^2}{1 - \theta_s} \right] / (1 - \theta_s)^2.$$
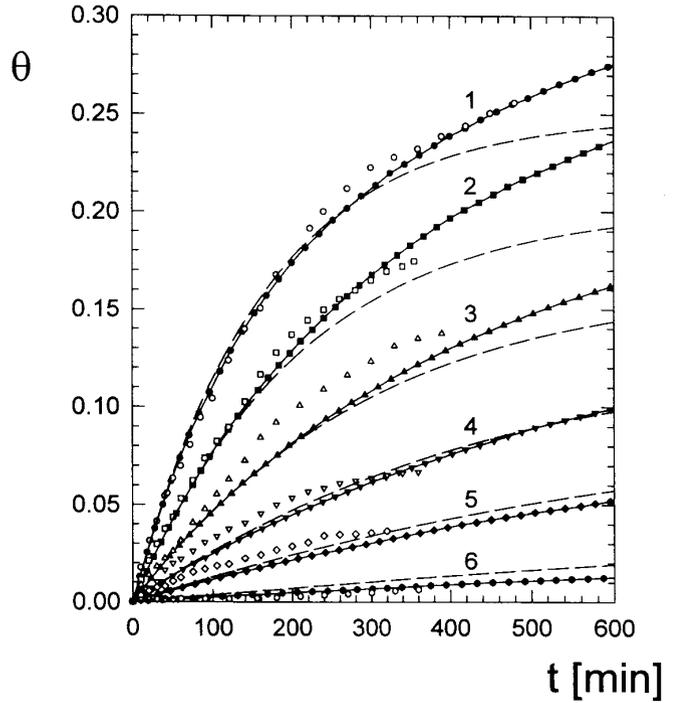
FIG. 1. The kinetics of polystyrene latex adsorption (larger particles $2a_1 = 1.48$ μm) at mica surface precovered by various amounts of smaller particles ($2a_s = 0.68$ μm) for $I = 10^{-4}$ M, $Re = 4$: (1) $\theta_s = 0$ (uncovered surface), (2) $\theta_s = 5.8\%$, (3) $\theta_s = 10\%$, (4) $\theta_s = 15\%$, (5) $\theta_s = 20.5\%$, (6) $\theta_s = 27\%$. The solid lines denote the RSA simulations and the broken lines the analytical results stemming from Eq. [5].

Substituting Eq. [4] into Eq. [3] one obtains

$$\theta_1 = \frac{1}{C_1'} [1 - e^{-B_0(\theta_s)C_1\pi a_1^2 j_0 t}]. \quad [5]$$

The analytical predictions stemming from Eq. [5] are also plotted in Fig. 1 (dotted lines). As can be seen they are in good agreement with the numerical simulations and experimental results for $\theta_s > 5\%$, especially for shorter adsorption times ($t < 300$ min).

It should also be noted in Fig. 1 that for longer adsorption times ($t > 300$ min) the kinetic curves seem to approach stationary (saturation) values. This is, however, an apparent saturation effect because from the numerical predictions one can deduce that the true limiting values of θ are much higher as discussed extensively in (13). However, the physical adsorption time needed to approach the true jamming limits becomes excessively long, especially for higher θ_s values (on the order of days for the bulk suspension concentration equal 4×10^8 cm^{-3}). For such long-lasting experiments, however, the chances of contaminating the system are increased which makes them less reliable.

Therefore, the kinetic runs like those shown in Fig. 1 are not suitable for determining the maximum surface coverages. They can be used, however, with good accuracy to derive the initial flux at covered surfaces. We used the least-squares nonlinear fitting procedure to determine the initial flux $j_0'(\theta_s)$ as the derivative of the θ vs time dependence in the limit $t \to 0$. The results are shown in Fig. 2 in the reduced form as the dependence j_0'/j_0 on θ_s. According to Eq. [2] this quantity can be treated as the blocking parameter of larger particles at surfaces precovered by small particles. The experimental results are compared with the numerical RSA simulations performed for both interacting and hard particles. The solid line in Fig. 2
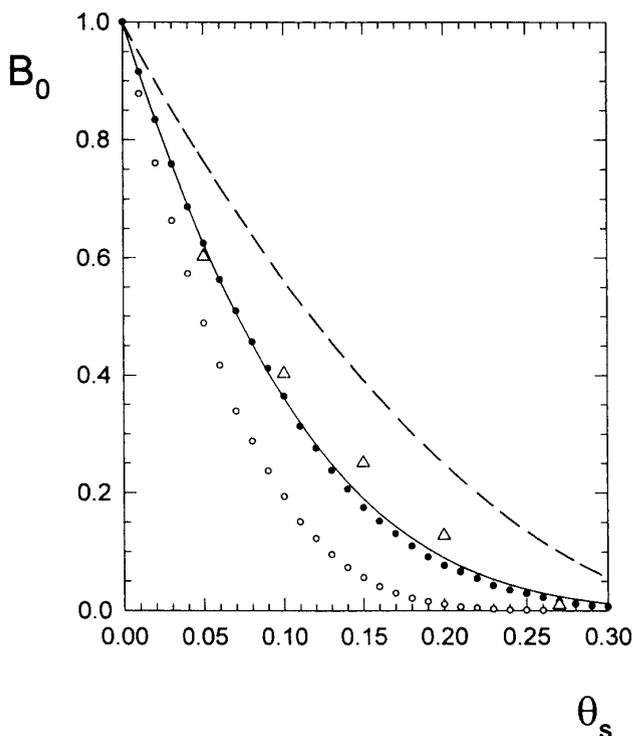
FIG. 2. The dependence of the reduced initial flux $j'_0/j_0 = B_0$ of larger latex particles on surface coverage θ_s of smaller particles preadsorbed at mica surface ($I = 10^{-4}$ M, $Re = 4$); the triangles denote the experimental results, the empty and filled circles represent the RSA simulations performed for interacting and hard spheres, respectively, the broken line represents the theoretical predictions for monodisperse particles, and the solid line shows the analytical results calculated from Eq. [2] valid for equilibrium adsorption.

represents the theoretical results stemming from the analytical expression Eq. [2] whereas for comparison the theoretical values of j'_0/j_0 calculated for the case of monodisperse particles, i.e., when $\gamma = 1$ are depicted by the broken line.

In accordance with the previous discussion the experimental results are well reflected for low θ_s values by the RSA simulations for interacting particles, whereas for higher θ_s the hard particle RSA model, which agrees well with the analytical formula Eq. [2], seems more appropriate.

In any case, however, the results shown in Fig. 2 demonstrate that the presence of smaller particles can exert a profound effect on adsorption kinetics of larger particles. The initial flux for θ_s as low as 10% was found to be almost three times smaller than for clean surfaces. For θ_s equal to 20% the initial flux at precovered surfaces is reduced by more than ten times. It is also interesting to note that this considerable flux reduction is mainly due to the size difference between preadsorbed (smaller) and ad-

sorbing (larger) particles since for monodisperse spheres the analogous flux reduction is significantly smaller (cf. the broken line in Fig. 2).

It should be mentioned that the effects measured in our work, which are stemming from the surface exclusions effects, exceed by orders of magnitude the effects predicted theoretically by Dąbroś and van de Ven (2) originating from hydrodynamic corrections due to the presence of adsorbed particles.

The large sensitivity of j'_0 to surface coverage of smaller particles (especially for the region of low θ_s) suggests that in particle adsorption experiments in which surface cleanness is not satisfactory controlled (in respect to smaller colloid particles) the initial flux measurements will be charged with a considerable error.

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