Deposition of latex particles at heterogeneous surfaces

Z. Adamczyk*, B. Siwek, K. Jaszczółt, P. Weroński

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-239 Kraków, Niezapominajek 8, Poland

Available online 12 October 2004

Abstract

Irreversible adsorption (deposition) of colloid particles at heterogeneous surfaces was studied experimentally. The substrate surfaces of desired heterogeneity were produced by covering mica surfaces by positively charged polystyrene latex particles. Then, deposition kinetics of negatively charged latex was studied under diffusion-controlled transport conditions. Particle distributions over surfaces and coverage were quantitatively evaluated using the direct microscope observation technique. Using this method, jamming coverage of colloid particles as a function of the heterogeneity degree (smaller particle coverage) was determined. These experimental data confirmed, in accordance with numerical simulations that the adsorption site multiplicity exerted a pronounced effect on the structure of adsorbed layers and the jamming coverage.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Adsorption of colloids; Colloid adsorption; Heterogeneous surfaces; Irreversible adsorption; Random site adsorption

1. Introduction

Adsorption and deposition (irreversible adsorption) of colloids, proteins and other bio-materials on solid/liquid interfaces is of large significance for many practical and natural processes such as filtration, paper-making, chromatography, separation of proteins, viruses, bacteria, pathological cells, immunological assays, thrombosis, biofouling, biomineralisation, etc. The effectiveness of these processes is often enhanced by the use of coupling agents bound to interfaces, e.g. polyelectrolytes [1–5]. In biomedical applications special proteins (antibodies) attached to the surface are applied for a selective binding of a desired ligands from protein mixtures as is the case in the affinity chromatography [6], recognition processes (biosensors) [7–8], immunological assays [9–10], etc.

On the other hand, many of experimental studies on colloid particle adsorption have been carried out for surfaces modified by adsorption of polymers, surfactants, polyvalent ions, or chemical coupling agents (silanes), which change the natural surface charge of substrate surfaces [11–12]. A characteristic feature of all these processes, also comprising chemisorption of gases on solids, is that the solute (particle or protein) adsorption occurs at heterogeneous surfaces bearing isolated adsorption sites.

Despite significance of particle adsorption at heterogeneous surfaces, this subject has little been studied experimentally in a systematic manner. The existing results were obtained for polystyrene latex adsorbing at mica under the convection-dominated transport conditions in the impinging-jet cell [13–14]. On the other hand, preliminary results concerning the diffusion-controlled adsorption of colloid particles at heterogeneous surfaces have been reported in Ref. [15].

The aim of this work was to check experimentally if the recently elaborated theoretical model [16–17] is adequate for describing irreversible particle adsorption at heterogeneous surfaces bearing adsorption centres of well-defined density and distribution. Besides direct applications for predicting biocolloid adsorption at heterogeneous surfaces, the results obtained can be exploited for elucidating the mechanism and modelling the kinetics of molecular adsorption.

2. Experimental

Particle deposition experiments have been carried out using the direct microscope observation method in the diffu-

sion cell described in Ref. [15]. The main part of the cell was a Teflon container of dimensions $1.5\,cm \times 2.5\,cm \times 8\,cm$ (height) with a rectangular window of the dimension of $2\,cm \times 6\,cm$ made of the mica sheet, used as the substrate for particle adsorption. The cell was placed on an optical microscope stage (Nikon) that was attached to a special metal table, which could be inclined (rotated) by an angle reaching $90°$. In this way, the microscope can be oriented horizontally with the objective perpendicular to the substrate surface, so the gravity force was directed parallel to the mica surface, eliminating effectively the particle sedimentation effect. Deposition kinetics and particle distribution over the substrate was followed in situ using a long-distance objective coupled with a CCD camera (Hamamatsu C-3077) and an image analysing system.

As model colloids in our deposition kinetic studies, two samples of polystyrene latex were used. The negatively charged latex was synthesized according to the polymerisation procedure described in Ref. [18] using a persulfate initiator. Particle size distribution and concentration in the dilute samples used in experiments were determined by the Coulter-Counter and by laser diffractometer with an accuracy of a few percent. The averaged size $2a_p$ of the negative latex used in our experiments was $0.9\,\mu m$ with standard deviation of $0.06\,\mu m$. The positively charged latex suspension (used for modelling adsorption sites) was produced and cleaned according to a similar procedure with the azonitrile initiator in place of the persulfate initiator. The averaged size $2a_s$ of the latex was $0.45\,\mu m$ with the standard deviation of $0.04\,\mu m$ as determined by a laser difractometer. Zeta potential of latex samples was determined by the Brookhaven zetasizer. For $I = 10^{-3}\,M$ KCl and pH = 5.5 (particle deposition experimental conditions) zeta potential of the negative latex was $-50\,mV$, whereas for the positive latex $54\,mV$, respectively.

The substrate surfaces were prepared of mica provided by Mica & Micanite Supplies Ltd., England. Zeta potential of this mica was determined by the streaming potential method in the plane-parallel channel cell [19]. For the above experimental conditions zeta potential on mica was $-80\,mV$.

The experimental procedure was the following: a freshly cleaved mica sheet was cut to the appropriate size and mounted into the cell's window without using any adhesive. Then the positive latex suspension was carefully poured into the cell. Particle deposition was carried out for a desired time (typically 1 h) until the prescribed surface concentration of particles was attained. The surface concentration was determined by a direct microscope counting over statistically chosen areas. For sake of convenience the surface concentration of particles was expressed as the dimensionless coverage $\Theta_s = \pi a_s^2 \langle N_s \rangle$ (where N_s is the average surface concentration of adsorbed smaller particles). In our experiments Θ_s varied between 0 and 0.25. After preparing the heterogeneous substrate, the positive latex suspension was replaced by $10^{-3}\,M$ KCl solution and then by the negative latex suspension and the

particle deposition run was continued for a period reaching 48 h. The bulk suspension concentration of the negative latex n_b used in experiments was typically $(2–5) \times 10^9\,cm^{-3}$. Images of adsorbed particles were collected in situ at prescribed time intervals. Adsorption kinetics of latex was followed by determining the averaged surface concentration $\langle N_p \rangle$ of particles found on these images after a prescribed deposition time t.

It was proven in separate experiments that larger particle adsorption was perfectly irreversible and localised. No lateral motion or particle desorption was observed when rinsing particle monolayers with electrolyte (10^{-3} KCl) in situ by a prolonged period of time.

3. Results and discussion

As mentioned, a desired site coverage was attained by performing deposition of positive latex for a prescribed time interval under the diffusion-controlled transport conditions. It was found that the coverage Θ_s up to the value of 0.25 increased linearly with the square root of the deposition time t, in accordance with theoretical predictions [12,20]. A typical site configuration produced in these experiments is shown in Fig. 1. It was confirmed via statistical analysis that the site distribution for this range of coverage was random over macroscopic areas of square centimetre size.

After establishing conditions for obtaining the desired coverage Θ_s a series of adsorption experiments of larger (negative) latex at heterogeneous mica was performed. The ionic strength prevailing in these experiments was rather high, i.e. $10^{-3}\,M$, that practically eliminated the lateral, electrostatic interactions among larger particles. The bulk density of particles in these experiments was $4.79 \times 10^9\,cm^{-3}$. The distribution of particles, kinetics of adsorption and maximum (jamming) coverage of larger particles as a function of site
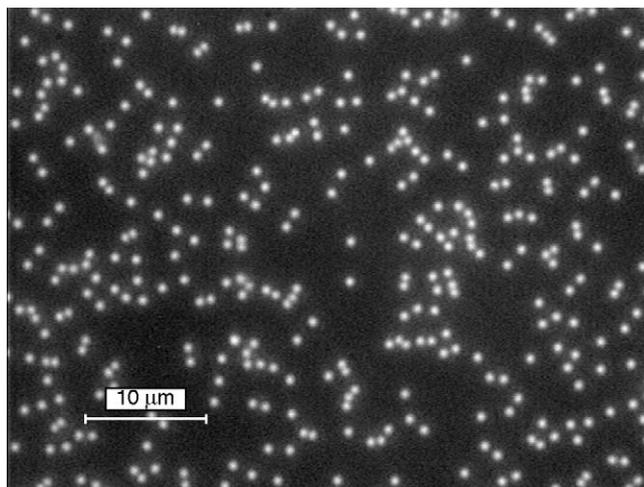

Fig. 1. A micrographs of sites (positive latex particles adsorbed at mica) at the coverage $\Theta_s = 0.0281$.
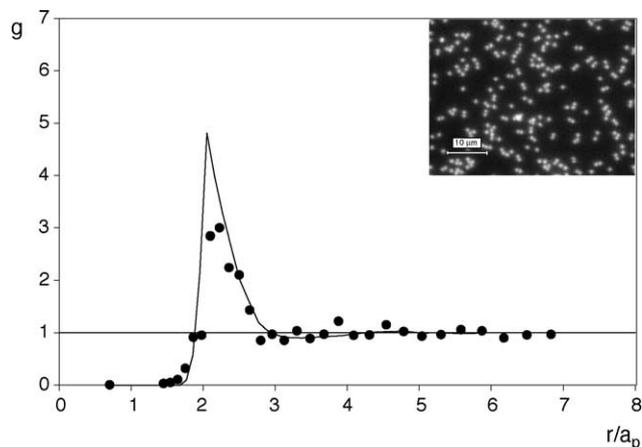
Fig. 2. The pair correlation function $g(r/a)$ of polystyrene latex particles (average diameter 0.9 μm) adsorbed at mica pre-covered by smaller-sized latex, $I = 10^{-3}$ M, $\Theta_s = 0.017$, $\Theta_p = 0.079$. The solid line denotes the theoretical results derived from Monte Carlo simulations [17].

Fig. 3. The dependence of the maximum (jamming) coverage of larger latex particles Θ_p on the smaller latex coverage Θ_s, the points represent the experimental results and the solid line denotes the theoretical Monte Carlo simulations (smoothened), the broken line shows the analytical results derived from the dependence $\Theta_p = \lambda^2 \Theta_s$.

coverage Θ_s was systematically studied. A quantitative characterisation of particle distributions was achieved in terms of the pair correlation function $g(r)$ (referred often to as the radial distribution function) [16,20]. The function was calculated from the constitutive relationship

$$g(r) = \frac{\pi a_p^2}{\Theta_p} \left\langle \frac{\Delta N_p}{2\pi r \, \Delta r} \right\rangle \qquad (1)$$

where $\langle \ \rangle$ means the ensemble average, $\Theta_p = \pi a_p^2 \langle N_p \rangle$ is the dimensionless surface coverage of larger particles and ΔN_p the number of particles adsorbed within the ring $2\pi r$ Δr drawn around a central particle. The function can be interpreted as an averaged probability of finding a particle at the distance r from another particle (with the centre located at $r = 0$) normalised to the uniform probability at large distances. A typical $g(r)$ function determined experimentally for $\Theta_s = 0.017$ and $\Theta_p = 0.079$ is presented in Fig. 2, (for the sake of convenience r was normalized by using the particle radius a_p as the scaling variable).

As can be observed a very high peak appears at close separations between particles that indicates strong correlations among particle positions. This contrasts previously found results for homogeneous surfaces [20] when the peak height for this value Θ_p was practically negligible. A characteristic feature of the $g(r)$ function shown in Fig. 2 is that it vanishes at the distance 1.75 rather than for $r/a_p = 2$ as is should be expected for homogeneous particle adsorption. This behaviour predicted theoretically [17] spectacularly confirms the fact that particles are adsorbed in various planes (quasi 3D) due to the finite size of the adsorption sites. This means that their projections on the adsorption plane can overlap. It is also interesting to observe that the experimental data in Fig. 2 are well reflected by the theoretical simulations performed according to the model described in Ref. [17].
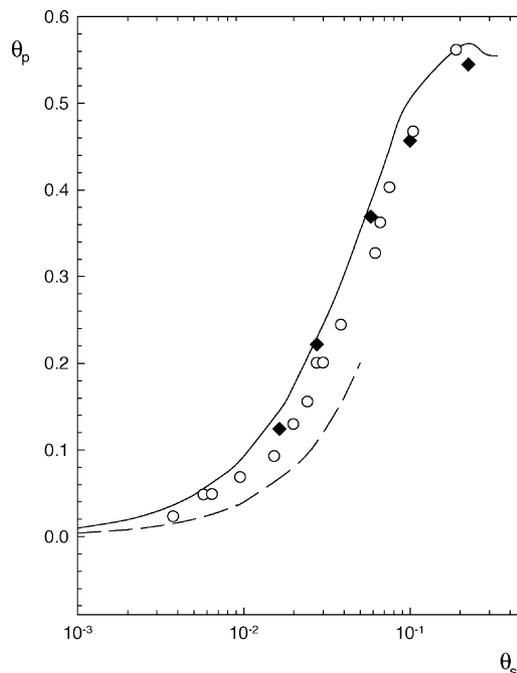
Besides studying the structural aspects, the main goal of this work was to determine the long time limiting particle coverage, referred to as the maximum or jamming coverage denoted by Θ_p^{mx} [13,17]. The dependence of Θ_p^{mx} on the site coverage Θ_s determined from long-lasting kinetic runs is plotted in Fig. 3.

As can be noticed, the experimental results are in a quantitative agreement with the theoretical simulations (depicted by the solid line) for the entire range of Θ_s. A very interesting feature of these results is that the maximum coverage of larger particles attains a maximum for $\Theta_s = 0.22$. The height of this maximum, 0.58, exceeds the jamming limit predicted theoretically for homogeneous surfaces equal 0.547 [21]. This is so because particle adsorption at random site (heterogeneous surfaces) is a three-dimensional process with particles adsorbing in various planes. Thus, the results shown in Fig. 3 confirm the significance of three-dimensional effects in particle adsorption on heterogeneous surfaces.

It is interesting to observe in Fig. 3 that both experimental and theoretical results collected for low site coverage range deviate significantly from the asymptotic expression $\Theta_p = \lambda^2 \Theta_s$ (where $\lambda = a_p/a_s$ is the particle size ratio) expected to be valid if one site could accommodate only one adsorbing particle. This deviation confirms the site multiplicity effect suggested previously by the large maximum of the pair correlation function (see Fig. 2). Therefore, the site multiplicity can be evaluated quantitatively by plotting the jamming coverage Θ_p versus $\lambda^2 \Theta_s$ for the range of low coverage. It was

found in this way that the site multiplicity factor $n_s = 2.35$. This agrees well with the theoretical value found from simulation, equal 2.45 in the limit of $\Theta_p \to 0$. These results can be efficiently interpreted in terms of the geometrical model discussed in Ref. [22]. As was demonstrated, for $\lambda = 2$, at the jamming state, one site can be blocked by one, two, three or four particles. However, the one and four particle attachment event is highly improbable, so most of the sites bear two or there particles, as can be observed in Fig. 2. Assuming equal probability of these two configurations one obtains $n_s = 2.5$ that is quite close to the experimental and theoretical value.

4. Concluding remarks

It was demonstrated experimentally using the direct microscope observation method that the main features of colloid particle adsorption at random-site (heterogeneous surfaces) can well be reflected by the theoretical approach developed in Ref. [17]. In contrast to previous approaches [20,23], this model postulates a 3D adsorption that profoundly affects the structure of adsorbed particle monolayer and the jamming coverage.

Therefore, by determining experimentally the distribution of adsorbed particles, characterised in terms of the pair correlation function g and the jamming coverage of larger colloid particles the presence of adsorption sites invisible under microscope can be quantitatively evaluated.

Acknowledgment

References

[1] M.Y. Boluk, T.G.M. van de Ven, Colloids Surf. 46 (1990) 157.
[2] Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, J. Am. Chem. Soc. 117 (1995) 6120.
[3] T. Serizawa, H. Takashita, M. Akashi, Langmuir 14 (1998) 4088.
[4] J. Schmitt, P. Machtle, D. Eck, H. Mohwald, C.A. Helm, Langmuir 15 (1999) 3256.
[5] K.M. Chen, X. Jiang, L.C. Kimmerling, P.T. Hammond, Langmuir 16 (2000) 7825.
[6] H.A. Chase, Chem. Eng. Sci. 39 (1984) 1099.
[7] I. Willner, M. Lion-Dagan, S. Marx-Tibbon, E. Katz, J. Am. Chem. Soc. 117 (1995) 6581.
[8] E. Katz, A.E. Buckmann, I. Willner, J. Am. Chem. Soc. 123 (2001) 10752.
[9] H.D. Inerowicz, S. Howell, F.E. Reniger, R. Reifenberger, Langmuir 18 (2002) 5263.
[10] S.W. Howell, H.D. Inerowicz, R. Reifenberger, Langmuir 19 (2003) 436.
[11] Z. Adamczyk, M. Zembala, B. Siwek, J. Czarnecki, J. Colloid Interface Sci. 110 (1986) 188.
[12] Z. Adamczyk, B. Siwek, M. Zembala, P. Belouschek, Adv. Colloid Interface Sci. 48 (1994) 151.
[13] Z. Adamczyk, B. Siwek, E. Musiał, Langmuir 17 (2001) 4529.
[14] Z. Adamczyk, B. Siwek, P. Weroński, E. Musiał, Appl. Surf. Sci. 196 (2002) 250.
[15] Z. Adamczyk, B. Siwek, P. Weroński, K. Jaszczółt, Colloids Surf. A 222 (2003) 15.
[16] Z. Adamczyk, P. Weroński, E. Musiał, J. Chem. Phys. 116 (2002) 4665.
[17] Z. Adamczyk, P. Weroński, E. Musiał, J. Colloid Interface Sci. 248 (2002) 67.
[18] J.W. Goodwin, J. Hearn, C.C. Ho, R.H. Ottewill, Colloid Polym. Sci. 252 (1974) 464.
[19] M. Zembala, Z. Adamczyk, Langmuir 16 (2000) 1593.
[20] Z. Adamczyk, Irreversible adsorption of particles, in: J. Toth (Ed.), Adsorption: Theory, Modeling and Analysis, Marcel-Dekker, New York, 2002. Chapter 5, pp. 251–374.
[21] E.L. Hinrichsen, J. Feder, T. Jossang, J. Stat. Phys. 44 (1986) 79.
[22] Z. Adamczyk, K. Jaszczółt, B. Siwek, P. Weroński, J. Chem. Phys. 123 (2004) 11155.
[23] I. Langmuir, Phys. Rev. 6 (1915) 79.