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ORIGINAL CONTRIBUTION

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Synchronous alternate multilayered adsorption of poly(4-vinyl-*N*-*n*-butylpyridinium) cations and poly(styrene sulfonate) anions on polystyrene colloidal spheres

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Abstract Alternate multiple adsorbed layers of up to six macrocations [poly(4-vinyl-*N*-*n*-butylpyridinium bromide)] and macroanions [sodium poly(styrene sulfonate)] are formed on monodispersed polystyrene colloidal spheres above the critical concentration of the macroions, m^*. The m^* value is the minimum number of macroions needed to reverse the sign of the ζ potential of the spheres in the first adsorption step. Alternate sign reversal in the ζ potential and expansive–contractive thickness changes are observed on the repeated and alternate addition of macrocations first and macroanions next. When the macroanions are added first, sign reversal in the ζ potential and reversible expansion and contraction do not occur. Breaking of the alternate multiple-type adsorption also occurs when equivalency in the number of dissociative groups of macrocations and macroanions is broken. Synchronous conformational changes of macrocations and macroanions in the multiple-adsorbed layers occurs only when the conformational rigidities with the multiple electrostatic and hydrophobic attraction and/or repulsion between macrocations and macroanions are delicately balanced.

Key words Synchronous adsorption · Multiple adsorption · Polystyrene spheres · Electrophoretic measurement · Dynamic light scattering

Introduction

In our previous work [1, 2] the abrupt sign reversal in the ζ potential of a colloidal sphere, usually negatively charged at its surface, was observed on the addition of various kinds of oppositely charged macroions and their low valency simple ions, such as calcium and lanthanium ions. This suggests that the excess macroions compared to the charges on the colloidal surfaces are adsorbed in the manner of the so-called avalanche-type synchronous adsorption mechanism, i.e., adsorption of macroions occurs abruptly on the colloidal surfaces above the critical concentration (m^*) of the macroions added. Below m^* adsorption does not occur so significantly. It is now highly plausible to obtain multilayered adsorption of macroions on the surface of anionic colloidal spheres by the addition of macrocations first, then macroanions, further macrocations, macroanions, and so on. This alternate adsorption should occur because of the electrostatic attraction between the absorbed colloidal spheres and oppositely charged macroions. In a previous article [3] we reported the occurrence of the alternate changes in the charge sign and also in the thickness of the adsorbed layer observed for macroion–colloidal silica sphere complex systems. Here, we report the results of further studies to determine whether synchronous alternate adsorption takes place for strongly hydrophobic monodispersed polystyrene spheres or not.

We should note here that the similar layer-by-layer adsorption of oppositely charged molecules including polymers has been studied intensively by Decher and coworkers [4–7]. They observed the reversible thickness changes in the adsorbed layers. Several types of multiple adsorption of macromolecules have been investigated hitherto [8–19]. Quite recently, multilayered cationic particles of rhodamine-B-labeled melamine formamide with sodium poly(styrene sulfonate) (NaPSS) and poly(allylamine hydrochloride) were prepared and their Förster resonance energy transfer was discussed [20]. Furthermore, the ζ potential showed a nice alternate sign reversal of the spheres, though the thickness of the adsorbed layers was not measured. We should note here that addition of macroions to oppositely charged colloids may turn intersphere repulsion into attraction, leading to aggregation or flocculation [21–23]. To prevent aggregation, the macroion–colloid complexation experiments in our work were always done with as low concentrations of spheres as possible.

Experimental

Materials

Monodispersed polystyrene spheres of D1A19 were purchased from Dow Chemical Co. The diameter (d_0), the standard deviation (δ) from the mean diameter and the polydispersity index (δ/d_0) were 220 nm, 6.5 nm and 0.030, respectively. The size parameters were determined with an electron microscope. The charge density of the strongly acidic groups was 1.32 μC/cm^2. NaPSS (molecular weight = 18000, polydispersity index; $M_w/M_n = 1.14$) was obtained from Pressure Chemicals (Pittsburgh, Pa.). The details of the preparation and purification of poly(4-vinyl-*N*-*n*-butylpyridinium bromide) (C4PVP) were described previously [24, 25]. The degree of polymerization of the parent polymer, poly(4-vinylpyridine), was 3800 as determined by viscometry. The water used for the purification and suspension preparation was purified using a Milli-Q reagent-grade system (Milli-RO5 plus and Milli-Q plus, Millipore Co., Bedford, Mass.).

Dynamic light scattering measurements

The dynamic light scattering (DLS) measurements were performed on a DLS spectrophotometer (DLS-7000, Otsuka Electronics, Osaka) at 25 ± 0.02 °C in a cylindrical vat containing silicone oil. A 5-ml sample was prepared in a Pyrex cuvette cell (12-mm outside diameter and 130-mm long). Data analysis was made with the cumulant analyses. Histogram methods [26], including the nonnegative least square and the Marquadt analyses, were also used to discuss the size distribution of the effective size of the colloidal spheres including the adsorbed layers of the linear-type macroions.

Electrophoretic light scattering measurements

Electrophoretic light scattering (ELS) measurements were made on a Leza-600 ELS Zeta-meter (Otsuka Electronics, Osaka) at 25 ± 0.02 °C.

pH and conductivity measurements

The pH values of the sample suspension were measured on a model ϕ34 pH meter Beckman (Tokyo) with a glass electrode (model 6378-10D, Horiba, Kyoto) at 25 ± 0.5 °C. The conductivity of the suspension was measured on a model DS-14 conductivity meter (Horiba, Kyoto) with an electrode (no 3552, Horiba) at 25 ± 0.5 °C.

Results and discussion

Figure 1 shows the ζ potential and thickness of the adsorbed layers in the macroion–colloid complex formed by the alternate addition of C4PVP first and then NaPSS on D1A19 polystyrene spheres. Here, the equivalent ionic concentrations were 1×10^{-6} monomol/l for both C4PVP and NaPSS polymers. Sphere concentrations were 1×10^{-5} in volume fraction (ϕ) and 3.7×10^{-8} in equivalent concentration of sphere charges (Eq/l). m^* of C4PVP for the charge reversal of D1A19 spheres was 3×10^{-7} monoM at the same sphere concentration, $\phi = 1 \times 10^{-5}$ [2], where monoM indicates the molar concentration of monomer units of the macroion. We should note here that the equivalent charge concentration of the spheres is one-eighth of the m^* value of C4PVP. This strongly suggests that the excess adsorption of macroions takes place suddenly in the manner of the avalanche-type adsorption mechanism [2], when an excess of macroions exists compared with spheres in suspension. As is clear in the figure, the ζ potential repeated sign reversal beautifully up to six layers. The small and large circles show the two runs of the ζ potential measurements and their mean values, respectively. The reproducibil-

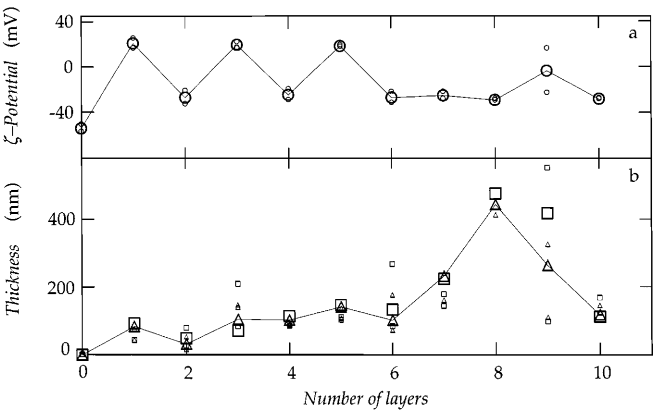

Fig. 1 ζ potential (*a*) and adsorbed layer's thickness (*b*) of D1A19 spheres at 25 °C. Poly(4-vinyl-*N*-*n*-butylpyridinium bromide) (*C4PVP*) (1×10^{-6} monoM) and sodium poly(styrene sulfonate) (*NaPSS*) (1×10^{-6} monoM) were added alternately. $\phi = 1 \times 10^{-5}$. C4PVP was added first. ζ potential (○), thickness from electrophoretic light scattering (*ELS*) (△), thickness from dynamic light scattering (*DLS*) (□). *Large symbols* indicate the mean of the two runs shown by the *small symbols*

ity of the ζ potential was excellent. The thickness of the adsorbed layers estimated from the ELS and DLS measurements also continued to expand and shrink, though the thickness increased stepwise slightly with increasing number of layers, when the effective charges of the spheres were positive and negative, respectively. In Fig. 1b, two runs of the ELS and DLS measurements and their mean values are shown by the small and large triangles and by the small and large squares, respectively. Surprisingly, agreement between the two methods was excellent. Reproducibility of the thickness was not so good compared with that of the ζ potential, especially at a number of layers greater than 7. It is highly plausible that weak aggregation of the macroion–colloid complexes took place when the number of layers was 7–9. It should be noted here that the sign reversal and the synchronous change in the thickness of the absorbed layers of C4PVP and NaPSS macroions took place beautifully up to ten layers on the surface of colloidal silica spheres [3]. It should be further mentioned here that almost all the macroions were bound on the colloidal surfaces in each adsorption steps and that the numbers of free macrocations, macroanions and/or macrocation–macroanion complexes were quite low. The equivalency in the charge amount of the macrocations and macroanions is very important for the alternate macroion–colloid complexation.

Expansion and contraction of the adsorbed layers supports several important facts. First, C4PVP molecules are bound more loosely than NaPSS. The rigidity of the polymer chain of the former is assumed to be greater than that of the latter. The bulkiness of the *N*-butylpyridinium moeities in the most outside layers of the macrocation rods is the main reason for the difficulty of stacking compactly. Second, synchronous balancing between the electrostatic attractions among the multiple interlayers of macrocations (n valent, for example) and macroanions (o valent) accompanied with the polymer chain contraction and the electrostatic repulsions with the chain expansion within the intralayers. The second factor should be the synchronous and cooperative interactions among the m valent silica surfaces and the adsorbed layers of the macroions having ionic valencies of n+ and o−. Let us consider a six-layered sphere with macrocations and macroanions, for example. The electrostatic attractive and repulsive interactions among the seven layers like [m−]-[n+]-[o−]-[n+]-[o−]-[n+]-[o−] must be taken into account. Intralayer electrostatic repulsion may contribute to the synchronization. Third, nonelectrostatic (hydrophobic, dipole–dipole interactions, for example) interlayer and intralayer attractive interactions are also important. Quaternary, flexibilities of macrocations and macroanions are important for the expansion forces in the intralayers. A theoretical consideration, where these factors are taken into account, is essential for understanding the synchronous nature of the adsorption.

The pH and conductivity of the complex suspensions were measured, though the graphs showing the data are omitted here. Interestingly, the former decreased slightly and continuously and the latter increased significantly and also continuously. The repeated expansion and contraction in the adsorbed layers observed in Fig. 1 did not affect these two parameters so much.

Figure 2 shows the ζ potential (curve a) and the adsorbed layer's thickness (curve b), when the NaPSS macroanions were added first to the suspension of the anionic polystyrene spheres. The ζ potential remained negative and increased very slightly from −53 to −30 mV stepwise but very slowly as is shown in the figure. The thickness of each of the macroion layers was small, except for the tenth layer. These results support the fact that clear-cut alternate adsorption does not take place when NaPSS is added first.

Figure 3 shows the ζ potential and thickness when the concentrations of both C4PVP and NaPSS are 3×10^{-7} monoM, i.e., at the critical concentration of the charge reversal. Clearly, the alternate change in the sign of the ζ potentials was observed at the first step of C4PVP addition only and was not observed for the other steps irrespective of the kind of macroions added in the first step. However, the thickness of the adsorbed layers was observed to be less than 100 nm and weak adsorption took place.

Figure 4 shows the ζ potential and the thickness when the concentrations of C4PVP and NaPSS are above the m^* value and the former is twice the latter. The alternate adsorption was not observed when C4PVP was added first as is clear in Fig. 4a. Furthermore, the thickness data show that the weak aggregation between the

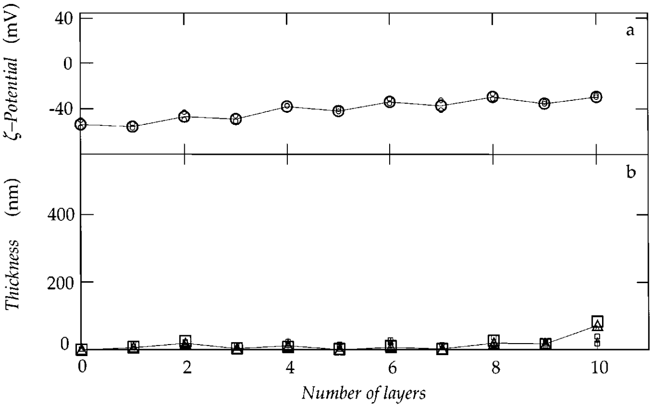

Fig. 2 ζ potential (*a*) and adsorbed layer's thickness (*b*) of D1A19 spheres at 25 °C. C4PVP (1×10^{-6} monoM) and NaPSS (1×10^{-6} monoM) were added alternately. $\phi = 1 \times 10^{-5}$. NaPSS was added first. ζ potential (○), thickness from ELS (△), thickness from DLS (□). *Large symbols* indicate the mean of the two runs shown by the *small symbols*

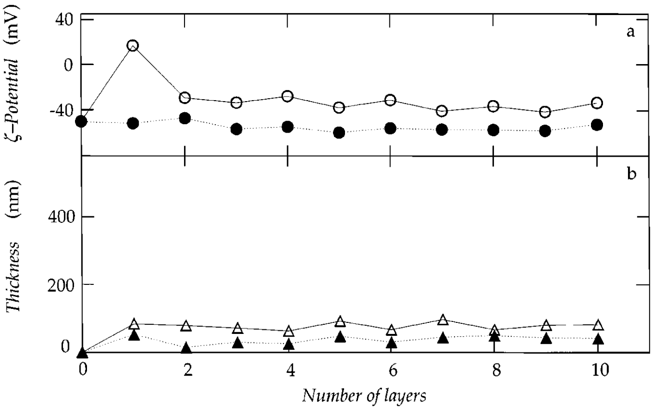

Fig. 3 ζ potential (*a*) and adsorbed layer's thickness (*b*) of D1A19 spheres at 25 °C. C4PVP (3×10^{-7} monoM) and NaPSS (3×10^{-7} monoM) were added alternately. $\phi = 1 \times 10^{-5}$. ζ potential with C4PVP added first (○), ζ potential with NaPSS added first (●), thickness from ELS with C4PVP added first (△), thickness from ELS with NaPSS added first (▲)

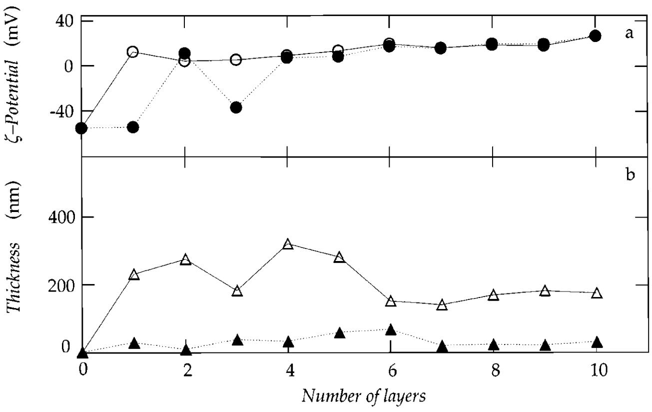

Fig. 4 ζ potential (*a*) and adsorbed layer's thickness (*b*) of D1A19 spheres at 25 °C. C4PVP (2×10^{-6} monoM) and NaPSS (1×10^{-6} monoM) were added alternately. $\phi = 1 \times 10^{-5}$. ζ potential with C4PVP added first (○), ζ potential with NaPSS added first (●), thickness from ELS with C4PVP added first (△), thickness from ELS with NaPSS added first (▲)

spheres occurs from the first to the fifth layer steps. These data support the fact that the formation of the macrocation–macroanion complex does not take place when equivalency in the number of dissociative groups of macrocations and macroanions is broken. Interestingly, the alternate adsorption took place from the second to fourth steps when the macroanions were added first as is clear in the data of the ζ potential of Fig. 1a. The thickness data shown by solid triangles in

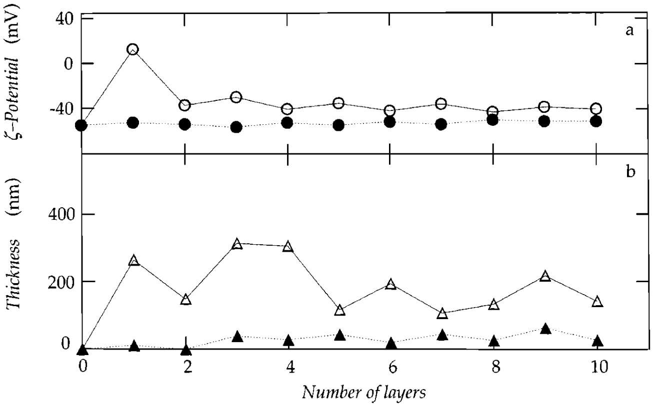

Fig. 5 ζ potential (*a*) and adsorbed layer's thickness (*b*) of D1A19 spheres at 25 °C. C4PVP (1×10^{-6} monoM) and NaPSS (2×10^{-6} monoM) were added alternately. $\phi = 1 \times 10^{-5}$. ζ potential with C4PVP added first (○), ζ potential with NaPSS added first (●), thickness from ELS with C4PVP added first (△), thickness from ELS with NaPSS added first (▲)

Fig. 1b suggests that weak expansion and contraction in the adsorbed layers take place from the second to the fourth layers. It should be mentioned here that the equivalency of the charges between macrocations and macroanions is important for the alternate sign reversal in the ζ potential and the synchronous expansion and contraction in the adsorbed layers.

Figure 5 shows the ζ potential and the thickness when the concentrations of C4PVP and NaPSS are above the *m** value and the former is half the latter. When the macrocations were added first alternate adsorption did not occur and weak aggregation between spheres and/or macrocation–macroanion complexation took place. When the macroanions were added first, on the other hand, no alternate adsorption was observed.

In conclusion, the alternate sign reversal in the ζ potential and the expansion and contraction for the polystyrene colloidal sphere systems were also observed when the macrocation was added first, when the ionic concentrations of macrocations and macroanions were equivalent and when the macroion concentrations were above the *m** value. Balancing of the electrostatic, hydrophobic and dipole–dipole interactions between the colloidal spheres and the macroions must be important for synchronous expansion and contraction.

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References

1. Okubo T (1990) Polym Bull 23:211
2. Okubo T, Suda M (1999) J Colloid Interface Sci 213:565
3. Okubo T, Suda M (1999) Colloid Polym Sci 277:813
4. Decher G, Hong JD (1991) Makromol Chem Symp 46:321
5. Decher G, Hong JD (1991) Ber Bunsenges Phys Chem 95:1430
6. Decher G, Hong JD, Schmitt J (1992) Thin Solid Films 210/211:831
7. Sukhorukov GB, Schmitt J, Decher G (1996) Ber Bunsenges Phys Chem 100:948
8. Schmitt J, Grunewald T, Kjaerk K, Pershan P, Decher G, Losche M (1993) Macromolecules 26:7058
9. Decher G, Lvov Y, Schmitt J (1994) Thin Solid Films 244:772
10. Decher G, Lehr B, Lowack K, Lvov Y, Schmitt J (1994) Biosens Bioelectron 9:677
11. Ferreiva M, Cheung JH, Rubner MF (1994) Thin Solid Films 244:806
12. Gao M, Zhang X, Yang Y, Yang B, Shen J (1994) J Chem Soc Chem Commun 2777
13. Kleinfeld ER, Ferguson GS (1994) Science 265:370
14. Keller SW, Kim HN, Mallouk TE (1994) J Am Chem Soc 116:8817
15. Kong W, Zhang X, Gao ML, Zhou H, Li W, Shen JC (1994) Macromol Rapid Commun 15:405
16. Korneev D, Lvov Y, Decher G, Schmitt J, Yaradaikin S (1995) Thin Solid Films B 213/214:954
17. Onoda M, Yoshino K (1995) Jpn J Appl Phys 34:L260
18. Savemi F, Maassen E, Tieke B, Jordan G, Rammensee W (1995) Langmuir 11:1068
19. Lvov Y, Ariga K, Kunitake T (1995) J Am Chem Soc 117:6117
20. Caruso F, Donath E, Mohwald H (1998) J Phys Chem 102:2016
21. Joanny JF, Leibler L, de Gennes PG (1979) J Polym Sci 17:1073
22. Cabane B, Wong K, Wang TK, Lafuma F, Duplessix R (1988) Colloid Polym Sci 266:101
23. Dickinson E, Eriksson L (1991) Adv Colloid Interfare Sci 34:1
24. (a) Okubo T, Ise N (1973) J Am Chem Soc 95:2293; (b) Okubo T, Ise N (1973) J Am Chem Soc 95:4031
25. Ishiwatari T, Okubo T, Ise N (1980) J Polym Sci 18:1807
26. Okubo T, Kiriyama K, Nemoto N, Hashimoto H (1996) Colloid Polym Sci 274:93