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ORIGINAL CONTRIBUTION

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Synchronous multilayered adsorption of macrocations and macroanions on colloidal spheres. Influence of foreign salt and basicity or acidity of the macroions

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Abstract The influence of foreign salt, the basicity or the acidity of macroions and the equivalency of the number of ionic groups of macrocations and macroanions upon alternate multiple adsorption on surfaces of colloidal silica (CS91, 110 nm in diameter) and polystyrene spheres (D1A19, 220 nm) have been studied by electrophoretic light scattering measurements. The macrocations used were poly(4-vinyl-*N*-*n*-butyl pyridinium bromide (C4PVP, strongly basic), poly(4-vinyl-*N*-ethyl pyridinium bromide (C2PVP, strongly basic) and poly(allylamine) (PAL, weakly basic). Sodium poly(styrene sulfonate) (NaPSS, strongly acidic) and sodium polyacrylate (NaPAA, weakly acidic) were used as macroanions. The alternate adsorption disappears even in the presence of a small amount of sodium chloride. The alternate multiple adsorption takes place on the addition of C4PVP first and NaPSS next, PAL first and NaPAA next, NaPAA first and C4PVP next, and NaPAA first and PAL next on the CS91 spheres. The influence of the equivalency of the number of ionic groups of C2PVP and NaPAA has been studied for the adsorption on the D1A19 spheres. The synchronous delicate balancing of the electrostatic interactions among the macrocations, the macroanions and the surfaces of the colloidal spheres is important for the alternate multiple adsorption.

Keywords Multiple adsorption · Colloidal silica sphere · Polystyrene sphere · Electrophoretic light scattering measurement · Synchronization

Introduction

The multiple-adsorption phenomena of macrocations and macroanions on colloidal surfaces have been studied independently by Caruso and coworkers, Voigt et al. and Gao et al. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] and by Okubo and and coworkers [11, 12, 13]. It is well known that most colloidal spheres have negative charges on their surfaces in aqueous and polar solvents [14]. In our previous work [15, 16] the abrupt sign reversal in the ζ potential of colloidal spheres was observed on the addition of oppositely charged macroions. Thus, we expected to obtain multilayered adsorption of macroions on the surface of anionic colloidal spheres on the addition of macrocations first, then macroanions, and so on. We added the minimum amount of the macrocations required to reverse the sign of the ζ potential of the spheres in the first adsorption step. Furthermore, the same equivalent amounts of the macroanions and the macrocations were added successively. By this method no free macrocations and macroanions coexisted in the suspension of the alternate adsorption complexes. In the previous work we reported that the strongly basic macroions, poly(4-vinyl-*N*-*n*-butyl pyridinium bromide) first and then the strongly acidic macroions, sodium poly(styrene sulfonate) are adsorbed alternately on the colloidal surfaces of colloidal silica [11, 12] and polystyrene spheres [13].

Here, the influence of the foreign salt, the basicity the or acidity of the macrocations or macroanions and the equivalency of the number of the ionic groups of the macrocations and macroanions upon the layer-by-layer adsorption has been studied in detail.

Experimental

Materials

Colloidal silica spheres of CS91 gifts from Catalyst & Chemicals Ind. Co. (Tokyo). The diameter (d_0), the standard deviation (δ) from the mean diameter and the polydispersity index (δ/d_0) of these spheres were 110 nm, 4.5 nm and 0.041, respectively. These size parameters were determined using an electron microscope. The charge density of the strongly acidic groups was 0.48 μC/cm^2 as determined by conductometric titration. Monodispersed polystyrene spheres of D1A19 were purchased from Dow Chemical Co. d_0, δ and δ/d_0 were 220 nm, 6.5 nm and 0.03, respectively. The charge density of the strongly acidic groups was 1.32 μC/cm^2. These sphere samples were carefully purified several times using an ultrafiltration cell (model 202, membrane: Diaflo-XM300, Amicon Co.). Then, the samples were treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8 (D), 20–50 mesh] for more than 4 years before use, since newly produced silica spheres always released a considerable number of alkali ions from the sphere surfaces for a long time.

Sodium polyacrylate (NaPAA, degree of polymerization of 640) was a gift from Toa Gosei Chemicals Co. (Nagoya). Sodium poly(styrene sulfonate) (NaPSS, molecular weight of 18,000, polydispersity index:$M_w/M_n = 1.14$) was purchased from Pressure Chemicals (Pittsburgh, Pa.). The details of the preparation and purification of poly(4-vinyl-*N*-ethylpyridinium bromide) (C2PVP) and poly(4-vinyl-*N*-*n*-butylpyridinium bromide) (C4PVP) were described previously [17, 19]. The degrees of quaternization were 0.96 and 0.95, respectively. The degree of polymerization of the parent polymer, poly(4-vinylpyridine) was 3,800 as determined by viscometry. Poly(allylamine) (PAL) was a gift from Nitto Boseki Co. (Tokyo). The degree of polymerization was about 1,000. The water used for the purification and for suspension preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore Co., Bedford, Mass.).

Electrophoretic light scattering measurements

Electrophoretic light scattering (ELS) measurements were made using an electrophoretic spectrophotometer (ELS 8000, Otsuka Electronics, Osaka) at 25 ± 0.02 °C. First, 11 suspensions of colloidal spheres having the same sphere concentration, each 19 ml, were prepared in test tubes (disposable culture tube, 18×150 mm, Iwaki Glass Co., Tokyo). After 3 hours one sample was used for the ELS measurements. The ELS measurements were repeated three to four times. The remaining ten samples were added dropwise to 0.19 ml of the first macroion solution and mixed gently. After a further 3 hours, one sample suspension was used for the ELS measurements, and the remaining nine samples were mixed further with 0.19 ml of the solution of the second macroions. These procedures were repeated until the ELS measurements had been completed for all the samples corresponding to a number of layers from 0 to 10. The thickness of the adsorbed layer was obtained by subtracting the sphere radius from the observed effective radius from the ELS measurements. The reproducibility of the data was 20% in the thickness value.

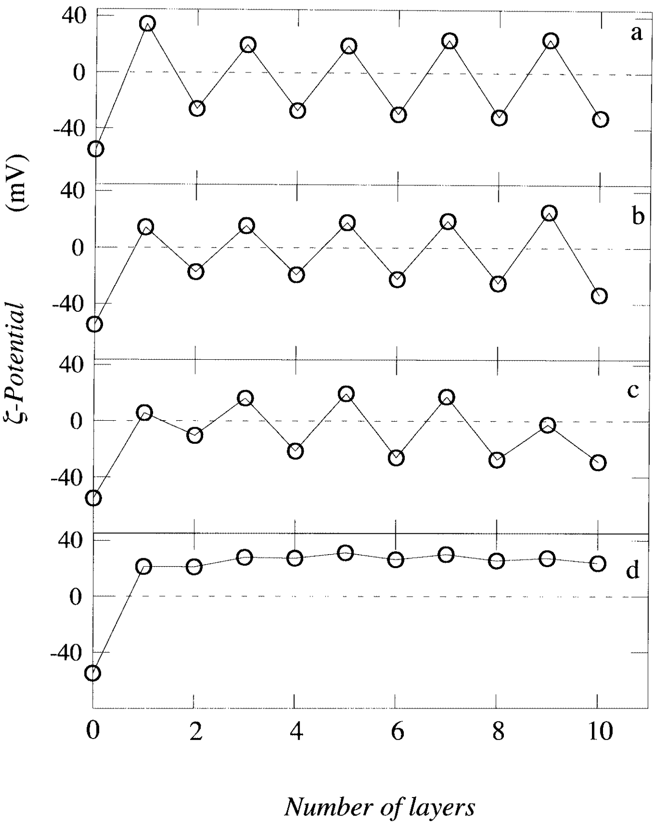

Fig. 1a–d ζ potential of CS91 spheres in the presence of NaCl (**a**: 0 M, taken from Ref. [12]; **b**: 1x10^{-6}; **c**: 3x10^{-6}; **d**: 1x10^{-5}) at 25 °C. Poly(4-vinyl-*N*-*n*-butyl pyridinium bromide (*C4PVP*) (8x10^{-6} monoM) and poly(styrene sulfonate) (*NaPSS*) (8x10^{-6}) were added alternately. $\phi = 7\text{x}10^{-5}$; C4PVP was added first

pH and conductivity measurements

The pH values of the sample suspensions were measured using a model ϕ34 pH meter (Beckman, Tokyo) with a glass electrode (model 6378-10D, Horiba, Kyoto) at 25 ± 0.05 °C. The conductivity of the suspension was measured using a model DS-14 conductivity meter (Horiba, Kyoto) with an electrode (no. 3552, Horiba) at 25 ± 0.05 °C.

Results and discussion

Influence of salt on the alternate adsorption

The ζ potential and the thickness of the adsorbed layer of CS91 spheres in the presence of sodium chloride are shown in Figs. 1 and 2. Figures 1a and 2a were taken from previous work [12]. Here, the equivalent ionic concentrations were 8x10^{-6} monoM for both C4PVP and NaPSS polymers. The sphere concentration was 7x10^{-5} in volume fraction and

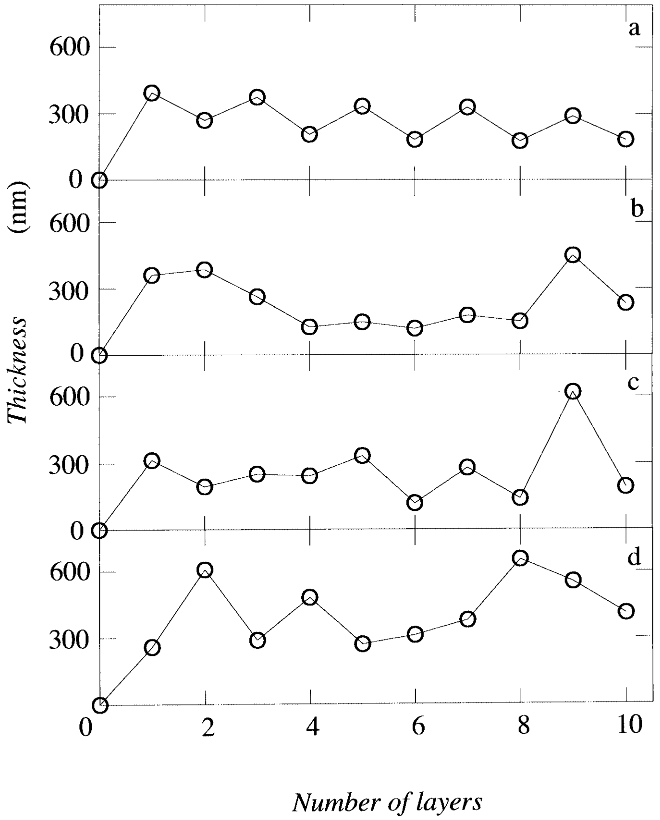

Fig. 2a–d Thickness of the adsorbed layer of CS91 spheres in the presence of NaCl (**a**: 0 M, taken from Ref. [12]; **b**: 1x10^{-6}; **c**: 3x10^{-6}; **d**: 1x10^{-5}) at 25 °C. C4PVP (8x10^{-6} monoM) and NaPSS (8x10^{-6}) were added alternately. $\phi = 7\text{x}10^{-5}$; C4PVP was added first

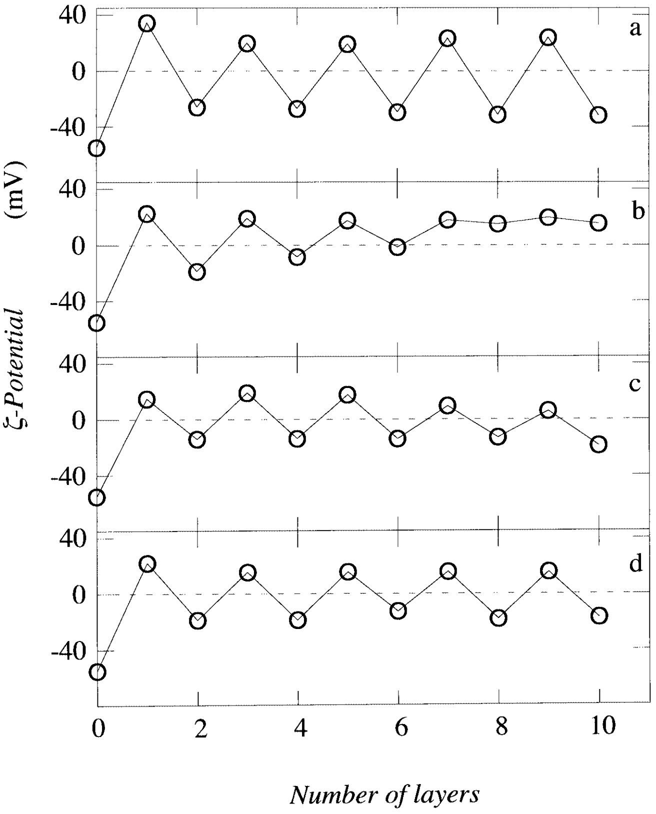

Fig. 3a–d ζ potential of CS91 spheres at 25 °C. **a** C4PVP (8x10^{-6} monoM) and NaPSS (8x10^{-6}) were added alternately (from Ref. [12]), **b** C4PVP (8x10^{-6} monoM) and sodium polyacrylate (*NaPAA*) (8x10^{-6}), **c** poly(allylamine) (*PAL*) (8x10^{-6} monoM) and NaPSS (8x10^{-6}), and **d** PAL (8x10^{-6} monoM) and NaPAA (8x10^{-6}). $\phi = 7\text{x}10^{-5}$; the macrocations were added first

1.9x10^{-7} M in ionic concentration. The critical concentration (*m**) of C4PVP for the charge reversal of CS91 spheres was 3x10^{-6} monoM [16]. The first adsorption step is clearly avalanche type, i.e., adsorption of the macrocations occurred abruptly above m*, which is an excess compared with the equivalent concentration of the sphere charges (1.9x10^{-7} M). In our experiments, the concentrations of the macrocations and the macroanions were the same, 8x10^{-6} monoM, which is 42 times higher than the ionic concentration of CS91 spheres.

When the concentrations of the salt were higher than 3x10^{-6} M, alternate complexation did not occur. It is clear that the first adsorbed layers of the macrocations were formed at a NaCl concentration of 1x10^{-5} M, but the successive alternate complexation did not occur. Clearly, the electrostatic shielding effect of the salt is important for the second and the successive adsorption steps. The strong shielding effect of the simple electrolytes upon the polyelectrolyte complexation has been clarified by one of the authors [20] from solubility measurements of the polyelectrolyte complex with sodium chloride and also from a theoretical discussion using Manning theory.

As shown in Fig. 2a, in the absence of the foreign salt a beautiful alternate expansion and contraction change in the thickness of the adsorbed layers was observed. This result supports two important facts. First, C4PVP molecules are bound more loosely than NaPSS. The rigidity of the polymer chain of the former is greater than that of the latter. The bulkiness of the *N*-*n*-butylpyridinium moieties in the outermost layers of the macrocation rods is the main reason for the difficulty of stacking compactly. Second, synchronous balancing between the electrostatic attractions holds among the multiple interlayers of macrocations and macroanions accompanied by the polymer chain contraction and the electrostatic repulsion with the chain expansion within intralayers. The second factor should be the synchronous and cooperative interactions among the silica surfaces and the adsorbed layers of the macroions. In the presence of the salt, however, the thickness was also significant but changed irregularly as the number of layers increased. This result suggests that the delicate

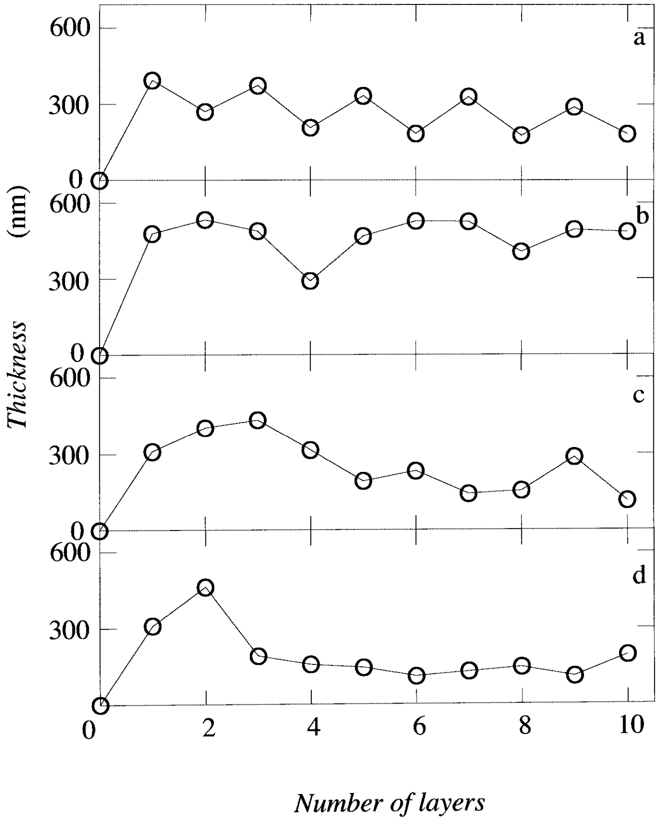

Fig. 4a–d Thickness of the adsorbed layer of CS91 spheres at 25 °C. **a** C4PVP (8×10^{-6} monoM) and NaPSS (8×10^{-6}) were added alternately (from Ref. [12]), **b** C4PVP (8×10^{-6} monoM) and NaPAA (8×10^{-6}), **c** PAL (8×10^{-6} monoM) and NaPSS (8×10^{-6}), and **d** PAL (8×10^{-6} monoM) and NaPAA (8×10^{-6}). $\phi=7\times10^{-5}$; the macrocations were added first

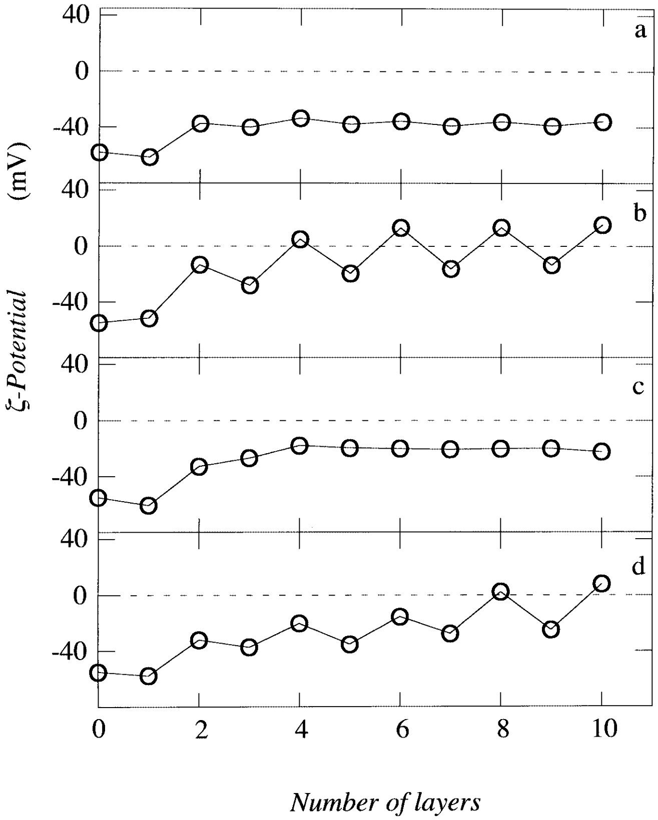

Fig. 5a–d ζ potential of CS91 spheres at 25 °C. **a** C4PVP (8×10^{-6} monoM) and NaPSS (8×10^{-6}) were added alternately (from Ref. [12]), **b** C4PVP (8×10^{-6} monoM) and NaPAA (8×10^{-6}), **c** PAL (8×10^{-6} monoM) and NaPSS (8×10^{-6}), and d PAL (8×10^{-6} monoM) and NaPAA (8×10^{-6}). $\phi=7\times10^{-5}$; the macroanions were added first

balance was broken by the electrostatic shielding effect of the salt. It should be noted that comparatively loose adsorbed layers reaching 600 nm in thickness were formed even in the presence of a tiny amount of sodium chloride of the order of 10^{-6} M.

The values of the pH and the conductance of complex suspensions containing sodium chloride ranging from 0 to 1×10^{-5} M decreased slightly and increased on the successive addition of the macroions, though the graphs showing these are omitted here. It should be noted that the pH and the conductance changed continuously, not zigzag, on the addition of the macroions. Furthermore, they were not so sensitive to the salt addition, though the pH and the conductance increased very slightly as the number of layers increased.

Influence of the basicity and the acidity of the macroions on the alternate adsorption

Figure 3 shows the ζ potential of CS91 spheres where the macrocations and the macroanions are strongly basic and strongly acidic (Fig. 3a), strongly basic and weakly acidic (Fig. 3b), weakly basic and strongly acidic (Fig. 3c) and weakly basic and weakly acidic (Fig. 3d), respectively. Here, the concentrations of the macroions were the same at 8×10^{-6} monoM. The macrocations were added first, and no salt was added. Clearly the alternate change in the ζ potential was quite regular through the ten-layer adsorption processes for the combinations shown in Fig. 3a and d, i.e., C4PVP first plus NaPSS next and PAL first plus NaPAA next. However, the alternate change was broken gradually for the combinations shown in Fig. 3b and c, and the ζ potential shifted toward positive and negative, respectively. These experimental results show clearly that the effective charge number of the strongly basic or acidic macroions ionized is large compared with those of weakly basic or acidic macroions in the suspensions. The equivalency of the basicity and the acidity of the macrocations and macroanions is important for the alternate complexation, in addition to the equivalency of the number of the ionic groups between the macrocations and macroanions.

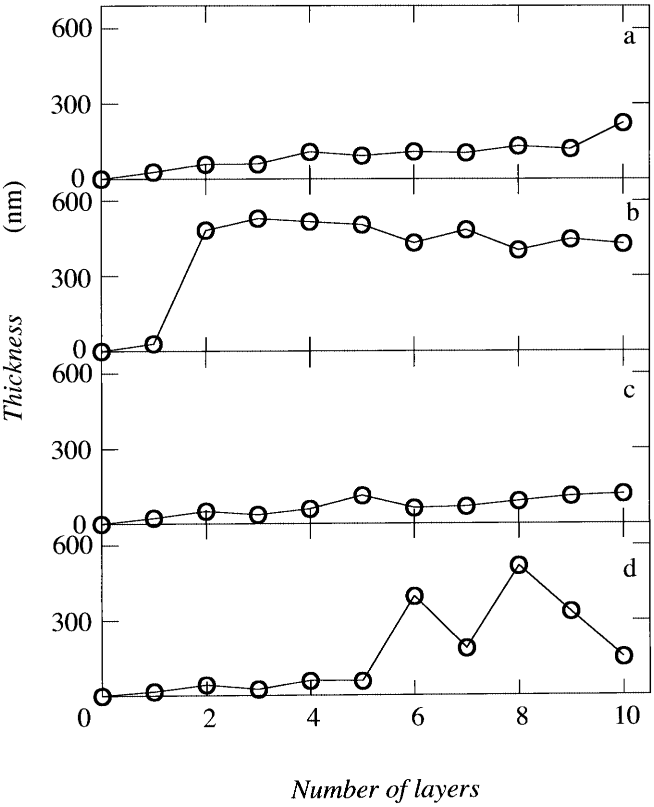

Fig. 6a–d Thickness of the adsorbed layer of CS91 spheres at 25 °C. **a** C4PVP (8×10^{-6} monoM) and NaPSS (8×10^{-6}) were added alternately (from Ref. [12]), **b** C4PVP (8×10^{-6} monoM) and NaPAA (8×10^{-6}), **c** PAL (8×10^{-6} monoM) and NaPSS (8×10^{-6}), and **d** PAL (8×10^{-6} monoM) and NaPAA (8×10^{-6}). $\phi = 7\times10^{-5}$; The macroanions were added first

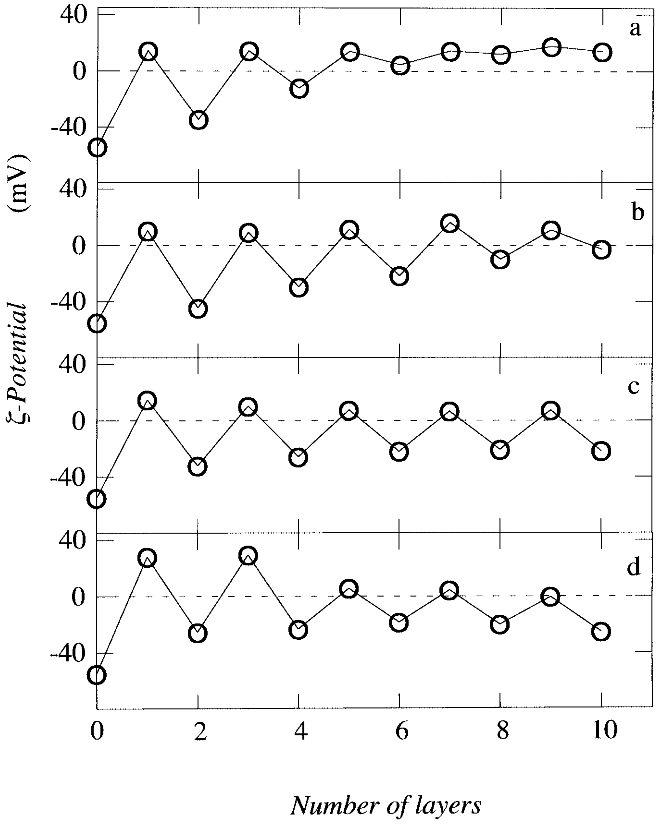

Fig. 7a–d ζ potential of D1A19 spheres at 25 °C. Poly(4-vinyl-*N*-ethyl pyridinium bromide (*C2PVP*) (1×10^{-6} monoM) and NaPAA (**a**: 7.14×10^{-7} monoM; **b**: 1×10^{-6}; **c**: 1.11×10^{-6}; **d**: 1.43×10^{-6}) were added alternately. $\phi = 1\times10^{-5}$; C2PVP was added first

The thickness of the adsorbed layers as a function of the number of layers is shown in Fig. 4. The reversible expansion and contraction occurred only for the strongly basic and strongly acidic macroions (Fig. 4a), and disappeared for other combinations (Fig. 4b–d).

The ζ potential and the thickness of the adsorbed layers for various combinations of the macroions having basicity and acidity, when the macroanions were added first, are shown in Figs. 5 and 6. It is highly plausible from Fig. 5 that the alternate adsorption occurs for combinations of C4PVP and NaPAA (Fig. 5b) and PAL and NaPAA (Fig. 5d) even when the macroanions are added first. However, only the combination of C4PVP and NaPAA (Fig. 5b) is clarified from Fig. 6 as giving alternately adsorbed complexes after the second layer. Figure 6 shows that the clear-cut alternate adsorption did not occur for the combination of PAL and NaPAA, however, the expanded complexes were formed between the sixth and ninth layers.

Influence of the concentration ratio of the macrocations and the macroanions on the alternate adsorption

Figure 7 shows the ζ potential of D1A19 polystyrene spheres when C2PVP (strongly basic) first and NaPAA (weakly acidic) were added alternately, where the concentration ratios (*r*) of the macrocations to the macroanions were 1.4 (Fig. 7a), 1 (Fig. 7b), 0.9 (Fig. 7c) and 0.7 (Fig. 7d). Here, *m** of C2PVP was 3×10^{-7} monoM at a sphere concentration of 1×10^{-5} in volume fraction [16]. The equivalent ionic concentration of the spheres, 3.7×10^{-8} M, is one-eighth of the *m** value of C2PVP. This strongly suggests that the excess adsorption of macroions takes place suddenly in the manner of the avalanche-type adsorption mechanism [11, 12, 13]. In the present experiments, the ionic concentration of C2PVP was 27 times higher than that of D1A19 spheres.

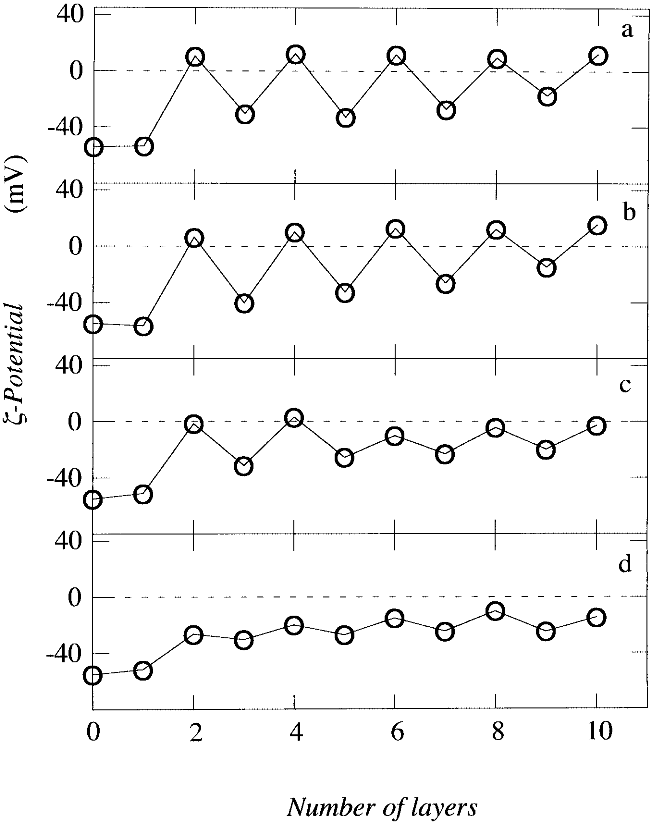

Fig. 8a–d ζ potential of D1A19 spheres at 25 °C. C2PVP (1×10^{-6} monoM) and NaPAA (**a**: 7.14×10^{-7} monoM; **b**: 1×10^{-6}; **c**: 1.11×10^{-6}; **d**: 1.43×10^{-6}) wereadded alternately. $\phi=1\times10^{-5}$; NaPAA was added first

For the combinations shown in Fig. 7a and d, alternate adsorption occurred for the first several layers, since sign reversal was observed; however, the ζ potential shifted to plus or minus, respectively, and the sign reversal disappeared as the number of layers increased further. When the values of *r* were 1 and 0.9, a beautiful charge reversal and then alternate adsorption occurred. These results clearly suggest that the electrostatic balance between macrocations and macroanions is achieved when the concentration of the strongly basic macrocations, C2PVP, is lower than that of weakly acidic macroanions, NaPAA, to within 10%.

The ζ-potential changes as a function of the number of layers, when the macroanions are added first, are shown in Fig. 8. Interestingly, alternate adsorption occurred even when the macroanions were added first, when the values of *r* were 1.4 and 1, as is clear in the figure. It should be noted that the combination of NaPAA first plus C4PVP at $r=1.0$ also gave alternate multiple adsorption as was discussed in the previous section.

Summarizing the experimental results obtained in this work, the electrostatic shielding effect of the simple electrolytes on the intermacroion interactions, the basicity or the acidity of the macrocations or macroanions, and also the equivalency of the number of ionic groups of the macroions play an important role for the alternate multiple adsorption on the surface of colloidal particles. The synchronous delicate balancing of the electrostatic interactions among the macrocations, the macroanions and the surfaces of the colloidal spheres is also very important for multiple complexation.

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References

1. Caruso F, Donath E, Mohwald H (1998) J Phys Chem 102:2016
2. Caruso F, Caruso RA, Mohwald H (1998) Science 282:1111
3. Donath E, Sukhorukov GB, Caruso F, Davis SA, Mohwald H (1998) Angew Chem Int Ed Engl 37:2202
4. Caruso F, Donath E, Mohwald H (1998) J Phys Chem B 102:2011
5. Caruso F, Mohwald H (1999) Langmuir 15:8276
6. Caruso F, Mohwald H (1999) J Am Chem Soc 121:6039
7. Voigt A, Lichtenfeld H, Sukhorukov GB, Zastrow H, Donath E, Baumler H, Mohwald H (1999) Ind Eng Chem Rev 38:4037
8. Caruso F, Trau D, Mohwald H, Renneberg R (2000) Langmuir 16:1485
9. Caruso F, Yang W, Trau D, Renneberg R (2000) Langmuir 16:8932
10. Gao C, Leporatti S, Moya S, Donath E, Mohwald H (2001) Langmuir 17:3491
11. Okubo T, Suda M, Morino S (1998) Polym Prepr Jpn 47:836
12. Okubo T, Suda M (1999) Colloid Polym Sci 277:813
13. Okubo T, Suda M (2000) Colloid Polym Sci 278:380
14. Okubo T (1988) Acc Chem Res 21:281
15. Okubo T (1990) Polym Bull 23:211
16. Okubo T, Suda M (1999) J Colloid Interface Sci 213:565
17. Okubo T, Ise N (1973) J Am Chem Soc 95:2293
18. Okubo T, Ise N (1973) J Am Chem Soc 95:4031
19. Okubo T, Ise N (1980) J Polym Sci 18:1807
20. Okubo T, Mohri N (1988) Macromolecules 21:2744