Colloid Polym Sci (2004) 282: 518–523
DOI 10.1007/s00396-003-0991-1

SHORT COMMUNICATION

Mitsuhiro Suda
Tsuneo Okubo

The influence of pH on the alternate multi-layered adsorption of macrocations and macroanions on colloidal spheres

Received: 28 April 2003
Accepted: 17 July 2003

M. Suda · T. Okubo (✉)
Department of Applied Chemistry and Graduate School of Materials Science, Gifu University, 501-1193 Gifu, Japan
E-mail: okubotsu@apchem.gifu-u.ac.jp
Fax: +81-58-2932628

Abstract The ζ-potential and thickness of the alternate multiple adsorption layers of macrocations and macroanions on the surfaces of colloidal spheres in suspension were measured at pH values ranging from 2.8 to 10.8 via electrophoretic light-scattering measurements. Colloidal silica spheres (110 nm in diameter) were used. The macrocations used were poly(4-vinyl-N-*n*-butyl pyridinium bromide) (C4PVP, a strongly basic macroion) and poly (allylamine) (PAL, which is weakly basic). Sodium poly(styrene sulfonate) (NaPSS, strongly acidic) and sodium polyacrylate (NaPAA, weakly acidic) were used as macroanions. The macrocations were added first in all of the experiments. The alternate adsorption of C4PVP and NaPSS takes place for a wide range of pH values, between 2.8 and 8.7. For C4PVP + NaPAA systems, alternate layers are formed only at neutral pH values and within three to six layers. Multiple adsorption phenomena are observed at acidic and neutral pH values for PAL + NaPSS and PAL + NaPAA systems, respectively. These results strongly support the theory that the synchronous delicate balancing of the electrostatic interactions among the macrocations, the macroanions, and the colloidal spheres is important for the alternate multiple adsorption.

Keywords Alternate multiple adsorption · Macroions · ζ-Potential and thickness of multiple-adsorption layers · Colloidal silica sphere · Electrophoretic light-scattering

Introduction

The alternate multiple-adsorption phenomena of macrocations and macroanions on colloidal surfaces have been studied intensively by the research group of Mohwald, Caruso et al. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Independently, Okubo and Suda [13, 14, 15, 16, 17] studied similar systems from a thermodynamic point of view. It is well-known that most colloidal spheres in aqueous and polar solvents have negative charges on their surfaces [18]. In our previous work [19, 20] the abrupt sign reversal in the ζ-potential of the colloidal spheres was observed by the addition of oppositely-charged macroions. This suggests that the excess macroions (excess compared to the charges on the colloidal surfaces) are adsorbed in the manner of the avalanche-type synchronous adsorption mechanism; in other words adsorption of macroions takes place abruptly on the colloidal surfaces above the critical concentration (m^*) of the macroions added. It should be noted that the m^*-values are always very large; several hundred to a thousand times the ionic concentration of the colloidal spheres. The authors expected to obtain the multi-layered adsorption of macroions on the surface of anionic colloidal spheres by the addition of macrocations first, then macroanions, and so on. The authors added the minimum amount of the macrocations required to reverse the sign of the ζ-potential in the first adsorption step. Equivalent amounts of the macroanions and the macrocations were added in successive steps. Using this method no free macrocation, free macroanion, and then macrocation-macroanion complexes were expected to co-exist in the suspension.

In previous papers, the authors reported that first the salt of strongly basic macrocations [poly(4-vinyl-N-*n*-butyl pyridinium bromide)]and then the salt of strongly acidic macroanions [sodium poly(styrene sulfonate)] were adsorbed alternately on the surfaces of colloidal silica [13, 14] and polystyrene spheres [15]. Furthermore, influences of the foreign salt, basicity or acidity of the macroions, and equivalency in the number of the ionic groups between the macrocations and macroanions upon the layer-by-layer adsorption have been studied in detail [16]. The delicate balance of the electrostatic interactions among the macrocations, macroanions and the surface of the colloidal spheres was important for the multiple adsorptions. In this work, the influence of pH on the alternate multiple adsorptions is further studied using strongly and weakly acidic or basic macroions.

Experimental

Materials

Colloidal silica spheres CS91 were gifts from Catalyst and Chemicals Ind. Co. (Tokyo). The diameter (d), standard deviation (δ) from the mean diameter, and polydispersity index (δ/d) 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 according to conductometric titration. The sphere sample was carefully purified several times using an ultrafiltration cell (model 202, membrane: Diaflo-XM300, Amicon Co.), and then treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8 (D), 20–50 mesh] *more than five years* before use, since newly-produced silica spheres release a considerable amount of alkali ions from their surfaces over a long time period.

Sodium polyacrylate (NaPAA, degree of polymerization = 640) was a gift from Toa Gosei Chemicals Co. (Nagoya). Sodium poly(styrene sulfonate), NaPSS, (degree of polymerization = 87, 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-*n*-butylpyridinium bromide) (C4PVP) have been described previously [21, 22, 23]. The degree of quaternization was 0.96. The degree of polymerization of the parent polymer, poly(4-vinylpyridine) was 3800, as determined by viscometry. Poly(allylamine) (PAL) was a gift from Nitto Boseki Co. (Tokyo). The degree of polymerization for PAL was ca. 600. Water used for the purification and preparation of the samples was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore Co., Bedford, MA).

Electrophoretic light-scattering measurements

The electrophoretic light-scattering (ELS) measurements were made on an ELS spectrophotometer (ELS-6000, Otsuka Electronics, Osaka) at 25 ± 0.02 °C. First, eleven suspensions of the same colloidal spheres having the same sphere concentration, each 19 mL, were prepared in the test tubes (disposable culture tube, 18x150 mm, Iwaki Glass Co., Tokyo). Three hours later one sample was used for the ELS measurement. The measurements were repeated two or three times. The first macroion solution (0.19 mL) was added drop-wise to the remaining ten samples. Three hours later, again, one sample suspension was used for the ELS measurements, and the second macroion solution (0.19 mL) was mixed further with the remaining nine samples. These procedures were repeated until the ELS measurements were completed for all the samples corresponding to the number of layers from zero to ten. The adsorbed layer's thickness was obtained by subtracting the sphere radius from the observed effective radius from the ELS measurements. The reproducibility for the ζ-potential and the thickness was within 5% and 25%, respectively.

pH measurements

pH values of the sample suspensions were measured on a Beckman pH meter (model ϕ34, Tokyo) with a glass electrode (model 6378-10D, Horiba, Kyoto) at 25 ± 0.5 °C. The apparent dissociation constants (K_a and K_b) of PAA and PAL were determined by pH titrations of the HPAA and PALOH with aqueous NaOH (1 M) and aqueous HCl (1 M), respectively, from the pH values at the half degree of neutralization. The acid and base forms of the polymers were obtained by the treatment of the corresponding polymer salts with excess amounts of Bio-Rad ion-exchange resins. The pK_a and pK_b values of PAA and PAL were 5.7 and 7.9, respectively.

The pH values of the sample suspensions were fixed at the given values by adding 0.1 M aqueous solutions of HCl or NaOH. The discrepancy was within ±0.2.

Conductivity measurements

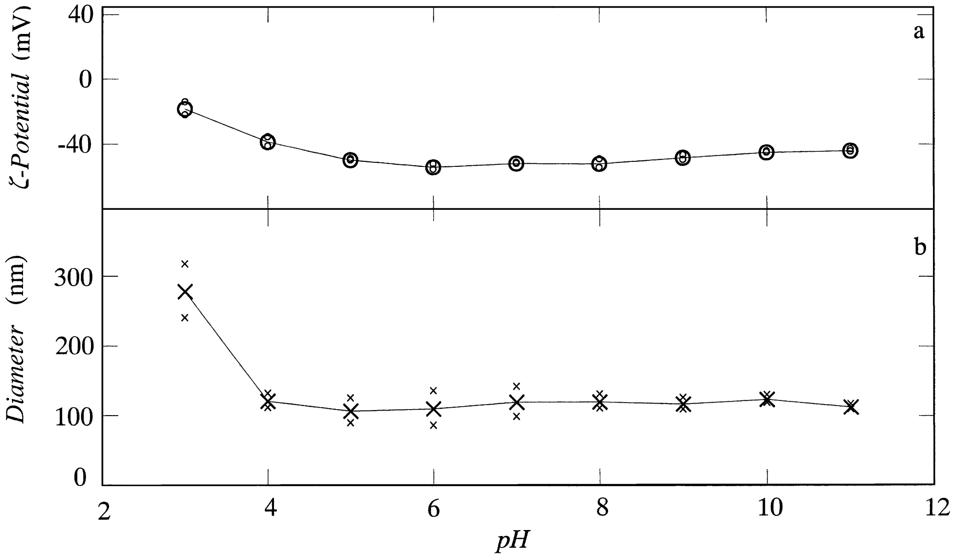
The conductivity of the suspension was measured on a model DS-14 conductivity meter (Horiba, Kyoto) with an electrode (code 3552, Horiba) at 25 ± 0.5 °C.

Results and discussion

Stability of the colloidal silica suspensions at pH values from 2.8 to 10.8

Fig. 1 shows the ζ-potentials and diameters estimated from ELS measurements for the colloidal silica spheres without macroion adsorption. Both parameters remained constant for pH values ranging from 4 to 10.8, and values at pH = 2.8 were large. It is clear that the silica spheres are suspended stably at pH values from 4 to 10.8. However, aggregation takes place in strongly acidic suspensions, since the silica spheres are close to neutral at pH = 2.8. In this case, electrostatic intersphere repulsion, which is very important for suspension stability, disappears.

Fig. 1 ζ-Potential (**a**) and diameter (**b**) of CS91 spheres at 25 °C. $\phi = 7\times10^{-5}$, large symbols indicate the mean values of two runs (shown by small symbols)



ζ-Potential of the alternate multi-layered complexes at pH values ranging from 2.8 to 10.8

Fig. 2 shows the change in the ζ-potential values for the CS91 + C4PVP + NaPSS system over the course of repeated adsorption processes. Clearly, the ζ-potentials undergo repeated sign reversal over the pH range from 2.8 to 8.7. The sulfonyl groups of NaPSS are strongly acidic anions and should dissociate irrespective of the pH values examined in this work. However, the quaternized pyridinium groups of C4PVP are strongly basic, but not as strongly basic as hydroxide ions. It is highly plausible that the C4PVP molecules are close to neutral at pH values of 9.5 and 10.8. The apparent dissociation constant (pK_b) of C4PVP was not measured by the pH titration, because the alkali form of C4PVP was chemically unstable. Therefore, alternate multiple adsorptions take place only when the silica spheres and NaPSS are *negatively* charged and C4PVP is *positively* charged. The delicate balance of the electrostatic interactions between the macrocations, macroanions and the colloidal spheres is important for the alternate multiple adsorption.

Fig. 3 shows the ζ-potentials for the CS91 + C4PVP + NaPAA system. The sign reversal occurred only at pH = 6.5 within three layers, and further alternate adsorption did not take place. In the previous work for the same system, sign reversal occurred until six layers [16]. The acidity of NaPAA is weak ($pK_a = 5.7$) and PAA molecules will not dissociate at pH = 2.8, and the sphere surfaces of CS91 also do not dissociate at pH = 2.8 as was discussed in Fig. 1.

The ζ-potentials of the CS91 + PAL + NaPSS system are shown in Fig. 4. Only in acidic conditions did alternate adsorption take place. The major reason

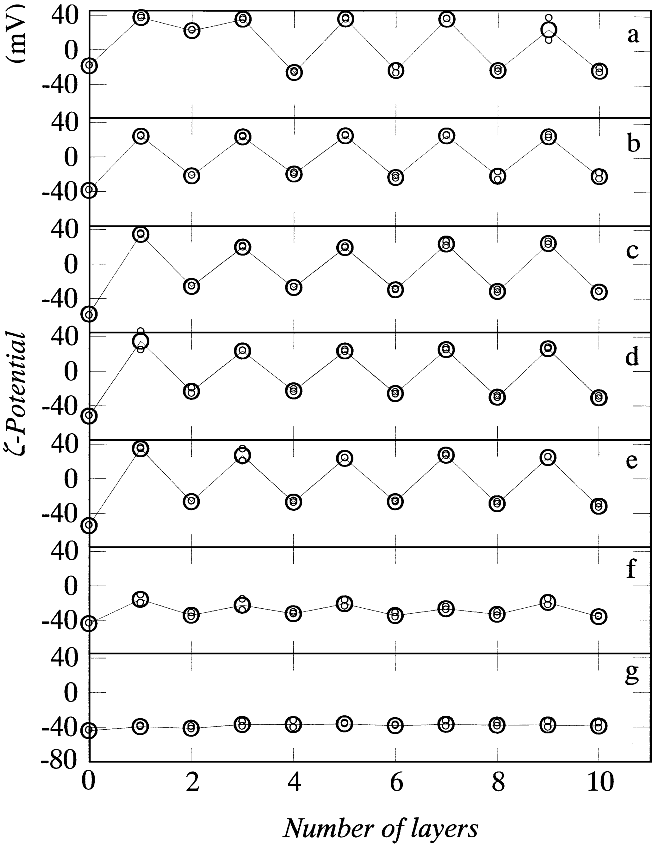


Fig. 2 ζ-Potential of CS91 spheres at 25 °C. C4PVP (8×10^{-6} monoM) and NaPSS (8×10^{-6} monoM) are added alternately. $\phi = 7\times10^{-5}$, C4PVP is added first, **a**: pH = 2.8, **b**: 4.1, **c**: 6.3, **d**: 6.5, **e**: 8.7, **f**: 9.5, **g**: 10.8, Large symbols indicate the mean values of two runs (shown by small symbols)

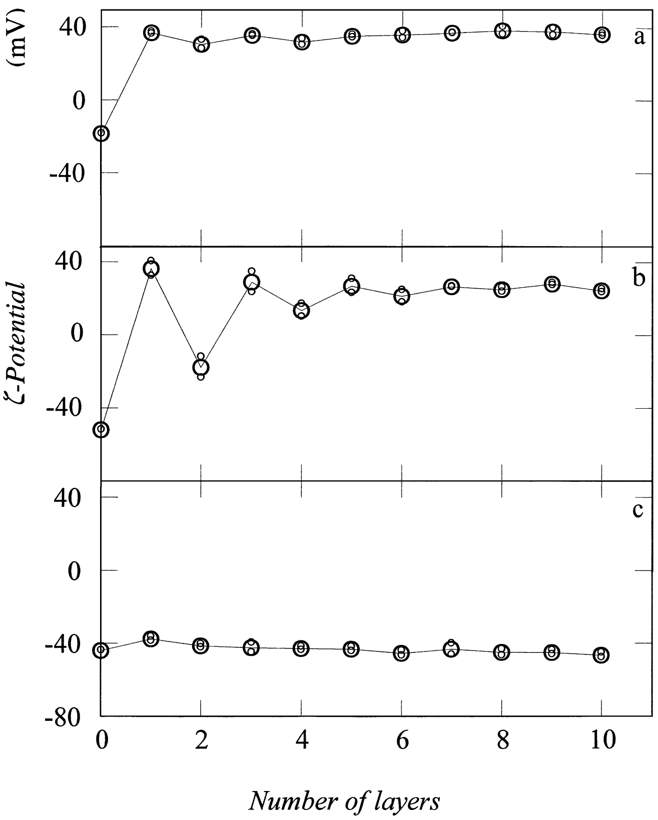


Fig. 3 ζ-Potential of CS91 spheres at 25 °C. C4PVP (8×10^{-6} monoM) and NaPAA (8×10^{-6} monoM) are added alternately. $\phi = 7\times10^{-5}$, C4PVP is added first, **a**: pH = 2.8, **b**: 6.5, **c**: 10.8, large symbols indicate the mean values of two runs (shown by small symbols)

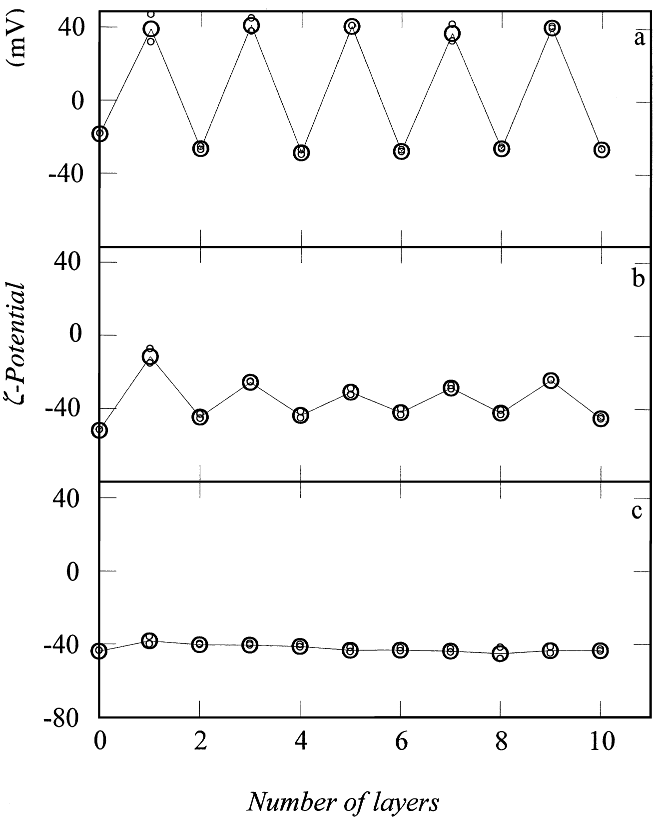


Fig. 4 ζ-Potential of CS91 spheres at 25 °C. PAL (8×10^{-6} monoM) and NaPSS (8×10^{-6} monoM) are added alternately. $\phi = 7\times10^{-5}$, PAL is added first, **a**: pH = 2.8, **b**: 6.5, **c**: 10.8, large symbols indicate the mean values of two runs (shown by small symbols)

for this observation is that the PAL dissociates only in acidic conditions, though PSS dissociates irrespective of pH values.

Fig. 5 shows the ζ-potentials for the weakly basic PAL and weakly acidic PAA system as a function of the number of layers. Interestingly, the multiple adsorptions occurred only at neutral pH.

Therefore, in summary, it is clear that the alternate multiple adsorption takes place only when all of the macrocations, macroanions and the colloidal spheres are dissociated and charged.

Adsorbed layer thickness at pH values ranging from 2.8 to 10.8

Fig. 6 shows the adsorbed layer's thickness for the four kinds of systems. At first glance, the results appear to be complex. However, the thickened adsorption layers were observed only for the systems where charge reversal took place. The mean values of the thickness per macroion layer are compiled in Table 1. Experimental errors were rather large, but thicknesses of several nanometers were obtained when the alternate multiple adsorption occurred.

It is clear from Table 1 that alternate adsorption of strongly acidic (PSS) and strongly basic macroions (C4PVP) on the colloidal spheres took place over a wide range of pH values between 2.8 and 8.7. This result shows that the macroions are dissociated over this range. However, the alternate adsorption did not occur at pH = 9.5 and 10.8, which indicates that C4PVP is not very strongly basic and does not dissociate (it is neutral) at these pH's.

The alternate complexation of PAL and NaPSS on CS91 spheres took place only at pH = 2.8, which clearly shows that both the macrocations and macroanions are dissociated at acidic pH only.

PAL and PAA are weakly basic and acidic macroions. Therefore, occurrence of complex formation at neutral pH is quite understandable, since PAL and PAA are not dissociated at basic and acidic pH's, respectively.

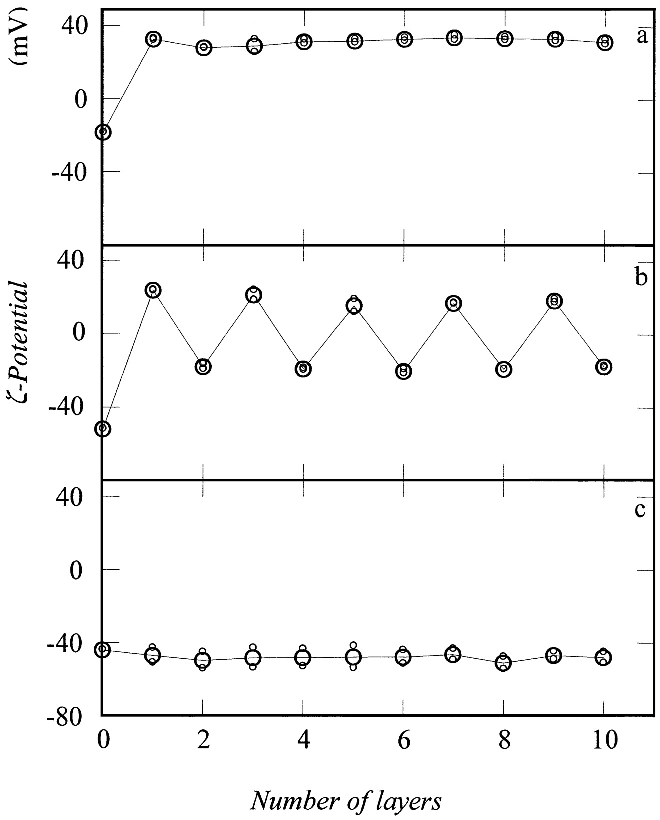


Fig. 5 ζ-Potential of CS91 spheres at 25 °C. PAL (8×10^{-6} monoM) and NaPAA (8×10^{-6} monoM) are added alternately. $\phi = 7\times10^{-5}$, PAL is added first, **a**: pH = 2.8, **b**: 6.5, **c**: 10.8, large symbols indicate the mean values of two runs (shown by small symbols)

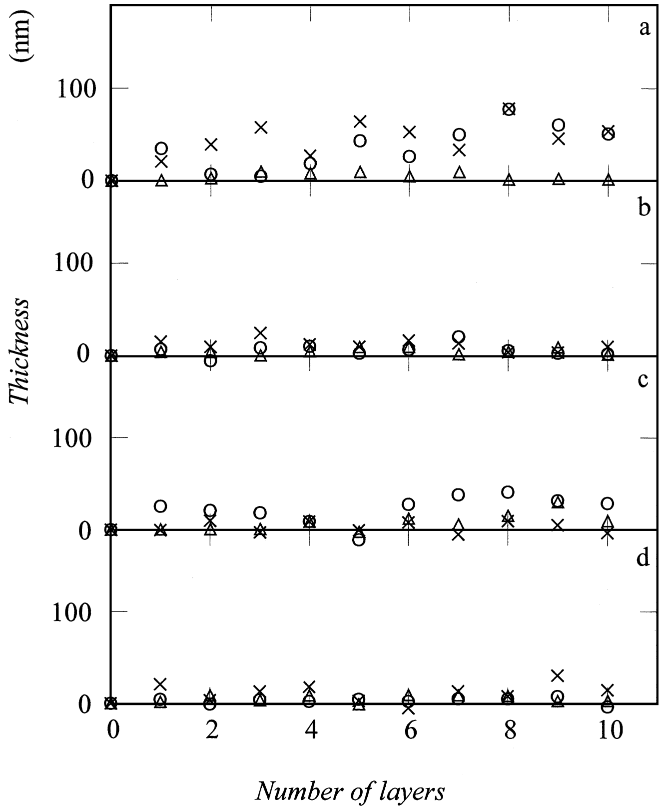


Fig. 6 Adsorbed layer's thickness of CS91 spheres at 25 °C. **a**: C4PVP (8×10^{-6} monoM) and NaPSS (8×10^{-6} monoM) are added alternately, **b**: C4PVP and NaPAA, **c**: PAL and NaPSS, **d**: PAL and NaPAA, $\phi = 7\times10^{-5}$, O: pH = 2.8, X: 6.5; Δ: 10.8

Conclusions

Summarizing the ELS data obtained in this work, alternate multiple adsorption takes place when the macrocations are added first and when equivalency holds for the number of ionic groups of macrocations and macroanions. In most cases, the three components: macrocations, macroanions, and colloidal spheres, must be charged positively, negatively, and negatively, respectively, in order to form the alternate multiple complex. Furthermore, the synchronous interactions and delicate balance of the electrostatic interactions among the three components are important. It should be mentioned here that the data regarding the ζ-potential from the ELS measurements reported previously were mostly reproducible and reliable. Only the layer thickness data from the ELS measurements contained rather large experimental errors.

Table 1 Mean thickness values per macroion layer, estimated from the ELS measurements at 25 °C. [C4PVP] = [NaPSS] = [PAL] = [NaPAA] = 8×10^{-6} monoM. The macrocations were added first, errors in pH values = ±0.02

pH	Mean thickness per macroion layer (nm)			
	CS91 + C4PVP + NaPSS	CS91 + C4PVP + NaPAA	CS91 + PAL + NaPSS	CS91 + PAL + NaPAA
2.8	6.5	0	3.7	0
4.1	6.8	–	–	–
6.3	9.7	–	–	–
6.5	7.3	1.5	0	1.9
8.7	8.3	–	–	–
9.5	0	–	–	–
10.8	0	0	0	0

Acknowledgements We wish to express our deep thanks to Drs. M. Komatsu and M. Hirai of Catalysts & Chemicals Ind. Co. (Tokyo) for providing the silica samples. We would also like to thank The Ministry of Education, Science, Sports and Culture for grants-in-aids of Scientific Research on Priority Area (A) (11167241) and for Scientific Research (B) (11450367).

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 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. Leporstti S, Gao C, Voigt A, Donath E, Mohwald H (2001) Eur Phys J E5:13
12. Dai Z, Mohwald H (2002) Langmuir 18:9533
13. Okubo T, Suda M, Morino S (1998) Polymer Preprints Japan 47:836
14. Okubo T, Suda M (1999) Colloid Polymer Sci 277:813
15. Okubo T, Suda M (2000) Colloid Polymer Sci 278:380
16. Okubo T, Suda M (2002) Colloid Polymer Sci, 280:533.
17. Okubo T, Suda M (2003) Colloid Polymer Sci, 281:782
18. Okubo T (1988) Acc Chem Res 21:281
19. Okubo T (1990) Polymer Bull 23:211
20. Okubo T, Suda M (1999) J Colloid Interface Sci 213:565
21. Okubo T, Ise N (1973) J Am Chem Soc 95:2293
22. Okubo T, Ise N (1973) J Am Chem Soc 95:4031
23. Okubo T, Ise N (1980) J Polymer Sci 18:1807