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Alternate multi-layered adsorption of macro-cations and -anions on the colloidal spheres. Influence of the deionization of the complexation mixtures with coexistence of the ion-exchange resins

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Abstract The alternate multiple adsorption layers of macrocations and macroanions on the surfaces of colloidal spheres, in which the complexation mixtures are deionized with ion-exchange resins are studied with help of the electrophoretic light-scattering, dynamic light-scattering and transmitted electron-microscopy techniques. The results are compared with those without resins. Colloidal silica spheres (110 nm in diameter) and monodispersed polystyrene spheres (220 nm) are used as colloidal spheres. The macrocations used are poly (4-vinyl-*N*-*n*-butyl pyridinium bromide) and poly (allylamine hydrochloride). Sodium poly (styrene sulfonate) and sodium polyacrylate are used as macroanions. The macroion-colloid complexations are formed firmly when the complexation suspensions are deionized with the resins.

Keywords Macroion-colloid multiple-adsorption layers · Deionization of the complexation suspension · Colloidal silica sphere · Polystyrene sphere · Dynamic light-scattering

Introduction

The alternate multiple-adsorption phenomena of macrocations and macroanions on the colloidal surfaces have been studied first by the two research groups of Mohwald, Caruso et al. [1–7] and Okubo and Suda [8,9] independently. It is well known that most of colloidal spheres have negative charges on their surfaces in aqueous and polar solvents [10]. In our previous work [11,12] the abrupt sign reversal in the ζ-potential of colloidal spheres was observed by the addition of oppositely charged macroions. Thus, 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. Furthermore, the same equivalent amounts of the macroanions and the macrocations were added successively. By this method it was expected that no free-macrocations, -macroanions, and then macrocation-macroanion complexes co-existed in the suspension.

In the previous papers, the authors have reported that the salt of strongly basic macrocations, poly (4-vinyl-*N*-*n*-butyl pyridinium bromide) (C4PVPBR) first and then the salt of strongly acidic macroanions, sodium poly (styrene sulfonate) (NaPSS) were adsorbed alternately on the surfaces of colloidal silica [8, 9] and polystyrene spheres [13]. Furthermore, influences of the foreign salt, basicity or acidity of the macroions and the equivalency in the number of the ionic groups between the macrocations and macroanions upon the layer-by-layer adsorption have been studied in detail [14]. In order to check the reliability of our data, we made a series of dynamic light-scattering (DLS) measurements and obtained the histograms showing the size distribution of the complexes [15]. Then, it became clear that our previous data from the cumulant analysis of the electrophoretic light-scattering (ELS) measurements on the thickness of the adsorption layers included the contribution from the small amount of the aggregated complexes. Our corrected thickness values obtained by eliminating the contribution from the aggregates support clearly the continuous thin layer's growing adsorption instead of the expansion-contraction type adsorption.

Recently, the authors studied the influence of pH of the complex mixtures on the alternate multi-layered adsorption [16]. In this work, influence of the simple ions expelled in the course of the complexation reaction is further studied in detail by the deionization of the complexation mixtures with the mixed beds of caion- and anion-exchange resins. Furthermore, electron-microscopic evidence for the alternate multiple-complexation is reported in this paper.

Experimental

Materials

Colloidal silica spheres CS91 were the gifts from Catalyst & Chemicals Ind. Co. (Tokyo). Diameter (d_o), standard deviation (δ) from the mean diameter, and polydispersity index (δ/d_o) of these spheres were 110, 4.5 and 0.041 nm, respectively. These size parameters were determined from an electron microscope. The charge density of the strongly acidic groups was 0.48 μC/cm^2 from conductometric titration. Monodispersed polystyrene spheres of D1A19 were purchased from Dow Chemical Co. d_o, δ and δ/d_o were 220, 6.5 and 0.03 nm, respectively. The charge density of the strongly acidic groups was 1.32 μC/cm^2. These spheres 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] more than 10 years before use, since the newly produced silica spheres always released a considerable amount of alkali ions from the sphere surfaces for a long time.

The details of the preparation and purification of C4PVP·Br were described previously [17–19]. The degree of quaternization was 0.96. The degree of polymerization of the parent polymer, poly (4-vinylpyridine) was 3,800 as determined by viscometry. Poly (allylamine hydrochloride) (PAL·HCl) was a gift from Nitto Boseki Co. (Tokyo). The degree of polymerization was ca. 1,000. Sodium polyacrylate (NaPAA, degree of polymerization = 640) was a gift from Toa Gosei Chemicals Co. (Nagoya). NaPSS, (molecular weight = 18,000, polydispersity index; $M_w/M_n = 1.14$) was purchased from Pressure Chemicals (Pittsburgh, PA, USA). 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, USA).

Electrophoretic light-scattering and dynamic light-scattering measurements

The ELS and the DLS measurements were made on a LEZA-6000 and DLS-7000 spectrophotometers, respectively ?(Otsuka Electronics, Osaka) at 25 ± 0.02°C. The adsorbed layer's thickness was obtained by subtracting the sphere radius from the observed effective radius. For the DLS measurements, the sample of 5 ml was prepared in a Pyrex tube cell (12 mm outside diameter and 130 mm long). Data analysis was made with the cumulant analysis. Histogram methods [20] including the non-negative least square (NNLS) and the Marquadt analyses were also made for discussing the size distribution in the effective size of colloidal spheres including the adsorbed layers. The reproducibility of the ζ-potential and the thickness was within 5 and 25%, respectively.

First 11 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). Ion-exchange resins (Bio-Rad, AG501-X8 (D), 20–50 mesh) were further added into the each tubes for the experiments with resins. Three hours later one sample was used for the ELS and DLS measurements. These measurements were repeated two to three times. The remaining ten samples were added drop-wisely with 0.19 ml of the first macroion solution and mixed gently. Three hours later, again, one sample suspension was used for the ELS and DLS 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 and DLS measurements completed for all the samples corresponding to the number of layers from 0 to 10. The adsorbed layer's thickness was obtained by subtracting the sphere radius from the observed effective radius by the histogram analyses of Marquadt and NNLS methods. The reproducibility of the data was within 25% for the thickness values. In this work, the experiments without resins were not made, and the reference values reported in the previous work were compared with the observed data with resins in this work.

Electron microscopy

Transmitted electron-microscopic observation was made on Hitachi H8000.

pH and conductivity measurements

pH values of the sample suspensions were measured on a Beckman pH meter (model f34, 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 (code 3352, Horiba) at 25 ± 0.5°C.

Results and discussion

Influence of the deionization of the complexation mixtures on the ζ-potential of the adsorbed spheres

Figure 1 shows the change in the ζ-potentials for the four kinds of complexation systems, i.e., CS91 + C4PVP + PSS, CS91 + C4PVP + PAA, CS91 + PAL + PSS and CS91 + PAL + PAA over the course of repeated adsorption processes. Clearly, the ζ-potential of the suspensions with resins undergoes repeated sign reversal more significantly than that of the suspensions without resins. This supports that the alternate multiple adsorptions take place much more firmly when the foreign ions repelled in the course of alternate complexations are deleted from the suspensions with the coexistence of the ion-exchange resins.

Influence of the deionization of the complexation mixtures on the adsorbed layer's thickness

Figure 2 shows the adsorbed layer's thickness observed from the ELS measurements. Rather scattered data of

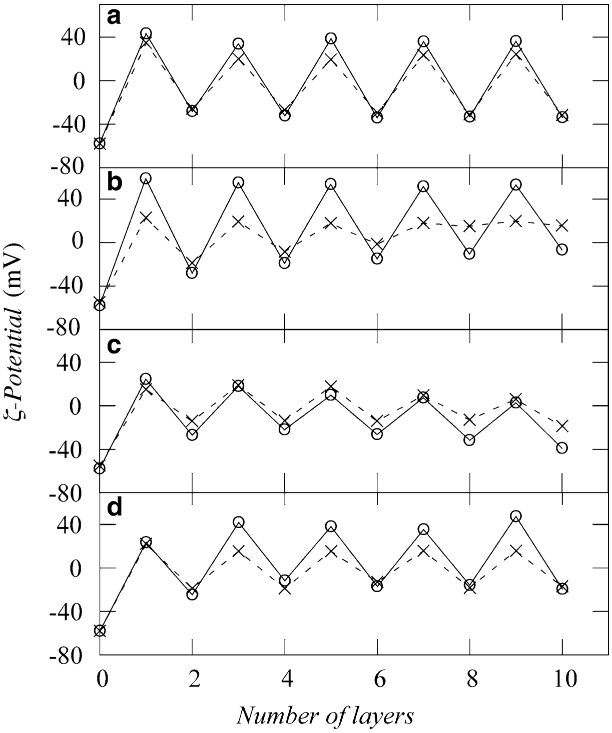


Fig. 1 ζ-Potential of the macroion-CS91 complexes estimated from ELS measurements at 25°C. **a** [C4PVP·Br] = [NaPSS] = 8×10^{-6} monoM, **b** [C4PVP·Br] = [NaPAA] = 8×10^{-6} monoM, **c** [PAL·HCl] = [NaPSS] = 8×10^{-6} monoM, **d** [PAL·HCl] = [NaPAA] = 8×10^{-6} monoM. Macrocation is added first. $\phi = 7\times10^{-5}$, *O* with resins, *X* without resins

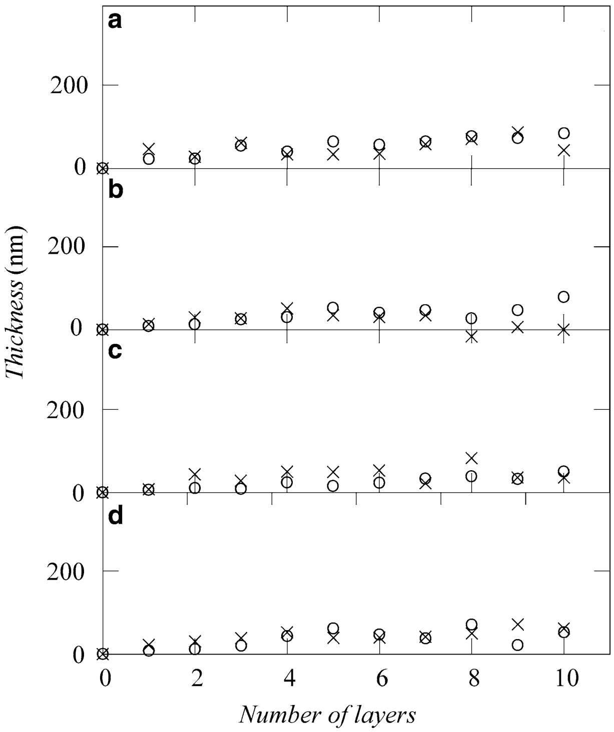
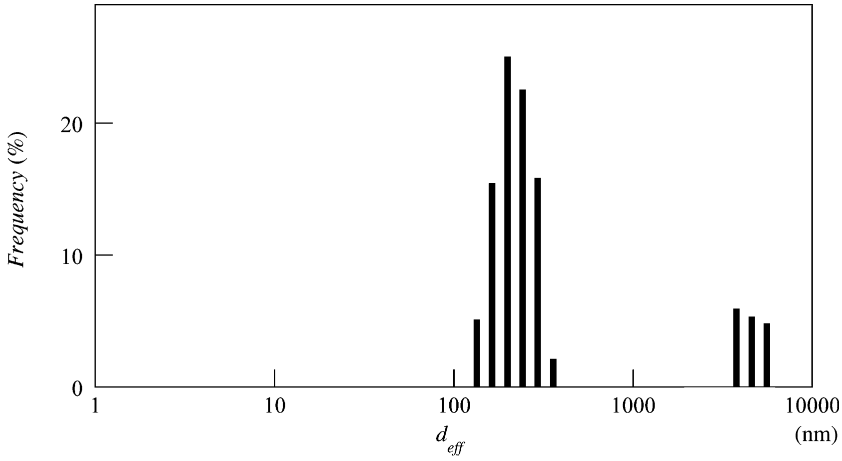


Fig. 2 Adsorbed layer's thickness of the macroion-CS91 complexes estimated from ELS measurements at 25°C. **a** [C4PVP·Br] = [NaPSS] = 8×10^{-6} monoM, **b** [C4PVP·Br] = [NaPAA] = 8×10^{-6} monoM, **c** [PAL·HCl] = [NaPSS] = 8×10^{-6} monoM, **d** [PAL·HCl] = [NaPAA] = 8×10^{-6} monoM. Macrocation is added first. $\phi = 7\times10^{-5}$, *O* with resins, *X* without resins

Fig. 3 Histogram showing the size distribution of CS91 + C4PVP + PSS complexes from NNLS analyses in the DLS measurements at 25 C. sixth layer, $\phi = 7\text{x}10^{-5}$, [C4PVP.Br] = [NaPAA] = $8\text{x}10^{-6}$ monoM, C4PVP.Br is added first



the thickness were obtained from the ELS method, and the quantitative discussion is regrettably impossible from the ELS method only.

More reliable data of the adsorbed layer's thickness were obtained from the DLS measurements. Figure 3 shows a typical example of the size distributions obtained from NNLS analysis. As discussed in a previous paper in detail [15], a small number of the aggregates, around 5,000 nm, coexisted as is shown in the figure. These aggregates will be the polyelectrolyte complexes and/or polyelectrolyte-colloid complexes associated. These aggregates were observed for most of the suspensions examined. Figure 4 shows the fractions in the frequencies of the main peak in the DLS measurements from NNLS analysis for the four complexation systems, (a) CS91 + C4PVP + PSS, (b) CS91 + C4PVP + PAA, (c) CS91 + PAL + PSS, and (d) CS91 + PAL + PAA. Clearly, the fractions of the main peak increased when the suspensions were deionized with the resins. This supports the idea that the macroion complezation reaction far from the colloidal spheres is diminished for the suspensions in the low ionic concentration of simple ions. In other words, the stable alternate adsorption takes place for the deionized suspensions compared with those coexisted with the foreign simple ions.

Corrected thicknesses of the alternate multi-layers thus obtained are compiled for CS91 + C4PVP + PSS systems in Table 1 with the data from the electron microscopy, which will be described later. Several characteristic features are observed in the table. First, the thicknesses in the beginning stage of the alternate adsorption within three to four layers were rather scattered and large compared with the final stage of the alternate adsorptions, especially the seventh to tenth layers. These results support strongly the fact that the first several adsorbed layers are rather soft and extended. Furthermore, the boundaries between the neighbored macroion layers will not be so clear and different macroions creep in to each other. The compact and distinct alternate layers must be formed in the progress of the alternate adsorptions. Secondly, the

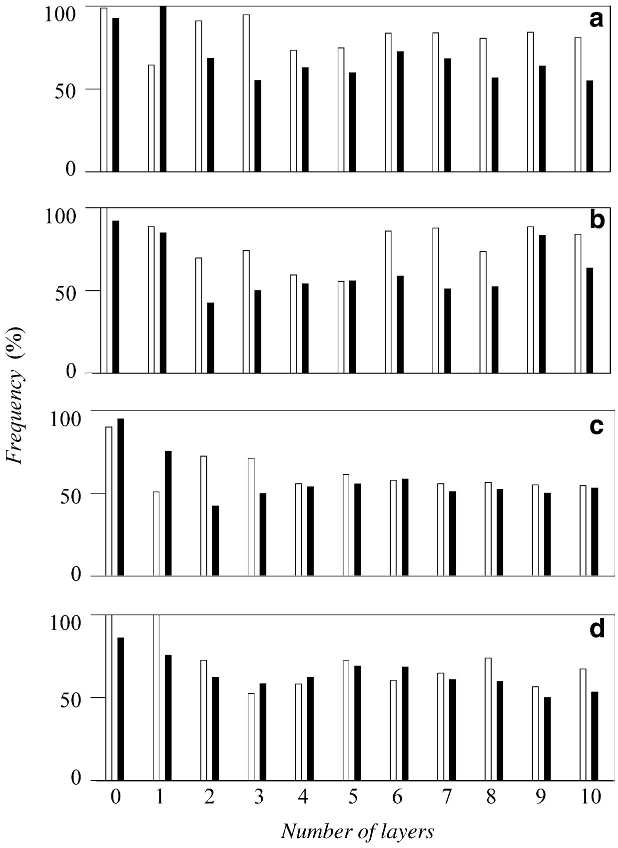


Fig. 4 Fractions in the frequencies of the main peak in the DLS measurements at 25°C. CS91 sphere, $\phi = 7\text{x}10^{-5}$, NNLS analyses, open poles: with resins, solid poles: without resins, **a** [C4PVP·Br] = [NaPSS] = $8\text{x}10^{-6}$ monoM, **b** [C4PVP·Br] = [NaPAA] = $8\text{x}10^{-6}$ monoM, **c** [PAL·HCl] = [NaPSS] = $8\text{x}10^{-6}$ monoM, **d** [PAL·HCl] = [NaPAA] = $8\text{x}10^{-6}$ monoM. Macrocations are added first

Table 1 Mean values of the thickness of the adsorbed layers for CS91 + C4PVP + PSS estimated from the DLS and TEM measurements at 25°C

Number of layers	DLS (nm)		TEM (nm)	
	With resins	Without	With	Without
0	0	0	0	0
1	22	46	–	16
2	22	28	–	10
3	54	61	13	16
4	40	34	18	8
5	64	33	–	7
6	56	35	–	8
7	64	58	–	10
8	76	71	–	–
9	73	86	14	12
10	84	44	20	12

[C4PVP.Br] = [NaPSS] = 8x10^{-6} monoM. ϕ = 7x10^{-5}. C4PVP is added first

thickness of the adsorbed layers still has rather large experimental errors. But, the tendency of the linear increase of the thickness was observed except the beginning steps of multiple adsorption processes. Thirdly, the thickness of the adsorbed layers estimated from the DLS measurements for the deionized suspensions was not so differ from those without ion-exchange resins.

Table 2 shows the thicknesses of the multiple adsorption layers estimated from the DLS method and also from TEM method for the CS91 + PAL + PSS systems. First and second features observed in Table 1 were also observed clearly in this table. Concerning the third feature, Table 2 shows clearly the thicknesses with resins being small compared with those without resins.

Table 2 Mean values of the thickness of the adsorbed layers for CS91 + PAL + PSS estimated from the DLS and TEM measurements at 25°C

Number of layers	DLS (nm)		TEM (nm)
	With resins	without	with
0	0	0	0
1	6	8	2
2	10	43	22
3	8	29	–
4	24	50	–
5	16	49	15
6	23	53	–
7	33	23	–
8	38	83	–
9	33	36	13
10	50	36	–

[PAL.HCl] = [NaPSS] = 8x10^{-6} monoM. ϕ = 7x10^{-5}. PAL is added first

Table 3 Mean values of the thickness per each macroion layer estimated from the DLS measurements at 25°C

Macrocation + macroanion	With resins (nm)	Without (nm)
C4PVP + PSS	11.6 ± 2	9.7 ± 2
C4PVP + PAA	7.6 ± 2	12.1 ± 2
PAL + PSS	5.3 ± 2	6.3 ± 2
PAL + PAA	8.0 ± 2	7.2 ± 2

CS91 spheres, [macrocation] = [macroanion] = 8x10^{-6} monoM

This supports that the firm and distinct multi-layers are formed with resins.

Table 3 compiles the thicknesses of the adsorbed layers per macroion layer estimated from the DLS measurements. The values for the multiple complexations with resins between the strongly basic and strongly acidic macroions (C4PVP + PSS) and those between weakly basic and weakly acidic macroions (PAL + PAA) were large compared with those without resins, whereas the thicknesses with resins between strongly basic and weakly acidic (C4PVP + PAA) and between weakly basic and strongly acidic macroions (PAL + PSS) were small compared with those without resins. These results will support that the alternate complexation proceeds firmly with the coexistence of the ion-exchange resins when the basicity of macro-cations and the acidity of the macro-anions are similar to each other.

Electron microscopic observation of the alternate multiple adsorption complexes

Figure 5 shows the TEM pictures of the alternate multiple complexes of C4PVP cations and PSS anions on the silica spheres without ion-exchange resins. The layers of the macroions were observed. Figure 6 shows the pictures of the same systems as Fig. 5, but with ion-exchange resins. Macroions were also coated on the surface of colloidal silica spheres.

The formation of the alternate complexes of the pairs of PAL cations and PSS anions with resins is supported from Fig. 7. It is interesting to note that the width of the multiple adsorbed layers increases by the progress of the adsorption, but turned to decrease at the ninth layers. This may support the fact that the layers at the beginning stages of adsorption are loose, whereas they are dense in the progress of the multiple adsorption. Figure 8 shows clearly that the firm complexation takes place between polystyrene spheres (D1A19) and the pairs of C4PVP cations and PSS anions, though the TEM pictures are for the dried complexes and highly plausible to differ from the real figure in suspension state.

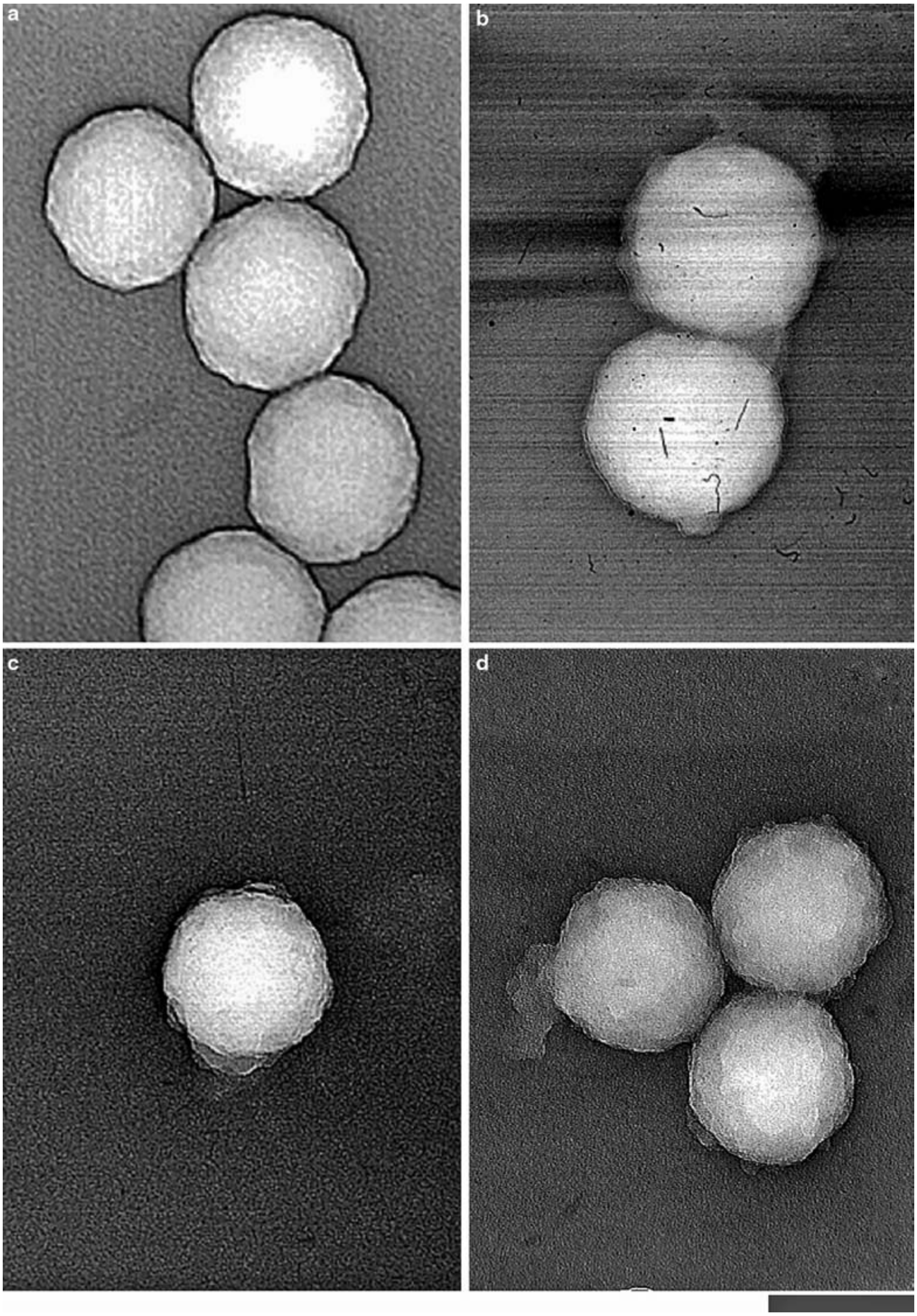


Fig. 5 TEM pictures of CS91 + C4PVP + PSS complexes. Without resins. [C4PVP·Br] = [NaPSS] = 8x10^{-6} monoM. C4PVP is added first. **a** CS91 only, **b** three layers, **c** seven layers, **d** nine layers. $\phi = 7\text{x}10^{-5}$, length of the *bar* is 100 nm

Influence of the deionization on the pH and the conductivity of the complexation mixtures

The pH-values of four systems of alternate complex suspensions, CS91 + C4PVP + PSS, CS91 + C4PVP + NaP-AA, CS91 + PAL + PSS and CS91 + PAL + PAA are measured at the each steps of the macroion addition. The

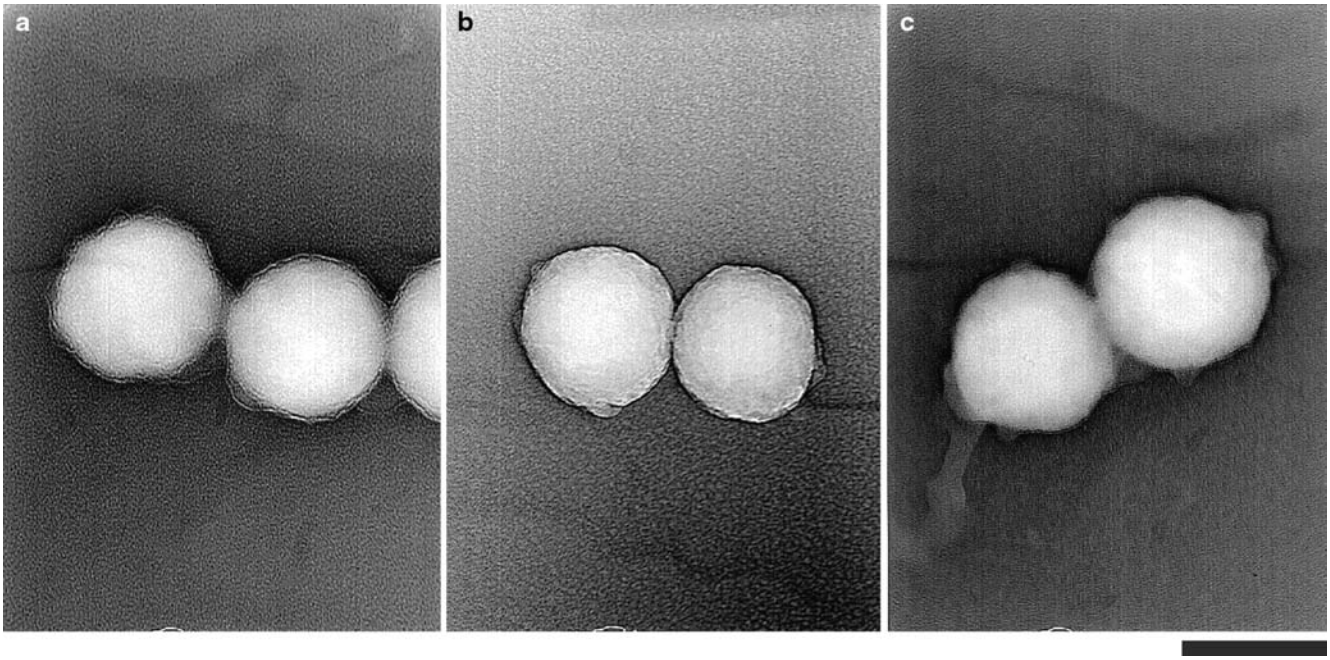
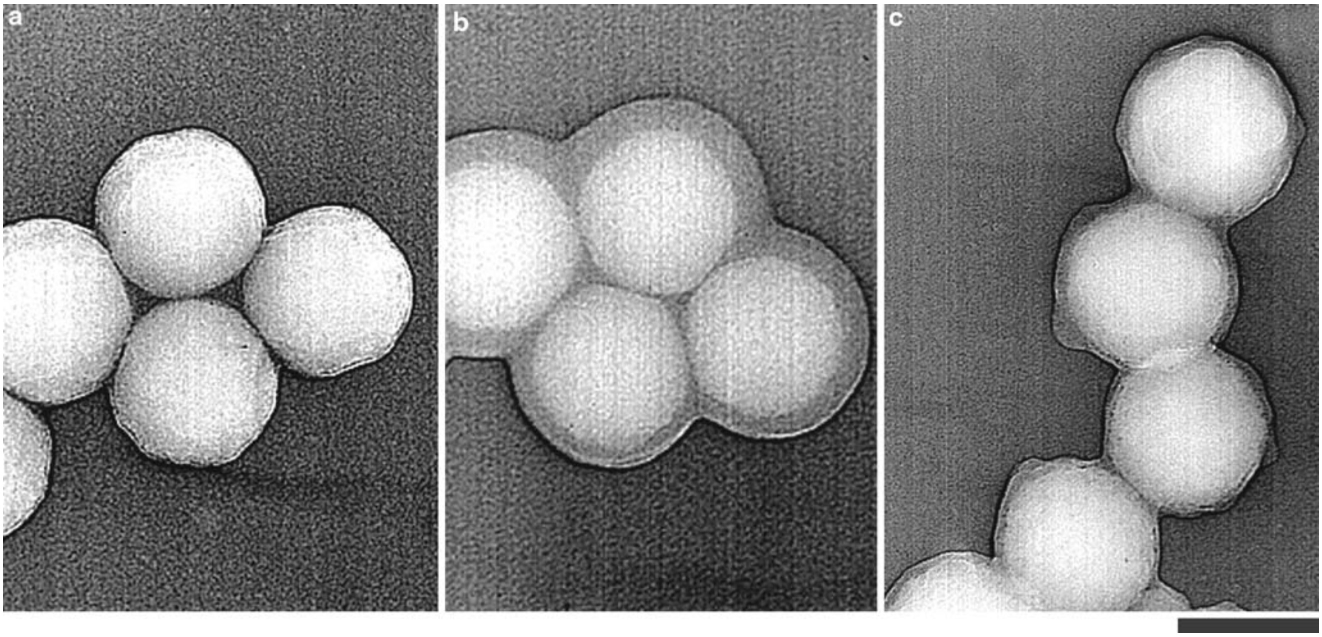


Fig. 6 TEM pictures of CS91 + C4PVP + PSS complexes. With resins. [C4PVP·Br] = [NaPSS] = 8x10^{-6} monoM. C4PVP·Br is added first. **a** three layers, **c** four layers, **d** nine layers. $\phi = 7x10^{-5}$, length of the *bar* is 100 nm

observed pH values of the suspensions with resins kept constant around seven irrespective of the stepwise complexation steps, and those with the resins were always large compared with those without resins within two. The graphs showing these were, however, skipped in this paper.

The conductivities of the suspensions with and without the ion-exchange resins increased in the progress of the macroion adsorption steps. Furthermore, the conductivities of all the systems with resins were small by the factor of five to seven compared with those without resins, though the graphs demonstrating these were skipped again in this report. Decrease in the conductivities is, of course, due to the subtraction of the

Fig. 7 TEM pictures of CS91 + PAL + PSS complexes. With resins. [PAL·HCl] = [NaPSS] = 8x10^{-6} monoM. PAL·HCl is added first. **a** one layers, **b** two layers, **c** nine layers. $\phi = 7x10^{-5}$, length of the bar is 100 nm



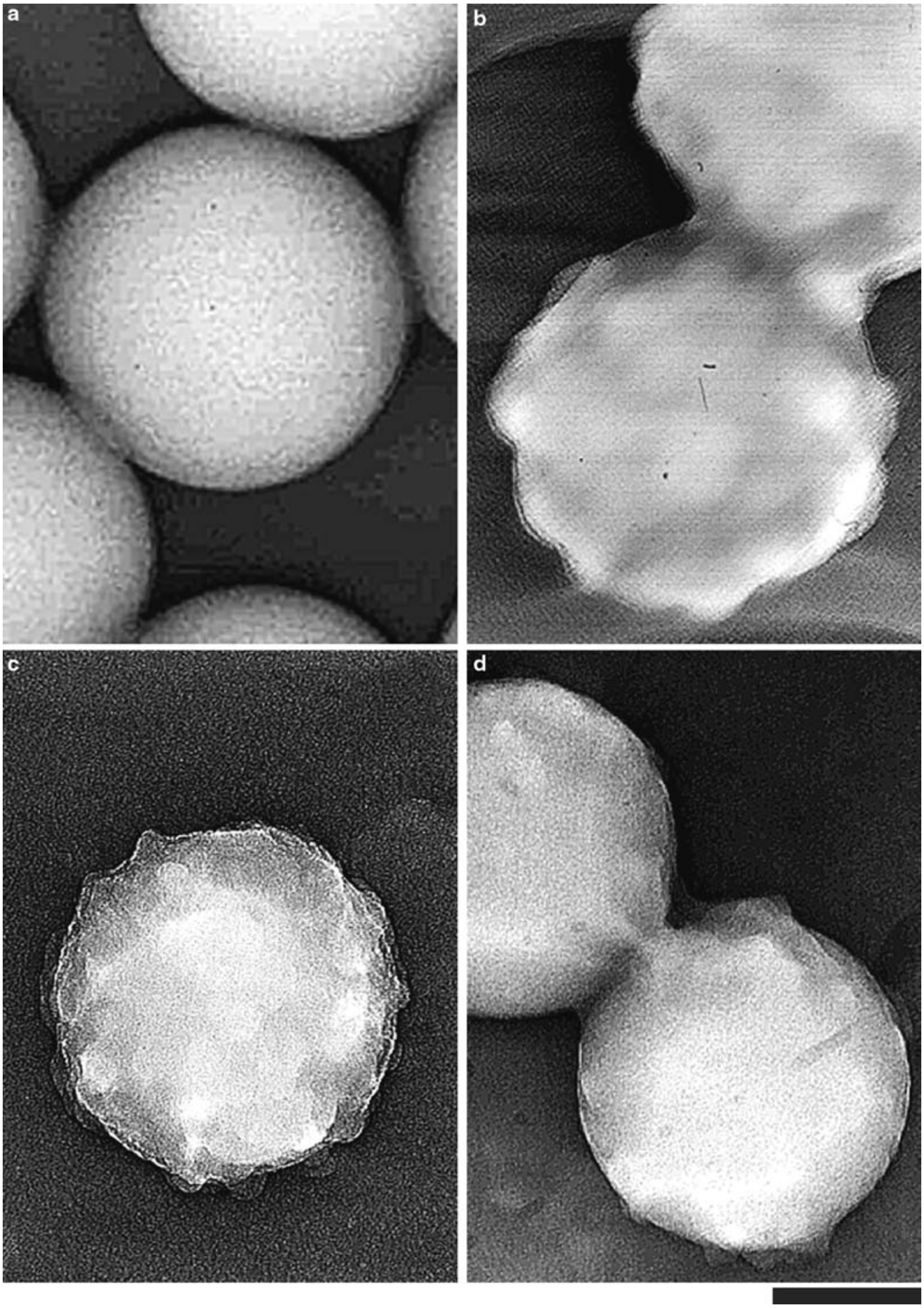


Fig. 8 TEM pictures of D1A19 + C4PVP + PSS complexes. Without resins. [C4PVP·Br] = [NaPSS] = 1x10^{-6} monoM. C4PVP·Br is added first. **a** D1A19 only, **b** two layers, **c** three layers and **d** nine layers. $\phi = 1\text{x}10^{-5}$, length of the *bar* is 100 nm

released simple ions in the course of macroion-colloid complexation. The coexistence of the resins introduces the firm colloid-macroions complex, since the electrostatic shielding effect of the simple ions released in the complexation step between unlikely charged macroions becomes weak.

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