

Polyelectrolytes at Charged Particles: Particle Number Density, Molecular Weight, and Charge Ratio Effects[†]

E. A. O. Reis,[‡] J. C. Caraschi,[§] A. M. Carmona-Ribeiro,[‡] and D. F. S. Petri^{*,‡}

*Instituto de Química, Universidade de São Paulo, P.O. Box 26077, São Paulo, SP, 05513-970 Brazil, and
Departamento de Química, Universidade Estadual de Maringá, CEP 87020-900 Maringá, PR, Brazil*

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The effect of molecular weight, particle number density, and charge ratio on the colloidal behavior of positively charged polystyrene particles (PSA) in the presence of the natural polyanion carboxymethyl cellulose (CMC) was investigated by zeta potential and light scattering measurements. For low ionic strength, a phase diagram with three distinct regimes was proposed. Flocculation is favored for R values close to 1, where R is the ratio of the total negative charge (N_{in}) to the total positive charge (N_{p}). Colloidal stabilization is achieved in the R range of 2.5–200 and with polyelectrolytes chain length smaller than the critical chain length (L_{crit}), which is the contour length corresponding to the particle mean perimeter. For R values larger than 200, isolated particles and/or doublets are present in the dispersion and with polyelectrolytes chain length smaller than L_{crit} , whereas doublets and/or aggregates are observed when the polyelectrolytes chain length is larger than L_{crit} . The effect of the particle number density on the colloidal stabilization was weak. The adsorption behavior of CMC onto PSA particles was not comparable to that of CMC onto PSA films.

Introduction

The adsorption of polyelectrolytes onto solid surfaces plays an important role in the colloidal behavior.¹ Electrosteric stabilization takes place when polyelectrolyte chains adsorb onto surfaces charged with opposite charges. Natural polyelectrolytes have been explored as colloidal stabilizers or flocculant agents because of their low environmental impact and low cost. Chitosan, a natural polycation, has been recently^{2,3} used as flocculant agent for negatively charged polymeric latex particles of variable size. The optimum flocculation concentration was close to charge neutralization and independent of molecular weight or charge density. Chitosan concentrations higher than the optimum led to charge reversal and electrostatic stabilization. Carboxymethyl cellulose (CMC) is a polysaccharide, which can behave like a polyanion under acidic pH. The adsorption of CMC onto inorganic^{4–8} and organic⁹ substrates has been reported in the literature. Hoogendam⁴ and co-workers performed a systematic study on the adsorption of CMC onto TiO₂ and Fe₂O₃ particles under variable ionic strength and pH. They observed that the adsorbed amount of CMC on TiO₂ and Fe₂O₃ increased with salt concentration but decreased with pH, indicating an electrostatic contribution to the adsorbing energy, although no dependence on the degree of substitution was found. The adsorption of CMC onto kaolin,⁸ hydroxyapatite,⁷ and barium sulfate⁶ particles was also driven by electrostatic interaction. The flocculation of negatively charged polystyrene particles occurred at the critical CMC concentration of 0.02%.⁹ This result was supported by the potential-energy calculation as a function of interparticle distance, which involved van der Waals, electrostatic, esteric, and depletion forces.

The complexation between charged particles and semiflexible polyelectrolytes has been studied theoretically.¹⁰ The conformation adopted by the adsorbed polyelectrolyte is a function of polymer charge density, particle size, and charge and ionic strength, so that a phase diagram based on these parameters was proposed. Most experimental reports on the literature^{2,3,9} are devoted to a charge ratio close to 1.0 (charge neutralization), where flocculation is favored. The aim of the present work is to study the effect of a broad range of charge ratios, CMC molecular weights, and particle number densities on the colloidal behavior of positively charged polystyrene particles (PSA), keeping the ionic strength and polyelectrolyte persistence length constant. Moreover, the adsorption behavior of CMC onto PSA particles is compared to that onto PSA flat films.

Experimental Section

Materials. Samples of carboxymethyl cellulose (CMC), sodium salt with nominal mean degree of substitution (DS) of 0.9, molecular weight in the range of 76 000 to 250 000 g/mol (see the samples characteristics in Table 1). Polystyrene amidine (PSA) particles, nominal mean diameter of 74 nm, 7900 charge group (C(NH)NH₂) per particle, area of 2.16 nm² per NH₂ charge group and 7.7×10^5 cm² g⁻¹ specific surface area, were purchased as batch no 800 from Interfacial Dynamics Corporation (Portland, OR). The particle number density (N_{p}) varied from 1.0×10^{15} to 4×10^{13} particles/L. Silicon (100) wafers purchased from Crystec (Berlin, Germany) with native oxide layer approximately 2 nm thick were used as substrates.

Methods. The PSA particles characterization was performed by means of a ZetaPlus- Zeta Potential Analyzer (Brookhaven Instruments Corporation, Holtsville, NY) equipped with a 570 nm laser. The zeta potential value, ξ , was determined from the electrophoretic mobility, μ , in KCl 0.001 mol L⁻¹ and Smoluchowski's equation: $\xi = \mu\eta/\epsilon$, where η is the medium viscosity and ϵ is the medium dielectric constant. The particle diameter D of 83 ± 3 nm was obtained by dynamic light scattering at

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^{*} To whom correspondence should be addressed. E-mail: dfsp@quim.iq.usp.br. Phone: 0055 11 3091 3831. Fax: 0055 11 3818 5579.

[‡] Universidade de São Paulo.

[§] Universidade Estadual de Maringá.

TABLE 1: Characteristics of the CMC Samples with DS 0.9 Used in This Work^a

sample	M_v (g/mol)	N	L_c (nm)	N_{nc}
CMC 76	76005	314	163	283
CMC 90	89300	369	192	332
CMC 114	113570	470	244	423
CMC 250	243180	1005	523	905

^a The average molecular weight M_v was determined by capillary viscometry in NaCl 0.1 mol L⁻¹ solution at 25.0° C, considering the Mark–Houwink–Sakurada constants²¹ as $a = 0.554$ and $k = 0.519 \times 10^{-3}$. N is the mean number of monomer units. L_c is the contour length calculated from the product of N by 0.52 nm. N_{nc} is the mean number of negative charges per chain calculated from the product of N by the DS.

TABLE 2: Total Number of Negative Charge (N_{tn}) Calculated for CMC 76, CMC 90, CMC 114, and CMC 250 at Different Concentrations^a

conc (g/L)	N_{tn} (CMC 76)	N_{tn} (CMC 90)	N_{tn} (CMC 114)	N_{tn} (CMC 250)	R
0.1	2.2×10^{20}	2.2×10^{20}	2.2×10^{20}	2.2×10^{20}	111.4
0.2	4.4×10^{20}	4.4×10^{20}	4.4×10^{20}	4.4×10^{20}	222.8
0.4	8.8×10^{20}	8.8×10^{20}	8.8×10^{20}	8.8×10^{20}	445.6
0.6	1.3×10^{21}	1.3×10^{21}	1.3×10^{21}	1.3×10^{21}	668.4
0.8	1.8×10^{21}	1.8×10^{21}	1.8×10^{21}	1.8×10^{21}	891.1
1.0	2.2×10^{21}	2.2×10^{21}	2.2×10^{21}	2.2×10^{21}	1114

^a The total number of positive charge (N_{tp}) calculated from the product of 7900 charge group (C(NH)NH₂) per particle and 2.5×10^{14} particles/L was constant and amounted to 1.975×10^{18} . The R values were obtained by dividing N_{tn} by N_{tp} .

90.0°. The PSA dispersions were prepared in KCl 0.001 mol L⁻¹ in the concentration range of 1.0×10^{12} to 1.0×10^{15} particles/L. CMC was added to the PSA dispersions in the concentration range of 0.1–1.0 g/L at pH 6.0. At this pH, carboxylate groups are charged. The PSA particles interacted with CMC during 18 h. After this, the PSA dispersions were characterized. The particle size distribution from analysis of quasi elastic light scattering (QELS) data was performed following well-established mathematical techniques.¹¹

PSA solution at the concentration of 10 g/L in toluene was prepared from dried particles. PSA films obtained by spin-coating (Headway Research, Inc., Garland, Texas) presented mean thickness of 45 ± 5 nm, as determined by ellipsometry. Ellipsometric measurements were performed in a vertical computer-controlled DRE-EL02 ellipsometer (Ratzeburg, Germany). The angle of incidence was set to 70.0°, and the wavelength λ of the laser was 632.8 nm. Contact angle measurements were performed in home-built equipment¹² with milli-Q water drops of 8 μ L for the advancing angles and 4 μ L for the receding angles. Adsorption experiments of CMC 250 onto PSA-covered substrates were carried out in an ellipsometric cell at the temperature of 24 ± 1 °C using CMC solutions in the concentration range of 0.002–2.0 g/L. The ellipsometric angles were recorded every 4 s. Changes in their values indicate the adsorption of CMC chains from solution to the PSA-covered substrate.^{13,14}

Results

Dispersion of PSA Particles and CMC with Constant Particle Number Density. The influence of concentration and molecular weight of CMC on the colloidal behavior of PSA particles was investigated in dispersions with constant particle number density N_p of 2.5×10^{14} particles/L. The charge ratio R showed in Table 2 is calculated by dividing the total negative charge (N_{tn}) by the total positive charge (N_{tp}) and seems to be

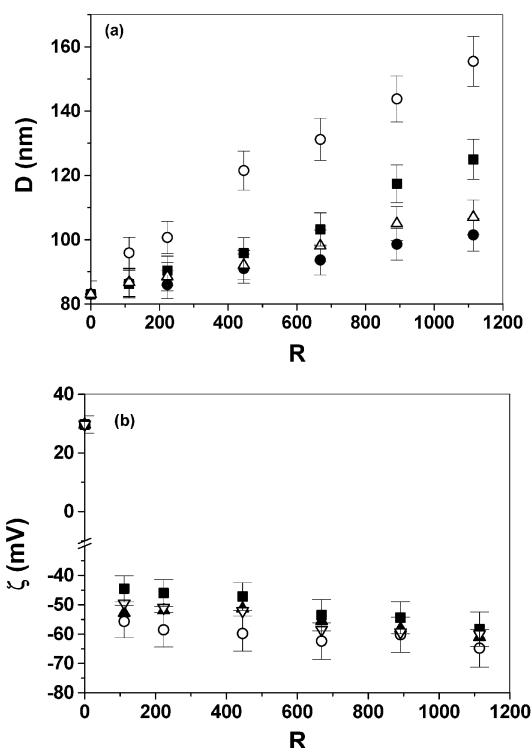


Figure 1. (a) Mean particle diameter D and (b) zeta potential ξ values as a function of the charge ratio R at constant particle number density (N_p) of 2×10^{14} particles/L. (●) CMC 76, (Δ) CMC 90, (■) CMC 114, and (○) CMC 250.

the controlling factor in colloidal systems where the electrostatic attraction is the main driving force.^{2,3} The total number of positive charge (N_{tp}) on the particles amounts to 1.975×10^{18} /L (=7900 charges per particle $\times 2.5 \times 10^{14}$ particles/L). Considering the Avogadro's constant, the number of total negative charge per liter of dispersion (N_{tn}) was calculated for CMC samples at different concentrations as shown in Table 2. The N_{tn} values do not depend on the molecular weight and show that under these conditions there is always charge overcompensation. Figure 1a shows the dependence of mean diameter D on the R values for different CMC molecular weights. Changes in the mean size upon adsorption might indicate colloidal stabilization or aggregation. For R values lower than 222.8, a maximum increase in D of 17 nm (21% of the original size) is observed just for the highest molecular weight (250 kg/mol). In the R range of 445.6 and 668.4, D increases up to 10% when the molecular weight of CMC does not exceed a value close to 114 kg/mol. Therefore, the particles stabilization is a process dependent on R , but also on a critical chain length. Above it, the increase in D reaches 34% of the original size, indicating the presence of particle doublets together with single particles. Aggregation due to bridging flocculation seems to be favored also when the R values exceed 891.1. In this case, even with the lowest CMC molecular weight, an increase of 20% in D is measured. The aggregation mechanism might be depicted as bridging flocculation, but it can also take place by the adsorption of CMC onto patches of opposite charges. For low ionic strength, as in this case, mutual repulsion between charged CMC segments can only be compensated by gaining adsorption energy in the first layer and the chains tend to adsorb in a flat conformation.^{15,4} The entropic gain associated with the release of the sodium counterions of the CMC is surely an important contribution to the adsorption energy.¹⁶ The persistence length of 5 nm was found for CMC (DS 0.88),¹⁷ indicating that CMC is a semiflexible polymer. A similar value was also determined

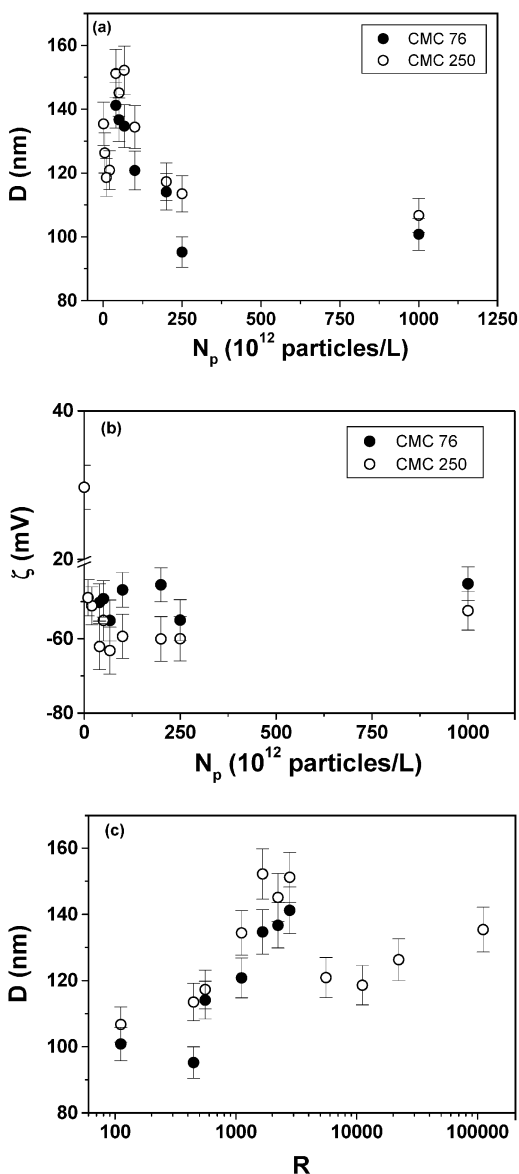


Figure 2. (a) Mean particle diameter D and (b) zeta potential ξ values as a function of the particle number density N_p for (●) CMC 76 and (○) CMC 250. (c) Mean particle diameter D as a function of the charge ratio R .

by Hoogendam et al.¹⁸ The increases observed in D might correspond to a mixture of particle doublets and single particles or they have been caused by tails of the adsorbed CMC chains. The former situation seems to be more reasonable, because the PS latex particles are optically much denser than dangling solvated CMC tails. Bare PS particles have an index of refraction of 1.59 for the working wavelength, whereas CMC presents an index of refraction of 1.50. In water, PS particles are hardly solvated, whereas CMC is highly solvated. Therefore, PS particles contribute much more strongly than CMC tails to the scattered intensity and, therefore, to the mean particle size.

For the PSA latex employed in this work, Interfacial Dynamics Corporation determined the area of 2.16 nm^2 per amidine charge group, which corresponds to a mean distance of 1.47 nm between two charge groups, whereas the length of a cellulose chain unit is 0.52 nm .¹⁹ Estimates about the contour length (the length of the stretched chain) and the mean number of negative charges per chain corresponding to the CMC samples with DS 0.9 used in this work are shown in Table 1. The PSA particles present mean perimeter of 261 nm . If the CMC chains

TABLE 3: Total Number of Negative Charge (N_{tn}) for CMC 76 and CMC 250 at 0.4 g/L , which Was Constant and Amounted to 8.8×10^{20a}

N_{tp}	R	N_{tp}	R	N_{tp}	R
7.9×10^{15}	111392	3.16×10^{17}	2780	1.58×10^{18}	557.0
3.95×10^{16}	22278	3.95×10^{17}	2228	1.98×10^{18}	445.6
7.90×10^{16}	11139	5.30×10^{17}	1663	7.90×10^{18}	111.4
1.58×10^{17}	5567	7.90×10^{17}	1114		

^a The total number of positive charge (N_{tp}) was calculated from the product of 7900 charge group ($\text{C}(\text{NH})\text{NH}_2$) per particle and the particle number density. The R values were obtained by dividing N_{tn} by N_{tp} .

adsorb flat on the particles, one CMC chain might wrap around them until a L_c value close to 260 nm , which corresponds to a molecular weight of 120 kg/mol . For longer chains, part of the segments adsorbs flat, whereas the nonadsorbing segments might dangle in the dispersion. The dangling segments are able to adsorb on a neighbor particle (bridging-flocculation), increasing the mean diameter (Figure 1a). Such a critical molecular weight is evidenced by the D values shown in Figure 1a, as discussed above. The present findings indicate that colloidal stabilization is controlled by charge overcompensation and chain length. It should also be remarked, that the critical chain length L_{crit} corresponds to the mean particle perimeter. Therefore, the larger the particles, the larger the L_{crit} values.

The zeta potential ξ values (Figure 1b) varied from $+(30 \pm 3) \text{ mV}$ (bare particles) to $-(55 \pm 5) \text{ mV}$ upon interacting with CMC. A very weak dependence of zeta potential values on R and on molecular weight is observed. The zeta-potential signal reversal evidences that the driving force for the adsorption of CMC onto PSA is mainly electrostatic in nature and charge overcompensation takes place.

Dispersion of PSA Particles and CMC with Variable Particle Number Density. The effect of particle number density (N_p) on the colloidal stabilization of PSA particles was studied in the range of 1.0×10^{12} to 1.0×10^{15} particles/L, in the presence of CMC 76 and CMC 250 at the concentration of 0.4 g/L . A maximum D value of 152 nm appeared for the N_p range of 3×10^{13} to 7×10^{13} particles/L, indicating the presence of doublets in this condition. For N_p higher or lower than 7×10^{13} particles/L, the mean D values indicate colloidal stabilization (Figure 2a). The particle number density N_p showed no influence on the zeta potential ξ values (Figure 2b). The ξ values measured for dispersions prepared with CMC 250 and CMC 76 amounted to $-57 \pm 5 \text{ mV}$ and $-50 \pm 4 \text{ mV}$, respectively. This small difference might be attributed to dangling CMC segments, as discussed above. The charge ratio varied from 111.4 to 111392, as shown in Table 3 and Figure 2c. Similarly to Figure 2a, a maximum in the mean D values was observed for the R range of 1600–2800, corresponding to the N_p range of 3×10^{13} to 7×10^{13} particles/L. The system might be stabilized at charge ratios higher and lower than this range.

Colloidal Behavior over a Broad Charge Ratio. Ashmore and Hearn^{2,3} proposed that the optimum flocculation for negatively charged particles is achieved close to the charge neutralization by the adsorption of chitosan, a natural polycation. At or close to a 1:1 stoichiometric ratio of positive to negative charge, the optimum flocculation takes place. An excess of positive charge (extra addition of chitosan) led to charge reversal and colloidal stabilization because of electrostatic repulsion. Figure 3, parts a and b, shows for the particle number density of 2×10^{14} particle/L the particles size distribution over the R range of 0.4–2000 for CMC 76 and CMC 250, respectively. The particle size distributions with the corresponding mean size (D) are presented. In the presence of CMC 76 and CMC 250,

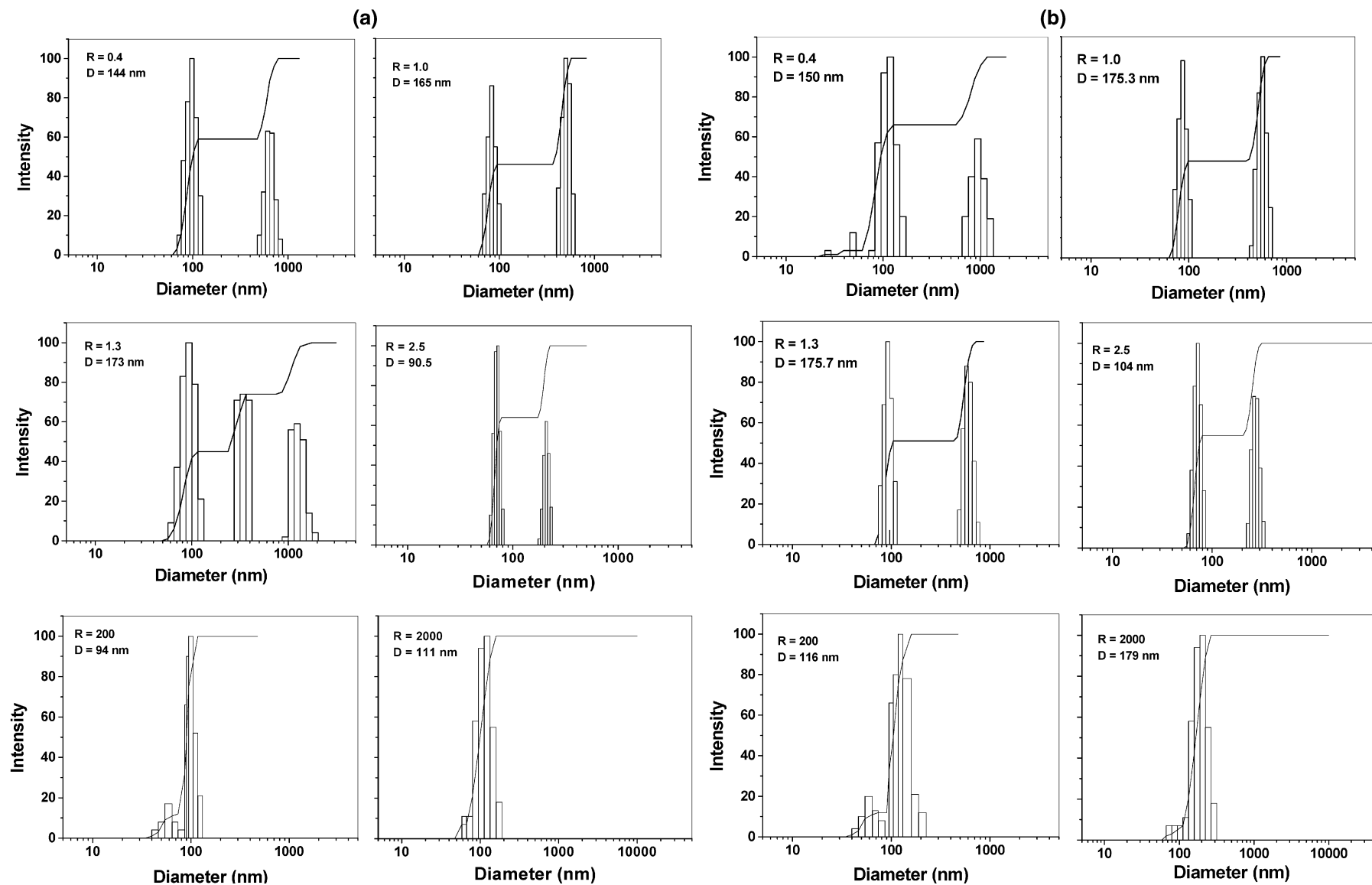


Figure 3. Particle size distribution obtained for R values varying from 0.4 to 2000 in dispersions prepared with N_p of 2×10^{14} particles/L and (a) CMC 76 and (b) CMC 250. R and D represent the charge ratio and mean diameter value, respectively.

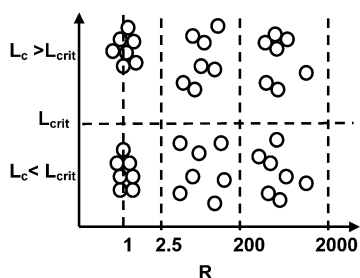


Figure 4. Schematic representation of the colloidal behavior considering the charge ratio R and the contour length L_c . L_{crit} is the critical contour length and correspond to the particle mean perimeter.

the highest D values are observed for R values of 1.0 and 1.3, which corroborate with Ashmore and Hearn findings.^{2,3} The disappearance of large aggregates upon increasing R values in the range of 2.5–2000 is observed only with CMC 76 and is attributed to overcompensation. There is an increase in the mean diameter of about 30 nm for an R value of 2000, indicating the mixture of isolated particles and doublets in the dispersion. The formation of CMC patches on the PSA particles might lead to the occurrence of doublets, because the chains are relatively short for bridging flocculation. In the presence of CMC 250, in the R range of 2.5–200, the mean diameter values are similar to those obtained in the presence of CMC 76 and would correspond to isolated particles and/or doublets. However, for R values larger than 200, the mean size distribution indicates the presence doublets and/or aggregates. This difference in colloidal behavior might be due to bridging flocculation because the CMC 250 chains are much longer than the CMC 76 chains, although patches formation cannot be discarded.

PSA Films. In situ ellipsometric measurements for the adsorption of CMC onto PSA-covered substrates showed no change in the ellipsometric angles over the whole CMC concentration range (0.002–2.0 g/L) in a period of 24 h. It means that the CMC does not adsorb onto the PSA films. PSA films spin-coated on silicon wafers are very hydrophobic,²⁰ with an advancing angle of $(86 \pm 5)^\circ$ measured for water drops. The amidine charge groups, which stem from the polymerization initiator, might be oriented to the hydrophilic silicon wafer during the film formation. If they were exposed to the air, the contact angle should be much smaller than that observed. Carboxymethyl cellulose is a very hydrophilic polymer because of the carboxylate and the hydroxyl groups. The adsorption process results from the competition between attractive interaction and loss of polymer conformational entropy.²¹ If there is no favorable interaction between CMC chains and the substrate, adsorption does not take place. Therefore, the comparison between the adsorption behavior of CMC onto PSA particles and that onto PSA flat films is not feasible.

Conclusions

The colloidal state of charged particles in the presence of oppositely charged polyelectrolytes is mainly controlled by the charge ratio R and polyelectrolyte molecular chain length. A phase diagram with three distinct regimes was proposed, as schematically shown in Figure 4. Flocculation is favored for

values close to 1 whatever the chain length (L_c). Colloidal stabilization is achieved in the R range of 2.5–200 and with polyelectrolytes chain length L_c smaller than critical chain length L_{crit} . For R values larger than 200, isolated particles and/or doublets are present in the dispersion and with polyelectrolytes chain length L_c smaller than L_{crit} , whereas doublets and/or aggregates are observed when the polyelectrolytes chain length L_c is larger than L_{crit} . The phase behavior suggested here considers (i) low ionic strength and (ii) semiflexible polyelectrolytes with constant persistence length. The samples were prepared in 0.001 mol/L KCl, and even after dissolving carboxymethyl cellulose (CMC), released counterions (Na^+) increased the ionic strength up to 0.005 mol/L ($R > 200$). Hoogendam et al.¹⁸ showed that the persistence length of CMC amounts to 5.9 and 5.8 nm for 0.002 and 0.01 mol/L NaCl, respectively.

The adsorption behavior of CMC onto PSA particles could not be compared with that of CMC onto PSA film because, in the latter, the charges are not exposed to the adsorbate.

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