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Effects of divalent salt on adsorption kinetics of a hydrophobically modified polyelectrolyte at the neutral surface–aqueous solution interface

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Abstract

Adsorption of a hydrophobically modified polyelectrolyte on hydrophobized silica surfaces in aqueous divalent salt solutions was studied using an ellipsometric technique. The results indicate three distinct stages in adsorption: a relatively short induction period, a surface accumulation region, and a plateau (quasi equilibrium) region. The induction period remains unchanged with increasing divalent salt concentration. The surface accumulation rate decreases while the equilibrium (quasi) adsorbed amount increases with increasing divalent ionic strength. Divalent salt ($CaCl_2$) produces much higher adsorbed amounts compared to a monovalent salt (NaCl). The analysis of kinetic data (surface accumulation rate) with a transport-limited regime model suggests the reduction of diffusion coefficient (i.e. the increase of size of the adsorbent) with increasing divalent salt concentration. At low concentrations of divalent salt (namely 0.01 M $CaCl_2$), it is possible that the substantially screened individual chains are predominantly adsorbed on the surface. On the contrary, at moderate and high concentrations of divalent salt (namely 0.075 M onwards), polyelectrolyte aggregates or micelles are predominantly adsorbed on the surface.

Keywords: Polyelectrolyte; Adsorption kinetics; Divalent salt

1. Introduction

Surface modification or regulation of surface characteristics using polyelectrolytes has been of prime importance due to the broad variability of their super molecular structures [1,2]. The surface modification improves or modifies surface hydrophilicity, biocompatibility, conductivity, surface roughness, surface hardness, adhesion, lubrication, antistatic, anti-fogging, and anti-fouling properties, etc. Originally, homopolymers were used for such surface modifications. The proliferation of block copolymers offers the possibility of selective adsorption on surfaces. In selective adsorption process, the less soluble blocks adsorb on surfaces from selective solvents while the more soluble blocks (charged) extend into the solution and behave as grafted chains. The adsorption and adsorbed layer characteristics of such diblock polyelectrolytes have been explored theoretically and experimentally to certain extend [3–16], however, very little is known about the kinetics of adsorption and other relevant characteristics [17,18].

The adsorption kinetics and equilibrium properties of neutral diblock copolymers in nonpolar solvents have been investigated in considerable level [19–24]. The process of adsorbed layer formation at a solid interface is essentially considered as two-stage process. Firstly, an initial fast process during which the polymer chains or aggregates diffuse from solution to bare substrate and thereby a monolayer is formed. Secondly, a subsequent slow buildup process where the chains penetrate through the existing monolayer in conjunction with conformational rearrangement of the chains.

The adsorption kinetics and equilibrium properties of neutral-charged diblock polyelectrolytes differ from those of neutral diblock copolymers due to the electrostatic interactions associated with the former ones. The experimental facts on the adsorption of neutral-charged diblock polyelectrolytes are few. Amiel et al. [17] studied the adsorption of a diblock polyelectrolyte, poly(*tert*-butyl polystyrene)-*b*-poly(styrene sodium sulfonate) [PtBPS-*b*-PSS], on a thermally grown silicon oxide surface in presence of NaCl. The kinetic data explained in terms of a two-stage process as in the case of neutral diblock copolymers. Abraham et al. [18] investigated the adsorption of a diblock polyelectrolyte, poly(*tert*-butyl methacrylate)-*b*-poly(glycidylmethacrylate sodium sulfonate) [PtBMA-*b*-PGMAS] on a hydrophobized silica under different NaCl concentrations. Their kinetic data revealed three distinct stages in the

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adsorption process: an induction period, a subsequent fast growth process of polymer layer, and a plateau (equilibrium) region. These three stages were appeared to be influenced by added salt concentration as well as counterion size. These two investigations [17,18] have also shown that the hydrophobic block plays a role in the adsorption of diblock polyelectrolyte on hydrophobized surfaces. Further, without revealing the kinetic aspects of adsorption, Zhang et al. [25] have shown that divalent salt ($CaCl_2$) produces much higher adsorbed amount of PtBPS-*b*-PSS compared to monovalent salt (NaCl). The present investigation addresses the issue of kinetic aspects of adsorption of a diblock polyelectrolyte, PtBMA-*b*-PGMAS, on a hydrophobized substrate under different divalent salt ($CaCl_2$) concentrations. This endeavor aims to improve our current level of understanding of the role of divalent salt in polyelectrolyte adsorption, specifically their effects on adsorption process and adsorbed layer structures at interfaces.

2. Experimental

2.1. Materials

Silicon wafers were obtained from MEMC Electronic Materials Inc., Spartanburg, with a native oxide layer of thickness 2 nm and were used as substrate in the ellipsometric measurements. Calcium chloride, ultra purity grade (99%+) was purchased from Merck. The diblock polyelectrolyte, poly(*tert*-butyl methacrylate)-*b*-poly(glycidylmethacrylate sodium sulfonate) [PtBMA-*b*-PGMAS] was supplied by Prof. Jérôme's research group, University of Liège, Belgium. The synthesis is described elsewhere [16,18]. The molecular weights and molecular weight distribution are: $M_{n(PtBMA)} = 3700$, $M_{n(PGMAS)} = 23\,900$ (g/mol), and $M_w/M_n = 1.10$. PtBMA-*b*-PGMAS exhibits amphiphilic characteristics. The critical micelle concentration (cmc) determined by surface tension measurement is found to be approximately 0.02% w/w.

2.2. Substrate preparation

Silicon wafers cut into rectangular pieces of dimension $2.1 \times 1.5\ cm^2$. The slides were then cleaned with dichloromethane in ultrasonic bath for 15 min. at about 50°C in order to remove possible organic surface contamination. Afterwards, the wafers were rinsed with Milli-pore water. This was followed by a cleaning step in an oxidation bath with a mixture of H_2O_2, NH_3 and water at 75°C for about 30–45 min. After rinsing thoroughly with Milli-pore water, the slides were dried with clean nitrogen. This treatment rendered the surface hydrophilic by generating silanol groups (Si–OH). Hydrophobic slides were prepared by treating hydrophilic slides with 0.2% v/v dichlorodimethyl silane in trichloroethane for 2 h. They were then rinsed several times with trichloroethane and ethanol. Afterwards, the surfaces were kept in absolute ethanol. Before use, they were rinsed with Milli-pore water and dried with purified nitrogen.

In order to check the hydrophobic character of the substrate, the contact angle measurements were conducted using a standard microscope. The contact angle for hydrophobized surfaces was found to be in the range of 85–90°. A phase interference microscope purchased from LOT/ZYGO was used to characterize the sample surfaces with a lateral resolution of approximately 1 μm and a height resolution of 0.6 nm. The magnification used was 100 times. The principle of operation is described elsewhere [26]. The hydrophobized substrate was found to be smooth and the roughness is less than 0.8 nm. The substrates have also been characterized by ellipsometric measurements. The oxide layer thickness (before silane treatment) and the silane layer thickness (after silane treatment) were found to be 1.2 ± 0.2 and 0.6 ± 0.1 nm, respectively. The ellipsometric readings for a given substrate at different locations were found to be very much consistent, therefore both oxide layer as well as silane layer can be considered as smooth and homogenous.

2.3. Ellipsometry

The ellipsometric measurements were performed with home built computer controlled null ellipsometer in a polarizer–compensator–sample–analyser (P–C–S–A) arrangement [19]. A He–Ne laser ($\lambda = 632.8$ nm) was used as light source. The angle of incidence was set to 70.0° to obtain the best sensitivity for our system. Using a motorized linear polarizer (P) and a compensator (C), a state of elliptical polarization is generated, which after reflection becomes linear polarized light. The reflected light is extinguished by an analyzer (A), which is in fact a second polarizer. The intensity of reflected light passing through analyzer is detected by the photomultiplier and the computer control of polarizer and analyzer allows the automated search for the null settings or minimum intensity. At the null settings, the position of polarizer gives the ellipsometric angle Δ and the position of analyzer gives the ellipsometric angle Ψ. The Δ and Ψ contain information about the relative phase shift and the attenuation of component waves perpendicular (s-wave) and parallel (p-wave) to the plane of incidence, respectively. Thus, both the relative phase difference (Δ) and amplitude ratio ($\tan \Psi$) corresponding to the change in reflection are obtained from the ellipsometer readings.

The adsorption experiments were performed in a specially designed trapezoidal teflon cell at room temperature (22 ± 2°C). Initially, the cell containing substrate rigidly mounted to a teflon table was filled with an aqueous solution at a desired salt concentration. The ellipsometric angles Ψ and Δ were measured as a function of time to check the stability of silane layer with and without salt. A pair of ellipsometric angles was recorded at every 21 s. In order to assure homogeneity of the system, a small magnetic stirrer was kept under the substrate-mounting table for gentle stirring. A known volume of concentrated PtBMA-*b*-PGMAS solution (0.344% w/w) was added in order to obtain a final concentration of 100 ppm solution and from that time the changes in Ψ and Δ were recorded as function of time. The measurements were conducted until the equilibrium was reached i.e. until no more changes in ellipsometric angles were detected.

The ellipsometry data were analyzed assuming that the adsorbed polymer molecules form a homogenous isotropic layer on the hydrophobized silicon wafer [18]. In this case, the fundamental equation of ellipsometry is [27]

$$\tan(\Psi)e^{i\Delta} = \frac{R^P}{R^S} = f(n_1, d_1, n_2, d_2, n_3, d_3, N_4, n_0, \phi_0, \lambda) \quad (1)$$

where R^P and R^S are the complex reflectances for the substrate parallel and perpendicular to the plane of incidence, N_4 is the complex refractive index of the silicon substrate ($N_4 = n_4 + ik$), n_1, n_2, n_3 and n_0 are the refractive indexes of the polymer layer, the silane layer, the silicon oxide layer and the surrounding solution respectively, d_1, d_2 and d_3 are the thickness of the polymer, silane and silicon oxide layers, respectively, and ϕ_0 is the angle of incidence and λ is the wavelength of light. In principle, from the ellipsometric angles (Ψ and Δ) measured at null intensity of reflected light, one can obtain the refractive index (n_1) and the adsorbed layer thickness (d_1) of the polymer. Since the adsorption leads to the formation of a thin adsorbed layer and consequently the optical contrast between the adsorbed polymer layer and the solution is small, unique values of refractive index (n_1) and thickness (d_1) of the adsorbed layer could not be found. Instead, a reasonable value for refractive index was guessed and the corresponding thickness (d_1) was calculated [17,18]. The product $n_1 d_1$, which is related to the adsorbed amount of polymer is found to be invariant. The adsorbed amount A (mg/m^2) can be calculated using the following equation [28]

$$A = \frac{d_1(n_1 - n_0)}{(dn/dc)_{\text{polymer}}} \quad (2)$$

To obtain the refractive index of solution (n_0), one has to take into account contributions of all solution components (water, copolymer and salt) [18]

$$n_0 = n_{\text{water}} + \left(\frac{dn}{dc}\right)_{\text{salt}} c_{\text{salt}} + \left(\frac{dn}{dc}\right)_{\text{polymer}} c_{\text{polymer}} \quad (3)$$

where n_{water} is the refractive index of water and $(dn/dc)_x$ is the refractive index increment of species x and c_x is the concentration of species x. The refractive index increments, dn/dc (ml/g) of each species used in this study were determined using a differential refractometer: PtBMA-*b*-PGMAS, 0.1440; CaCl$_2$, 0.177.

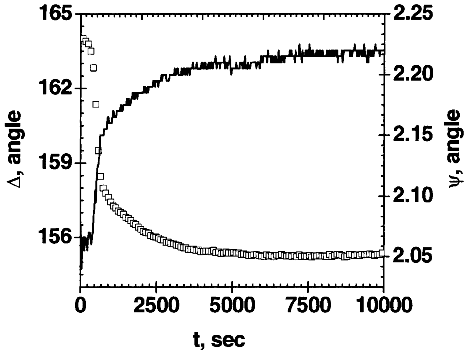

Fig. 1. Measured ellipsometric angles, Δ and Ψ, as a function of time t in presence of 0.01 M CaCl$_2$ over a prolonged period of adsorption. Keys: (□) ellipsometric angle Δ vs. time; (—) ellipsometric angle Ψ vs. time. PtBMA-*b*-PGMAS concentration was 100 ppm.

3. Results and discussion

3.1. Adsorption on hydrophobized surface

There is only very little changes in ellipsometric angles when the polymer solution was injected to the cell containing hydrophobized silica substrate and pure water or 0.001 M CaCl$_2$ solution even after 12 h.[1] When the salt concentration increased to 0.01 M, a significant decrease in Δ (Fig. 1) and a simultaneous increase in Ψ (Fig. 1) occurred after a certain period (induction period), indicating the formation and subsequent growth of polymer layer. The adsorbed polymer amount increased monotonically after a short induction period (ca. 5–6 min) and reached a plateau value as shown in Fig. 2a and b. At 0.075 M CaCl$_2$, the initial short induction period to initialize the surface accumulation remained the same[2] as in the case of 0.01 M CaCl$_2$. However, the differences were apparent in surface accumulation rates (transport limited regime) and equilibrium (quasi) adsorbed amounts. At 0.075 M CaCl$_2$, the surface accumulation rate was found to be relatively low compared to 0.01 M CaCl$_2$ but produced higher equilibrium (quasi) adsorbed amount. Further increase of salt concentrations to 0.15 and 0.5 M CaCl$_2$, marginally altered the initial accumulation rate and equilibrium (quasi) adsorption

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[1] There is a very little change in ellipsometric angles with no added and 0.001 M CaCl$_2$ and the corresponding adsorbed amount is found to be ≤ 0.1 mg/m^2 (obtained when the measured values are averaged over four points). Scatter in data is too high to judge the pattern of adsorption. The adsorbed amount may be very small to be detected by ellipsometry method due to the sparse tethering of diblock polyelectrolyte on the substrate. Since the adsorbed amount values are very little and the initial adsorption region hard to identify, the data are not considered in further kinetic analysis.

[2] In contrast to the experimental observations with CaCl$_2$, in the case of monovalent salt (NaCl) the induction period appears to increase with increasing salt concentration with an exponent of 1/2. The exact reasons for the existence of induction period are not known. Specific experiments, for instance adsorption measurements as a function of polyelectrolyte concentration, temperature etc may reveal the molecular details concerning the induction period. See Ref. [18] for details.

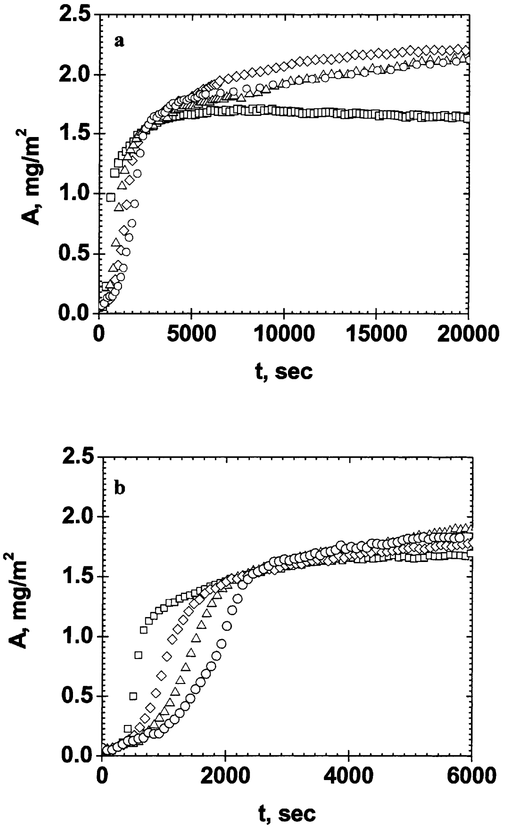

Fig. 2. (a) Adsorsbed amount A of PtBMA-*b*-PGMAS on hydrophobic surface as a function of time t for various salt concentrations over a prolonged period of adsorption. (b) Adsorbed amount A of PtBMA-*b*-PGMAS on hydrophobic surface as a function of time t for various salt concentrations on short time scale. PtBMA-*b*-PGMAS concentration was 100 ppm. Keys: (□) 0.01 M $CaCl_2$; (◇) 0.075 M $CaCl_2$; (Δ) 0.15 M $CaCl_2$ (○) 0.5 M $CaCl_2$.

region. It is also evident that the adsorbed amounts corresponding to quasi equilibrium region are nearly the same from 0.075 to 0.5 M $CaCl_2$ (Fig. 2a).

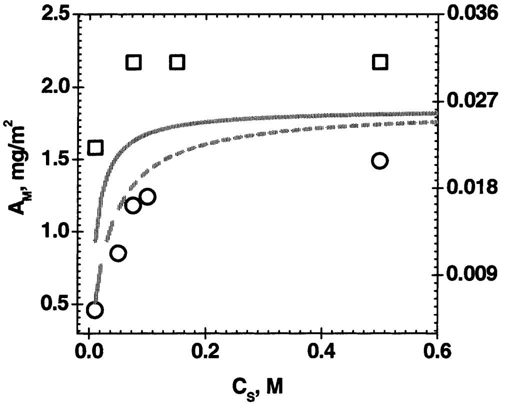

Fig. 3. The plateau value of adsorbed amount A_m (on left Y axis) obtained for various salt concentrations on hydrophobic surface as a function of ionic strength C_s. Keys: (□) $CaCl_2$; (○) NaCl. On right Y axis, the theoretically calculated equivalent surface density Γ is plotted as a function of ionic strength C_s. Keys: Gray solid line is meant for $CaCl_2$; Gray broken line is meant for NaCl. See text for details.

3.2. Effects of counterion valancy and ionic strength on equilibrium (quasi) adsorbed amount

Fig. 3 compares the effects of $CaCl_2$ and NaCl concentrations on equilibrium (quasi) adsorbed amount of PtBMA-*b*-PGMAS on a hydrphobized surface. The divalent salt produces much higher adsorbed amounts. Compared to monovalent salt (NaCl), even at the low concentration of divalent salt $CaCl_2$ (0.01 M) the adsorbed amount is substantial (see Fig. 3). It is interesting to note that, at 0.01 M $CaCl_2$, the adsorbed amount is approximately three times of that measured at 0.01 M NaCl.

The addition of salt, in general, facilitates the adsorption process by two simultaneous effects: (a) firstly, the added salt reduces the electrostatic interaction within and between the polyelectrolyte chains which in effect diminishes the barrier for close approach of chains; (b) secondly, the added salt worsens the solvent quality of polyelectrolyte chains which may promote the adsorption at solid–liquid interface. In addition to these effects, compared to monovalent salts, the divalent salts have an ability to produce intra- and inter-chain association of polyelectrolyte chains. The combination of these effects compensates for the loss of entropy and that produces significant amount of adsorption.

There are various models predicting the effects of added salt on conformational properties of polyelectrolyte chains [21]. According to a length scale based on persistence length [21], the mean square end-to-end distance $\langle R_0^2 \rangle$ is given by:

$$\langle R_0^2 \rangle = 2 l_P a N \tag{4}$$

Here a is the monomer size, N is the number of monomer units and l_P is the total persistence length which is

$$l_P = l_0 + l_E \tag{5}$$

l_0 is the persistence length in the absence of electrostatic interactions and l_E represents electrostatic contribution which is

$$l_E = \frac{l_B}{4 l_{eff}^2} \left(\frac{1}{\kappa} \right)^2 \tag{6}$$

Here l_B is the Bjerrum length, $1/\kappa$ is the Debye length and l_{eff} is the effective distance between charges. For high charge density polyelectrolytes,

$$l_{eff} = z l_B \tag{7}$$

where z is the valance of monomer charge. The size of hydrophilic block (polyelectrolyte block) can be roughly estimated using Eqs. (4)–(7) assuming that l_0 is equal to 1.0 nm [29]. From $\langle R_0^2 \rangle$, one can estimate the equivalent surface density (Γ) by:

$$\Gamma = \frac{1}{(\pi \langle R_0^2 \rangle / 4)} \tag{8}$$

The equivalent surface densities (Γ) calculated for both monovalent and divalent salt are plotted as a function of ionic strength in Fig. 3. At 0.01 M $CaCl_2$, the calculated equivalent surface coverage (Γ) is about 2.0 times higher than at 0.01 M NaCl. With increasing salt concentrations, the Γ values reach a plateau regime and the difference in Γ values between NaCl and $CaCl_2$ narrows down (see Fig. 3). This is because of the fact that the contribution of electrostatic component (l_E) to overall chain dimension decreases dramatically with increasing salt concentration. Thus, the chain becomes neutral at moderate or higher ionic strengths irrespective of the valancy of the salt. Accordingly, both monovalent and divalent salts give nearly the same equivalent surface densities (Γ) at moderate or higher salt concentrations. However, experimentally that is not the case. The measured adsorbed amounts (A_M) in presence of $CaCl_2$ (from 0.075 to 0.5 M) are about 1.5–2.0 times higher than those obtained from similar NaCl concentrations (see Fig. 3). This confirms the ability of divalent salt ions to produce association between polyelectrolyte chains, reducing electrostatic repulsions in away which monovalent ions cannot perform.

Although the above mentioned salt effects (i.e. electrostatic screening effects, worsening the solvent quality, the possibility of formation of aggregates) are more pronounced at higher divalent ionic strengths, it is noticeable that the equilibrium adsorbed amounts are nearly the same from 0.075 to 0.5 M in the case of divalent added salt $CaCl_2$. This can be explained as follows. When the adsorbed amount is sufficiently high, the already adsorbed chains or aggregates offer a steric barrier, which may hinder further adsorption with increasing divalent salt concentration. Such steric barrier due to the presence of short range excluded volume factor of polymer segments could be relevant especially when the surface is over crowded with the adsorbed chains.

The adsorption data presented here is qualitatively in agreement with the currently available literature information dealing with the adsorption of similar diblock polyelectrolyte (PtBPS-*b*-PSS) on a thermally grown silicon oxide surface [25]. It is, however, interesting to note that Zhang et al. [25] have not identified any measurable adsorbed amount below 0.03 M $CaCl_2$. This inconsistency can be attributed to two reasons: (a) firstly, the diblock polyelectrolyte used in their studies has relatively lower hydrophobic-to-charged block ratio; (b) secondly, the substrate used their studies has relatively lower hydrophobicity. This observation once again reaffirms the role of hydrophobic block in promoting the diblock polyelectrolyte adsorption on hydrophobized substrates [17,18].

3.3. Adsorption kinetics: transport limited regime

Let us apply a possible model for polyelectrolyte adsorption assuming that the adsorption process only is controlled by chain or aggregate (inter-polyelectrolyte complex) diffusion near the interface in the initial stages of adsorption. Ward and Tordai [30] proposed that the adsorption of molecules at the interfaces is a diffusion-controlled process. Initially, the surface is bare and the kinetics of adsorption is governed by the diffusion of chains from the bulk of the solution to the surface. Every chain that arrives at the surface is assumed to be adsorbed on the surface. Accordingly, in the initial stages of adsorption, the surface excess $A(t)$ can be related to the apparent diffusion coefficient near the surface, D_{sur} by an equation [30]

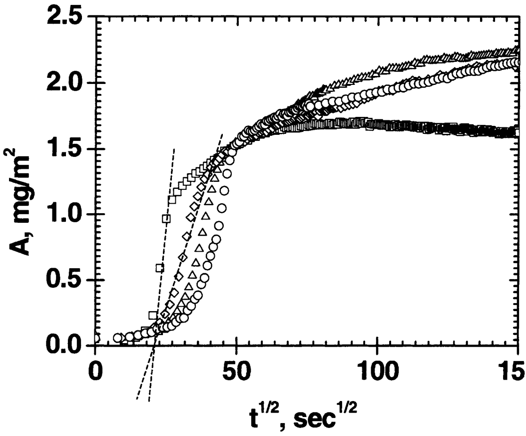

Fig. 4. Adsorbed amount A as a function of square root time $\sqrt{t}$. The broken lines represent fit based on Eq. (9). The PtBMA-*b*-PGMAS concentration was 100 ppm. Keys: (□) 0.01 M $CaCl_2$; (◇) 0.075 M $CaCl_2$; (Δ) 0.15 M $CaCl_2$ (○) 0.5 M $CaCl_2$.

$$A(t) = \frac{2}{\sqrt{\pi}} c_0 \sqrt{D_{sur} t} \tag{9}$$

where c_0 is the polyelectrolyte bulk concentration. In Fig. 4, $A(t)$ is plotted as a function of $\sqrt{t}$ for all $CaCl_2$ concentrations. From the slope of these curves corresponds to the initial period of adsorption (as shown in Fig. 4), the diffusion coefficients (D_{sur}) were determined. The values are plotted as a function of divalent salt concentration in Fig. 5. The diffusion coefficient of screened polyelectrolyte

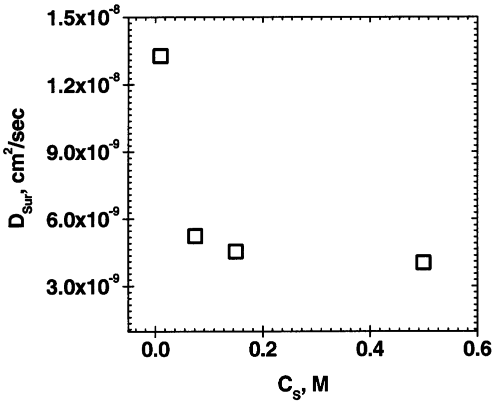

Fig. 5. The diffusion coefficient of polyelectrolyte chains or aggregates near the surface D_{sur} as a function of $CaCl_2$ concentration C_s.

chains or aggregates (D_{sur}) near the surface decreases with increasing divalent salt concentration. At low salt concentration, 0.01 M $CaCl_2$, the diffusion coefficient is nearly 2.5–3 times higher than that observed at 0.075 M $CaCl_2$ concentration. In addition, it can be noticed that the diffusion coefficient of chains or aggregates at 0.075, 0.15 and 0.5 M are nearly the same.

According to Eqs. (4)–(7), the overall dimension of the chains $\langle R_0^2 \rangle$ decreases with increasing salt concentration. Therefore, one may presume an increase in surface diffusion coefficient (D_{sur}) with increasing divalent salt concentration. On the contrary, the diffusion model analysis (Fig. 5) shows the reduction of surface diffusion coefficient (i.e. increase of the size of adsorbents) with increasing divalent salt concentration. This implies the aggregation or association of diblock polyelectrolyte chains with increasing divalent salt concentration.

Polyelectrolyte conformation in solution is known to be influenced by the counterion valancy of added salts [1]. Many authors have shown that divalent counterions cause much stronger polyelectrolyte coil shrinkage than monovalent salts [31–33]. More importantly, it is known also that the presence of divalent ions causes the formation of inter-polyelectrolyte aggregates [34]. Considering the macromolecular characteristics of the polymer used in this study (i.e. hydrophobic–electrolytic diblock), the aggregation or association could occur through two possible mechanisms. Firstly, the divalent cations (Ca^{++}) could promote association of polyelectrolyte blocks leading to the formation of polyelectrolyte aggregates. Secondly, the substantial screening of polyelectrolyte blocks with divalent cations (Ca^{++}) could facilitate the formation of aggregates (micelles) through the physical interactions among hydrophobic blocks. Note that experiments were performed at 100 ppm diblock polyelectrolyte solution, which is about 50% of cmc measured in the absence of salt (see Section 2.1 for details). These two mechanisms, which lead to the formation of polyelectrolyte aggregates or micelles, predominate with increasing divalent salt concentration. Possibly, at low concentration of divalent salt (0.01 M $CaCl_2$), only the shrinkage of individual chains is taking place through the effective screening with divalent cations. However, at moderate and high concentrations of added divalent salt (0.075 M $CaCl_2$ onwards), the shrinkage of individual chains and the association of polyelectrolyte chains (i.e. the formation of polyelectrolyte aggregates or micelles) are taking place simultaneously or the latter processes are predominating. Consequently, at low concentrations of divalent salt (namely 0.01 M $CaCl_2$), the electrostatically screened individual chains are adsorbed on the substrate. On the contrary, at moderate and high concentrations of divalent salt (namely 0.075 M $CaCl_2$ onwards), polyelectrolyte aggregates or micelles rather than individual chains are predominantly adsorbed on the substrate (Fig. 6). Therefore, one may conclude that the adsorption process in presence of divalent salts is a concentration dependent phenomenon. Hence, the adsorbed layer structures under these conditions can be different.

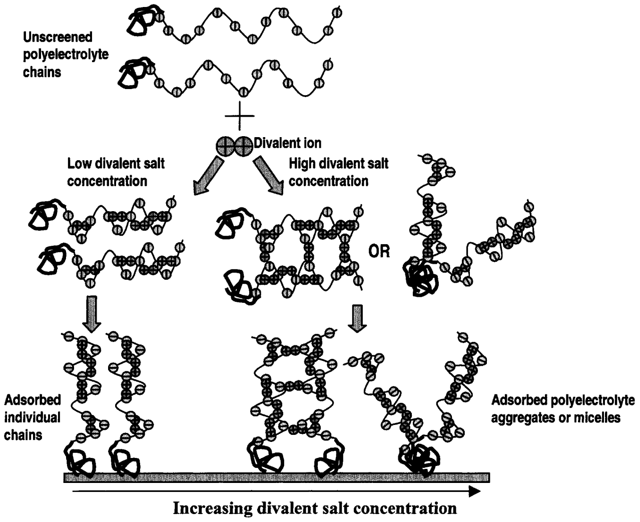

Fig. 6. Schematics show the proposed adsorption mechanisms. At low concentrations of added divalent salt, screened individual chains are adsorbed on the surface. At moderate or high concentrations of added divalent salt, polyelectrolyte aggregates are adsorbed on the surface. See text for details.

4. Conclusions

An ellipsomertic technique was used to study the kinetic aspects of adsorption of a diblock polyelectrolyte [PtBMA-*b*-PGMAS] on a hydrophobized silica substrate under different added divalent salt ($CaCl_2$) concentrations. It has been shown that the adsorption kinetics and adsorbed layer structure of such diblock polyelectrolytes depend on added divalent salt concentrations. The adsorption kinetic data reveal three distinct stages in adsorption process: a relatively short induction period, a surface buildup, and a plateau region. The induction period appears to be independent of added salt concentration, whereas the surface accumulation rate and equilibrium adsorbed amount are found to be influenced by added divalent salt concentration. Compared to a monovalent salt (NaCl), the divalent salt ($CaCl_2$) produces much higher adsorbed amounts. This can be attributed to the ability of the divalent salt ions to produce association between polyelectrolyte chains, reducing electrostatic repulsions in away, which monovalent ions cannot perform. A model calculation based on the dimension of polyelectrolyte chain confirms the proposed mechanism. It is interesting to note that the quasi-equilibrium adsorbed amounts are nearly the same from 0.075 to 0.5 M in the case of divalent added salt. This can be attributed to the steric barrier offered by already adsorbed chains or aggregates. Attempt has been made to explain adsorption kinetics assuming that the adsorption process is governed by the diffusion of chains or aggregates. The analysis suggests, the aggregation or association of polyelectrolyte chains with increasing divalent salt concentration. It is possible that, at low concentrations of divalent salt (namely 0.01 M $CaCl_2$), substantially screened individual chains are adsorbed on the surface. On the other hand, at moderate and high salt concentrations (namely 0.075 M onwards), polyelectrolyte aggregates or micelles are predominantly adsorbed on the surface.

As an effort to corroborate the adsorbed diblock polyelectrolyte layer structures under different added divalent salt concentrations, it would be interesting to take the atomic force microscope (AFM) images of lateral structure under these conditions. In addition, it would be interesting to probe the process of aggregation of diblock polyelectrolytes in solution under different added divalent salt concentrations using various light scattering techniques.

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