Colloid Polym Sci 275:655–660 (1997)

ORIGINAL CONTRIBUTION

V. Shubin
Yu. Samoshina
A. Menshikova
T. Evseeva

Adsorption of cationic polyelectrolyte onto a model carboxylic latex and the influence of adsorbed polycation on the charge regulation at the latex surface

Received: 3 December 1996
Accepted: 20 January 1997

V. Shubin (✉) · Yu. Samoshina
Department of Colloid Chemistry
Chemical Faculty
St. Petersburg University
198904 St. Petersburg, Russia

A. Menshikova · T. Evseeva
Institute of Macromolecular Compounds
of Russian Academy of Science
199004 St. Petersburg, Russia

Abstract Adsorption of a well-characterized cationic polyacrylamide (CPAM) onto the surface of a model colloid (monodisperse polystyrene latex with carboxylic functional groups) was studied over a wide range of pH (4–9) and KCl concentration ($c_s = 10^{-3}$–0.3 M). The surface charge density of the latex particles with and without adsorbed CPAM was also measured over the same range of electrolyte compositions. The adsorbed amount of CPAM increases with increase in c_s and pH. The polyelectrolyte adsorption alters substantially the surface charge density of the latex particles as compared to the polymer-free case. A large overcompensation of the surface charge by the adsorbed polyelectrolyte is established at high c_s and low pH. A qualitative explanation of the observed features is put forward.

Key words Polyelectrolyte – adsorption – latex – surface charge

Introduction

An efficient and successful use of polyelectrolytes in various technological processes such as ore processing, water treatment, papermaking and in the manufacture of different commercial products (cosmetics, paints, foodstuff, etc.) requires a deep understanding of the complex phenomenon of polyelectrolyte adsorption at solid surfaces. An exhaustive overview of theoretical and experimental achievements in the field can be found in a recent book by Fleer et al. [1].

The complexity of the adsorption process, the variety of factors involved, the diversity of real systems imply that not all aspects of polyelectrolyte adsorption are fully explored or well understood. This applies, for instance, to the kinetics of adsorption or to the influence of adsorbing macromolecules on electrochemical equilibrium at the interface. The latter aspect, however, is crucial as the surface charge is one of the major factors determining adsorption of charged macromolecules. In our opinion, further progress in the field depends largely on the availability of experimental results obtained from well-characterized systems and over as wide a range of experimental conditions as possible.

A latex as a substrate for polyelectrolyte adsorption has been chosen in the present study. The choice is mainly due to the fact that latexes are generally considered to be good model colloids as they are highly monodisperse, have particles of a regular spherical shape, can be obtained in a wide range of particle sizes and with different types and quantity of surface functional groups. Different types of latexes have been extensively used also in polyelectrolyte adsorption studies [2–7]. Negatively charged latexes are normally synthesized according to a procedure developed by Furusawa et al. [8]. This yields latexes bearing at least two types of functional groups: sulfate and carboxylate. It is known, however, that sulfate groups undergo hydrolysis,

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which makes the surface composition ill-defined and time-dependent. Moreover, these latexes are believed to be "hairy" in that the functional groups reside at the ends of hydrocarbon chains dangling into solution. All this complicates interpretation of colloid-chemical behavior of sulfolatexes.

In attempt to circumvent the above disadvantages of the polymer colloids, the emulsifier-free polymerization of styrene in the presence of carboxyl-containing initiator was proposed and investigated in details [9]. This method allows a preparation of monodisperse latexes with particle sizes in the range from 200 to 2100 nm, and with surface concentration of carboxyl groups 1.5–4.5 μmol m^{-2}. These latexes are shown to be good model systems for colloidal studies [10, 11] and have been successfully used for immunoassay [12]. In both the above applications they do not exhibit any features which can be attributed to the existence of an extended hydrophilic layer. In the first case this allows to avoid complications in interpretation of electrosurface properties. In the second case – to exclude absorption and screening of small antigenes and, of particular importance, synthetic antigenic determinants. In addition, these latexes (with pH-dependent surface charge) can be considered as a good model of real charge-regulating surfaces (oxides, biocolloids), and possess the advantage of monodispersity, perfect geometrical shape of particles, well-defined chemical nature of functional groups, a total number of which is easily accessible via conventional titration techniques.

In the present paper we report the results of experimental study of (i) adsorption of cationic polyacrylamide (CPAM) on the surface of an oppositely charged carboxylic latex and (ii) surface charge density of the latex particles in the abscence and in the presence of adsorbed polyelectrolyte.

Materials and methods

Chemicals

Styrene was purified by distillation under reduced pressure. 4,4′-azobis (4-cianopentanoic) acid (CPA) (Fig. 1a) was recrystallized from distilled methanol. Cationic polyacrylamide (Fig. 1b) – a copolymer of acrylamide (AM) and (3-methacrylamido) propyl trimethylammonium chloride (MAPTAC) – was obtained from Allied Colloids Ltd (Bradford, U.K.) and was used as supplied. The polymer is not a commercial product and was synthesized for research purposes. The mean molecular weight specified by the manufacturer was $M_w = 10^6$. The fraction of MAPTAC units $\tau = 0.33$ was determined by polyelectrolyte titration [13] and is in perfect match with that reported for the same polymer elsewhere (polymer T in [7]). The polymer stock solutions (2000 ppm) were prepared in freshly distilled water every few days. Water used in all experiments was doubly distilled. Potassium polyvinylsulphate (KPVS) from Wako Pure Chem. Ltd (Japan), was also used as supplied. All other chemicals (KCl, HCl, KOH, NaOH) were of analytical grade and were used without further purification.

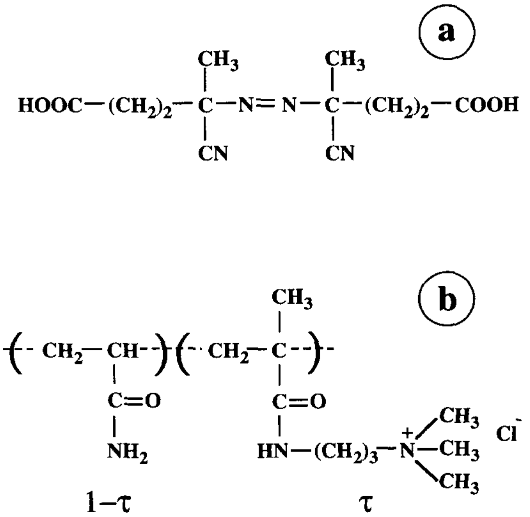

Fig. 1 Chemical structure of initiator of polymerisation used in the synthesis of carboxylated polystyrene latex (**a**) and of cationic polyacrylamide (**b**)

Latex

The latex was prepared by emulsifier-free polymerization of styrene using CPA as initiator. Polymerization was carried out in a four-neck glass reactor equipped with a glass paddle-type stirrer, condenser, nitrogen inlet and temperature controller. 1000 g of water, 70 g of styrene and 2 g of CPA were loaded into the reactor and purged with nitrogen. The pH was adjusted to 11.7 by addition of 0.1 M NaOH and the temperature was increased to 363 K. Continuous stirring at a rate of about 300 rpm was maintained during the polymerization process. After 7 h, a conversion of about 99% is normally reached, as was established gravimetrically. The washing of the latex was achieved via consecutive centrifugation–decantation–resuspension cycles. The latex was first washed a number of times with 10^{-4} M HCl and then with water until a neutral pH was reached. Finally the sample was ultrasonicated and kept in a form of a 10% suspension in water. The analysis of transmission electron micrographs of the sample gave the mean (by weight) diameter of particles

$d = 340$ nm and the polydispersity coefficient $\alpha = 1.029$. The particle size corresponds to a specific surface area $S_0 = 16.8\ \mathrm{m^2\,g^{-1}}$.

Methods

Surface charge density of latex particles was obtained by conventional acid–base potentiometric titration. In the absence of polyelectrolyte, titration was carried out in a "dynamic" regime with an interval of 2–3 min between consecutive titrant additions. In the presence of adsorbing polyelectrolyte, however, a "quasi-static" regime was adopted. Namely, pH was adjusted stepwise and was maintained at a desired level by continuous addition of titrants over a few first minutes. A typical lag between consecutive steps was ca. 10 min. In both titration and adsorption experiments the dilute latex suspension was added slowly to a solution of polyelectrolyte with a desired electrolyte concentration and pH under intensive stirring. The initial concentration of polyelectrolyte was always chosen to be sufficient to ensure a final bulk concentration of not less than 50 ppm. In adsorption experiments pH was kept constant by addition of titrants during the addition of latex. After 2 h of equilibration under continuous stirring, the suspension was centrifuged and supernatant analyzed for residual polyelectrolyte content by polyelectrolyte titration [13] using solution of potassium polyvinyl sulfate as a titrant and toluidine blue as an indicator.

Results and discussion

The surface charge density σ_0 of the latex particles in electrolyte solutions was measured in the pH range from 4 to 9 at background KCl concentrations $c_s = 10^{-3}$–1 M. The σ_0 vs. pH dependencies, presented in Fig. 2, exhibit two characteristic features. Firstly, the surface charge is already measurable at pH 4–4.5 and, secondly, reaches a plateau value ($\sigma_0^{\max}$) at high pH and $c_s \geq 10^{-2}$ M. These features are due to a relatively high dissociation constant of the surface carboxylic groups. As a first approximation, the intrinsic dissociation constant can be assumed to be equal to that of long-chain carboxylic acids (pK_a = 4.8). The obtained value of the total titratable charge $\sigma_0^{\max} = 0.149\ \mathrm{C\,m^{-2}}$ is typical for this type of latex [10] and corresponds to the surface density of functional groups $N_s = 9.3 \times 10^{17}\ \mathrm{m^{-2}}$ or to the area $A = 1.1\ \mathrm{nm^2}$ per group.

In order to describe quantitatively the charge formation at the solid–liquid interface, it is possible to apply the well-established and widely used theoretical approach usually referred to as "ion-complexation" or "site-binding" model [14, 15]. In this model two surface reactions – dissociation of surface functional groups and binding of counterions to the charged sites – are assumed to be responsible for the charge generation. Each of these reactions is characterized by its equilibrium constant (pK_a and pK_K, respectively). Two other model parameters are the surface density of functional groups N_s and a capacitance C_1 of the layer formed by the surface and the plane of location of bound counterions. Of the above four parameters (pK_a, pK_K, N_s, C_1), two are known: pK_a and N_s. To determine the remaining two parameters we used a fit of the theoretical prediction to the $\sigma_0 = f(c_s$, pH) experimental data. An initial estimate for the binding constant was obtained by graphical extrapolation technique (see [16, 17] for details). The values p$K_K = 0.1$ and $C_1 = 2.0\ \mathrm{F\,m^{-2}}$ were found to give the best fit to the experimental data. The above-estimated constants can be used in future in theoretical modelling of adsorption processes on the charge-regulating surface of the latex.

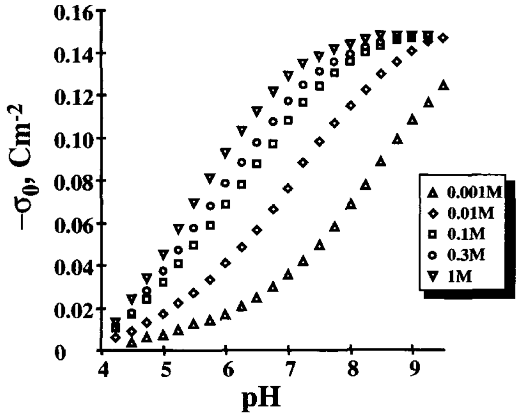

Fig. 2 Surface charge density of the latex particles as a function of pH at different KCl concentrations

Adsorption of CPAM on latex particles was measured over the same range of pH and c_s as the surface charge density except for $c_s = 1$ M. At this ionic strength polyelectrolyte titration did not give reliable results as the indicator color transition could not be clearly detected. The obtained results are summarized in Fig. 3. The general trend of adsorbed amount (Γ) change with c_s is the increase of adsorbed amount with increase of background electrolyte concentration from 10^{-3} to 10^{-1} M and some decrease at higher c_s (see Fig. 3a). Such a trend has been reported in a number of studies [18–21] and can be well rationalized via the analysis of the balance of different factors affecting adsorption, as it has been shown in Ref. [22]. Indeed, the Γ increase with increase of ionic strength can be explained by progressive screening of intralayer electrostatic repulsion. This favors accumulation of

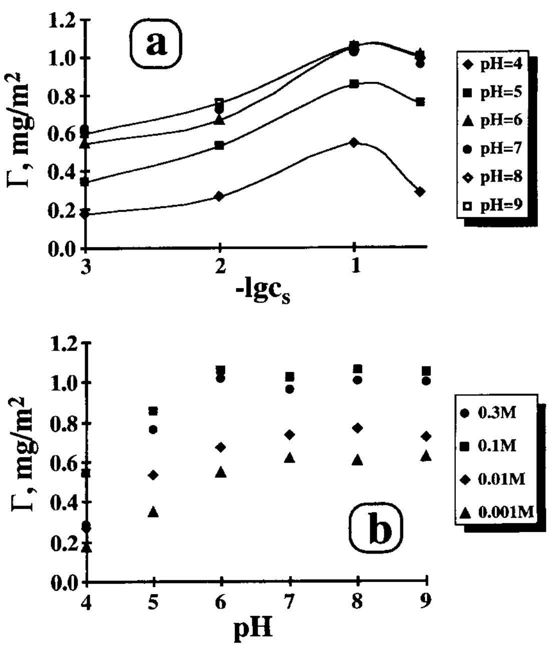

Fig. 3 The amount of CPAM adsorbed on latex particles from electrolyte solutions plotted as a function of concentration of background KCl solution (**a**) and pH of medium (**b**). Otherwise the data on panels **a** and **b** are identical

polyions in adsorbed layer. At the same time, increase in c_s implies a weakening of electrostatic attraction of polyelectrolyte to the surface and also enhances competitive adsorption of counterions. As a result, while at low electrolyte concentrations a rather flat conformation of adsorbed molecules is favorable, at high salt contents formation of large loops and tails is promoted, the number of contacts of the polyelectrolyte molecule with the surface decreases and progressive desorption of macromolecules ensue.

It is noted, that according to Ref. [22], the increase of Γ with c_s suggests nonelectrostatic polyelectrolyte–surface interaction to be operational. This assumption appears to be in contradiction with the absense of polyelectrolyte adsorption on polyestyrene latex, claimed in [7]. However, the latex used in [7] is somewhat different from ours in respect to the chemical surface composition. In our case at $\sigma_0 \ll \sigma_0^{\max}$ the surface bears a large fraction $\theta = 1 - \sigma_0/\sigma_0^{\max}$ of undissociated carboxylic groups which may form hydrogen bonds with acrylamide segments of the polymer in analogy with hydrogen bonding of acrylamide to free hydroxyl groups on silica [23]. Then, the higher θ is (at low pH) the stronger the influence of nonelectrostatic interactions will be. Indeed, at pH ≥ 7 CPAM adsorption increases by a factor of 1.7 upon increase in c_s from 10^{-3} to 10^{-1} M, at pH $= 6$ the factor is 1.9, at pH $= 5$–2.5 and at pH $= 4$–3.2.

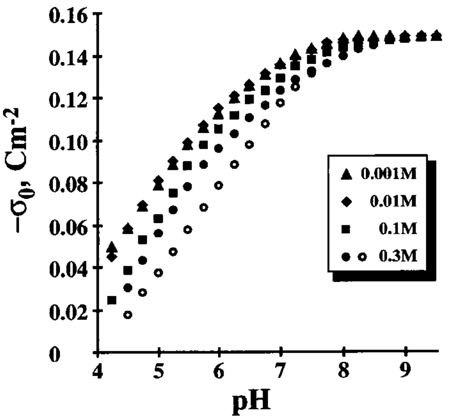

Fig. 4 Surface charge density of latex particles at diffrent KCl concentrations in the presence of adsorbed CPAM (filled symbols). Surface charge measured at $c_s = 0.3$ M in the absence of CPAM is shown for comparison (open symbols)

Upon increase of pH at constant c_s (see Fig. 3b), the adsorbed amount first increases in the pH interval from 4 to 6 and then levels off. This kind of behavior has been reported recently for other systems [9, 21]. The initial Γ increase is naturally explained by the increase of surface charge density with pH. As to the saturation at pH > 6, this can be due to electrostatic intersegmental repulsion which prevents further accumulation of polyions in the adsorbed layer.

In the above discussion, we assumed that the system under consideration is at (or close to) equilibrium. Another possibility, suggested in Ref. [24] and discussed also in Ref. [25], is that polyelectrolyte adsorption in kinetically controlled and adsorbed molecule conformation is close to that in solution prior to adsorption. Then the increase in Γ at constant pH upon change in c_s from 10^{-3} to 10^{-1} M observed in our experiment can be explained by the shrinking of macromolecules so that more of them can accomodate at the surface. The Γ saturation at $c_s =$ const can be simply attributed to a steric overlap of adsorbing molecules.

Now we will consider the results of surface charge measurements in the presence of adsorbed CPAM. The measurements were carried out over the same pH and electrolyte concentration range as adsorption experiments. The experimental σ_0 vs. pH dependencies are presented in Fig. 4. Unlike the case of the bare latex surface (see Fig. 2), the surface charge at constant pH is at its highest at low electrolyte concentrations (10^{-3}–10^{-2} M) and decreases as c_s increases. The last feature indicates clearly a reduction of the number of charged polymer segments in direct contact with the surface upon increase in c_s. The fact that at all electrolyte concentrations adsorption of polyelectrolyte leads to an increase of σ_0 as compared to the bare surface at the same electrolyte composition, means that the polycation is more efficient than small counterions in compensating the surface charge and, thus, in promoting its buildup. This is due to the connectivity of the polyion charges. At the same time, electrostatic attraction of polyelectrolyte to the oppositely charged surface is the main driving force for adsorption, so that polyelectrolyte adsorption on the charge regulating surfaces can be considered as a self-promoting process.

In order to elucidate, at least speculatively, the molecular mechanisms behind the mutual influence of polyelectrolyte adsorption and surface charge formation, we conducted a qualitative analysis of variations in the ratio $r = \sigma^{\mathrm{CPAM}}/\sigma_0$ (where σ^{CPAM} is a charge of adsorbed CPAM molecules per unit area) at varying solution composition (pH, c_s). The ratio r is often referred to as "charge ratio" and can be accessed if the adsorbed amount of well-characterized polyelectrolyte and the surface charge density of substrate with adsorbed layer are available. To date, such experimental data is rather scarce in literature.

As we can see from the Fig. 5b, at the lowest KCl concentration of 10^{-3} M, r is close to unity ($r = 1.2 \pm 0.1$) and does not depend on pH and, thus, on surface charge density. To explain this feature, let us consider first the geometry of an adsorbing CPAM molecule.

The charged groups of the molecule (see Fig. 1b) are located at the end of sidechains of a length of about 0.75 nm. The mean distance between the end groups, for a flatly adsorbed molecule with side chains extending in one direction from the backbone chain, will be about 1.5 nm, as was discussed in [7]. Taking into account flexibility of the side chains, it can reach 2.5 nm. Such a molecule, if lying fairly flat at the surface, can compensate stoichiometrically ($r \approx 1$) the surface charge in a rather wide range of distances (Δ) between underlying charges. In our case the change in σ_0 from 0.035 C m^{-2} (pH = 4) to 0.148 C m^{-2} (pH = 9) corresponds to a Δ change from 2.0 down to 1.2 nm. Further, assuming that the mean distance between the polyelectrolyte charges is about 2.0 nm and taking into account that Debye length at $c_s = 10^{-3}$ M is 10 nm, we can conclude that at this ionic strength every charged segment "feels" ca. 10 neighbors. This results in a rather stiff molecule, with a low level of conformational entropy, which favors a flat conformation of the adsorbed macromolecule. From the plateau value of adsorption measured in 10^{-3} M KCl ($\Gamma = 0.61$ mg m^{-2}) we estimated the concentration of charged segments $c^s_{\mathrm{P+}}$ in the 0.5 nm thick layer next to the surface to be ≈ 3 M and hence it is clear that small counterions can hardly compete with polyelectrolyte at the interface.

Upon increase of ionic strength (up to 10^{-2} M), the screening of intersegmental electrostatic repulsion leads to the increase of the macromolecules's flexibility and, hence, of its conformational entropy. The entropic penalty paid upon adsorption becomes higher which increases probability of formation of larger loops and tails. Since the surface charge density does not change (see Fig. 4), this should result in the increase of Γ and, consequently, r at all pHs. Indeed, this was observed in our experiment (see Figs. 3 and 5). A characteristic feature of r vs. pH dependence at $c_s = 10^{-2}$ M is a monotonic increase of the charge ratio with decrease of pH (at pH = 4, r attains a value of 2). This trend can be again due to the increased flexibility of the molecule and to a more efficient screening of intralayer repulsion. Then on increase of the distance between surface charges, the probability of formation of larger loops and tails will be higher than that of stretching of the molecule as at lower c_s. The charge overcompensation will be also promoted by nonelectrostatic polymer–surface interaction which is expected to be stronger at low pH as was discussed before.

At even higher electrolyte concentration, 0.1 M, a substantial increase of both Γ and r is observed. This feature can be explained by the fact that, while mean distance between polyelectrolyte charges is about 2 nm, the Debye length changes from 3 nm in 0.01 M solution down to 1 nm in 0.1 M KCl. This means that at some intermediate concentration the situation is reached when electrostatic repulsion between the neighboring charges is efficiently screened. This favors formation of an extended adsorbed

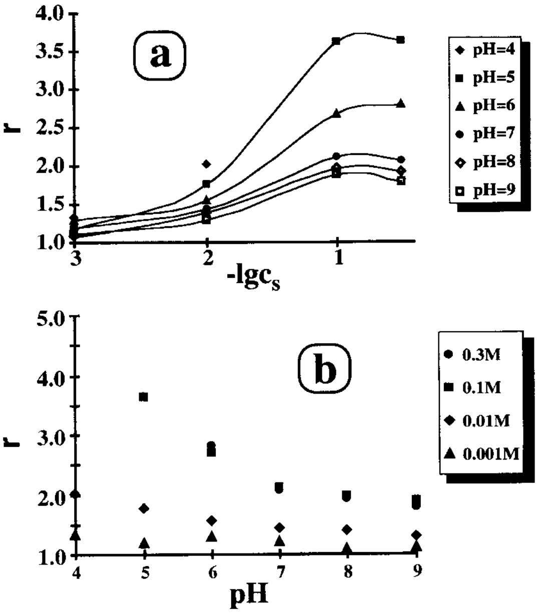

Fig. 5 The ratio of adsorbed CPAM charge to the surface charge plotted in function of KCl concentration (**a**) and pH (**b**). Otherwise the data on panels **a** and **b** are identical

layer with large loops and, if reduction of the number of contacts of polyelectrolyte molecule with the surface is not substantial, larger Γ can be expected. Such an explanation is in line with substantial range of interaction between two mica surfaces bearing highly charged polyelectrolytes adsorbed from 0.1 M salt solutions, as was observed in SFA experiments [26, 27].

At $c_s = 0.3$ M the surface charge density in the presence of the adsorbed layer is close to that for the bare surface (see Fig. 4). This means that at this electrolyte concentration small counterions are already close to polycation in their efficiency in compensating the surface charge and that their competitive adsorption cannot be neglected. Competition for the surface sites will eventually lead to desorption of polyelectrolyte at sufficiently high salt contents. Indeed, at $c_s = 0.3$ M we observe a slight decrease in Γ (see Fig. 3a).

The results presented here can be compared to those reported by Eriksson et al. [7]. They studied adsorption of a range of AM-MAPTAC copolymers with different τ on latexes with known and constant surface charge. Thus, for $c_s = 10^{-2}$ M, $\tau = 0.3$ and $\sigma_0 = 0.087\,\mathrm{C\,m^{-2}}$, $\Gamma \approx 0.55\,\mathrm{mg\,m^{-2}}$ and $r \approx 1.6$ were found. These values are in perfect agreement with our results for corresponding σ_0 (this would be at pH somewhat higher than 5). The trends reported in [7], e.g. increase in Γ and r with increase in c_s, also corroborate our findings.

Conclusions

Thus, the analysis of the combination of experimental data on polyelectrolyte adsorption and substrate surface charge density allows us to rationalize the main features of polyelectrolyte adsorption on a charge-regulating surface from electrolyte solutions, as well as the mutual influence of the adsorption and the surface charge formation as a result of the interplay of different factors governing these processes.

Since the data presented in this paper are obtained on a well-defined system – a well-characterized, constant-charge polyelectrolyte and a model latex with pH-dependent charge – it allows at least a semiquantitative comparison of the experimental results with theoretical predictions within, for instance, a self-consistent mean-field lattice theory for polyelectrolyte adsorption [20, 22, 28, 29], which can be extended to charge-regulating substrates in a straightforward manner [30]. Such a theoretical modelling of real systems is called for as well as a continuation of collection of diverse and reliable experimental data.

Acknowledgments We are grateful to Leif Eriksson for providing us with the polymer sample, for his help with polyelectrolyte titration technique and for fruitful discussions. Per Linse is thanked for his valued comments. V.S. acknowledges financial support by EU-INTAS grant 93-3372-EXT.

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