Journal of Colloid and Interface Science 362 (2011) 439–449

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Interrelations between charging, structure and electrokinetics of nanometric polyelectrolyte films ☆

Jérôme F.L. Duval [a,*,1], David Küttner [b], Mirko Nitschke [b], Carsten Werner [b,c], Ralf Zimmermann [b,*,1]

[a] Laboratoire Environnement et Minéralurgie, Nancy-Université, CNRS UMR 7569, 15 Avenue du Charmois, B.P. 40, 54501 Vandoeuvre-lès-Nancy, Cedex, France
[b] Leibniz Institute of Polymer Research Dresden, Max Bergmann Center of Biomaterials Dresden, Hohe Strasse 6, 01069 Dresden, Germany
[c] University of Toronto, Institute of Biomaterials and Biomedical Engineering, 5 King's College Road, Toronto, Ontario, Canada M5S 3G8

ARTICLE INFO

Article history:
Received 28 April 2011
Accepted 28 June 2011
Available online 7 July 2011

This article is dedicated to Prof. Stanislav S. Dukhin on the occasion of his 80th birthday

Keywords:
Soft surface electrokinetics
Polyelectrolyte layers
Interfacial charge formation
Streaming current
Surface conductivity

ABSTRACT

Streaming current, surface conductivity and swelling data of poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI) thin films are analyzed on the basis of the theory for diffuse soft interfaces (J.F.L. Duval, R. Zimmermann, A.L. Cordeiro, N. Rein, C. Werner, Langmuir 25 (2009) 10691). Focus is put on ways to unravel the electroosmotic and migration contributions of the measured surface conductivity, which is crucial for appropriate electrokinetic analysis of films carrying high densities of dissociable groups. Results demonstrate that the osmotically-driven swelling of the PAA films with increasing pH is accompanied by an increase in diffuseness for the interphasial polymer segment density distribution. This heterogeneity is particularly marked at low ionic strength with a non-monotonous dependence of the streaming current on pH and the presence of a maximum at pH $\sim$ 6.5. The analysis of the PEI films evidences heterogeneous swelling with lowering pH, *i.e.* upon protonation of the amine groups. The characteristic decay length in the interphasial PEI segment density distribution is found to be nearly independent of the pH, which is in line with the moderate swelling determined by ellipsometry. A critical discussion is given on the strengths and limitations of electrokinetics/surface conductivity for quantifying the coupled electrohydrodynamic and structural properties of moderately to highly swollen polyelectrolyte thin films.

1. Introduction

Immobilization of polymers is a widespread method for tailoring the surface properties of bulk materials. This strategy for surface modification takes benefit of the broad spectrum of polymer properties and options for polymer immobilization. Applications of polymer-coated substrates include *e.g.* antimicrobial materials [1], protein-resistant surfaces [2], stimuli-responsive surfaces [3], biosensors [4], liquid displays [5], drug delivery [6] and tissue-engineering scaffolds [7]. The optimization of polymer coatings within the framework of these applications requires refine measurement, analysis and understanding of the physico-chemical properties of the film. These necessarily include the processes governing the formation and screening of the interfacial charge, the mechanisms defining the impact of that charge on the structure or conformation of the immobilized polymers, and the very interactions of the film with ionic components in aqueous environments.

Electrokinetics is a versatile tool for investigating charge formation at interfaces between polymers and aqueous solutions [8–10]. With the formulation of appropriate electric double layer (EDL) models, it is possible to relate the searched interfacial charge of the investigated system to the measured electrokinetic quantity, *i.e.* streaming potential or streaming current. The fundamental equations for the interpretation of electrokinetic measurements on hard (impermeable) surfaces were developed many years ago (see *e.g.* [8,11]) and were proven to provide valuable information on charging, ion-specific interactions, and adsorption or desorption phenomena. In contrast, theories for EDL and electrokinetic phenomena at soft (permeable) surfaces were mainly developed in the last two decades [12–27]. Dukhin was among the first who tackled this challenging task for planar soft surfaces. In his pioneering work [15], he investigated electrokinetic phenomena at

☆ *Foreword:* In February 2011, Stanislav S. Dukhin celebrated his 80th birthday. About 15 years ago, he encouraged and advised the authors of this article to develop a new device – the Microslit Electrokinetic Set-up (MES) – for the simultaneous determination of zeta-potential and surface conductivity at planar surfaces. Until today, the MES has been applied for the extended characterization of the electrohydrodynamic properties of various hard and soft (bio)surfaces. Stanislav Dukhin continuously supported those activities by developing new theories and by numerous valuable discussions of the experimental results. He continues to actively contribute to the progress in the field of soft surface electrokinetics. With this article, the authors would like to express their gratitude for the privilege of his most fruitful and inspiring collaboration over many years.

* Corresponding authors. Fax: +33 3 83 59 62 55 (J.F.L. Duval), +49 351 4658 533 (R. Zimmermann).

E-mail addresses: jerome.duval@ensg.inpl-nancy.fr (J.F.L. Duval), zimmermn@ipfdd.de (R. Zimmermann).

[1] These authors equally contributed to this work.

0021-9797/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2011.06.063

adsorbed neutral polymer phase with evenly distributed segments. Donath and Voigth developed a model for the streaming potential/streaming current and surface conductivity of hard surfaces covered by a charged, ion-permeable polymer layer [17]. Later, Ohshima and Kondo [18] presented a theory within Debye-Hückel approximation for quantifying streaming potential/streaming current and electroosmotic flow at soft surfaces in a microslit channel. This theory introduced two essential parameters for adequate soft surface electrokinetic modeling, namely the volume density of charges carried by the film and the hydrodynamic film softness that reflects the propensity of solvent flow penetration within the layer. The impacts of porosity and specific ion interactions on electrokinetics of hydrogels were further investigated by Starov and Solomentsev [19,20] who underlined the importance of considering internal flow in case of highly porous layers [19].

The theories mentioned above [15–20] differ according to their degree of sophistication in formulating electrostatic and hydrodynamic flow field distributions at soft interfaces. They provide various options, often valid within limited range of layer thickness, charge density or electrolyte concentration, for the derivation of the key electrohydrodynamic properties of hydrogel film from measured streaming current or streaming potential data. In an effort to further constrain electrokinetic data modeling, Dukhin et al. suggested an alternative approach for the characterization of soft polymer layers [21]. The proposed methodology [21] is based on surface conductivity measurements and allows for the determination of the charge density in homogeneous polymer layers. In this theory [21], he provided analytical expressions for evaluating Donnan and surface potential at any degree of ionization for the dissociable groups located in the film. Dukhin et al. extended their work with a generalization of the equations for Donnan potential and surface conductivity in case of non-uniform segment distribution [22]. In the latter paper, the limitations of traditional electrokinetics were extensively discussed for interfaces between polyelectrolyte layers and aqueous solutions. Following earlier work on electrokinetics of micrometer-thick hydrogels [23–25], Duval et al. recently provided a generalized theory for consistent evaluation of streaming current and surface conductivity of soft polymer films [26,27]. The proposed formalism is applicable for any segment distribution, density of charges in the soft surface layer [26], film thickness and electrolyte concentration. On the basis of streaming current, surface conductivity and swelling measurements collected over a broad range of pH, salt concentration or temperature, it was demonstrated how confrontation between experiment and theory may provide insights into the charging, hydrodynamic and structural properties of uncharged poly(N-isopropylacrylamide)-*co*-*N*-(1-phenylethyl)acrylamide thermoresponsive films [26], and moderately charged poly(N-isopropylacrylamid-*co*-carboxyacrylamid) stimuli-responsive surface layers [27].

In this article, we refine and extend the methodology detailed in [27] for the analysis of charging and structure of highly charged polycationic (poly(acrylic acid), PAA) and polyanionic (poly(ethylene imine), PEI) soft surface layers. For that purpose, the films were covalently attached to hard surfaces using a low-pressure plasma treatment, and were subsequently characterized with streaming current measurements at various pH and salt concentrations (0.1–10 mM KCl, pH 2.5–10). The study was complemented by measurements of surface conductivity and pH-dependent swelling. Based on this set of data, we consistently estimate the charge densities, characteristic pK values of the functional groups in the film, and the hydrodynamic softness. It is emphasized that this evaluation requires a cautious investigation of the respective migration and electroosmotic components of the surface conductivity for unambiguous determination of the relevant electrostatic and hydrodynamic film properties. In addition, we provide a comprehensive interpretation of the measured dependence of the streaming current and surface conductivity on pH and salt concentration. In particular, for the PAA films, the non-monotonous variation of the streaming current with pH and electrolyte concentration is unambiguously attributed to changes in polymer segment density distribution following heterogeneous swelling of chains from bulk film to outer periphery. For the immobilized PEI, this heterogeneity is shown to hardly depend on pH, in accordance to the limited swelling of the films measured by ellipsometry.

2. Theory

The basics of electrokinetic theory for charged, diffuse (heterogeneous) soft thin-films supported by hard charged surfaces in a symmetrical z:z electrolyte were reported by Duval et al. in [26]. The theory was recently extended to cases of wider practical interest where soft diffuse films carry (single type of) incompletely-dissociated groups in an electrolyte composed of N ions of valence z_i and bulk concentrations c_i ($i = 1, \ldots, N$) [27]. For the sake of completeness and readability, the assumptions underlying the theory are briefly reviewed below. The formalism is straightforwardly extended to account for the concomitant presence of different types of ionizable groups. The nomenclature introduced in [27] is adopted and we consider a hard/soft interface in a rectangular slit channel of width ℓ, length L_o, and height H, where a liquid flows under the action of an applied pressure gradient ΔP. The theory is valid for laminar flow regime, steady-state hydrodynamic and electrostatic fields on the premise that there is no overlap of the soft surface layers within the cell and edge effects are negligible. Besides, we only consider hydrogels of sufficiently high water-content. Under such condition, only the first-order term in the hydrodynamic volume fraction of polymer segments has to be taken into account for evaluating the friction exerted by segments on the flow.

2.1. Hydrodynamics

For typical arrangements of electrokinetic cells, the liquid flow in the channel is parallel to the surface (y dimension). The velocity field, $\upsilon(x)$, then depends on the dimension x perpendicular to the interface according to the generalized Brinkman equation [28,29]:

$$\frac{d^2V(X)}{dX^2} - (\lambda_o H)^2 f(X)V(X) = -1, \qquad (1)$$

where $X = x/H$, $V(X) = \upsilon(X)/\upsilon_o$ with $\upsilon_o = \Delta P H^2/(\eta L_o)$ and η the dynamic viscosity of water. In Eq. (1), f is a function reflecting the (normalized) polymer segment density distribution at the film/solution interphase. Following the arguments in [26] we use the following expression for f:

$$f(x) = \frac{\omega}{2}\left(1 - \tanh\left(\frac{x-d}{\alpha}\right)\right). \qquad (2)$$

The parameter α corresponds to the characteristic decay length for the segment distribution at the film/solution interphase [26,27]. The scalar quantity ω ensures that the total number of polymer segments within the soft layer remains constant irrespective of the segment distribution [26]. The factor $(\lambda_o H)^2 f(X)$ in Eq. (1) determines the position-dependent friction exerted by the polymer segments on the fluid flow. The quantity λ_o is the so-called hydrodynamic softness of the film, $1/\lambda_o$ is the Brinkman length that reflects the flow penetration within the thin film in the limit $\alpha \to 0$ and $\omega \to 1$ [27]. The boundaries associated to Eq. (1) are provided by the no-slip condition at the rigid supporting surface (*i.e.* at $X = 0$) and symmetry of the velocity field with respect to $X = 1/2$ [26,27].