Electrokinetics of soft polymeric interphases with layered distribution of anionic and cationic charges

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ABSTRACT

Soft surface coatings attract increasing attention due to the versatile options they provide in numerous applications *e.g.* in the flourishing nanomedicine and nanobiotechnology areas. Optimisation of the performance of such ion- and solvent-permeable polyelectrolytic materials requires a detailed understanding of their electrostatic properties. This task is rendered difficult by the inherent non-uniform distribution of their structural charges. In this article, we review recent advances made in the measurement and theory of the electrokinetics (electrophoresis/streaming current) of soft surface coatings that carry spatially-separated cationic and anionic charges. Examples of such charge-stratified systems are polyelectrolyte-coated particles, polyelectrolyte multilayers, particles with zwitterionic interfacial functionality, microbial cells or hard–soft composite interfaces. It is shown here that the electrokinetic features of such colloidal systems are remarkably different from those of their counterparts with homogeneously distributed cationic and anionic charges. In particular, the interplay between electrostatic and hydrodynamic flow fields developed under electrokinetic conditions in the bulk and interfacial compartments of charge-stratified colloids/films are shown to induce a reversal of their electrokinetic response (electrophoretic mobility/streaming current) that depends on the concentration of monovalent electrolyte in solution. The prerequisites for occurrence of such spectacular behaviour are theoretically identified in terms of the Debye length, the spatial length scales defining charge layering, and the typical length for flow penetration within the colloids/films. Electrophoresis and streaming current results recently reported for poly(amidoamine) carboxylated nanodendrimers, natural rubber colloids and poly(ethyleneimine)-supported lipid bilayers are further discussed to illustrate the generic electrokinetic properties of soft interfaces defined by a given stratification of their anionic and cationic structural charges.

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1. Introduction

Soft particulate or planar interfaces consist partly or entirely of charged polymer materials that are permeable to ions and solvent [1–3**]. Representative examples include polyelectrolyte (nano)colloids [4*], core–(bio)shell particles [5*], hydrogels or thin polymer films [6,7], which encompasses systems as diverse as humics [8], bacteriophages [9], bacteria [2], antibacterial coatings [10] or blood cells [11]. Due to the central role they play *e.g.* in naturally-occurring processes [12], in micro/nano-fluidics or medical applications [13,14], soft interfacial systems have now acquired a central place in surface and colloidal science in general, and more specifically in the field of electrokinetics. Since the pioneering work by

Ohshima and Dukhin on electrophoresis of soft particles [1,15] and on streaming potential of soft macroscopic polymer films [16,17], there has been a plethora of published studies that demonstrate the fundamental differences between electrokinetics of soft and hard (impermeable) colloids. In particular, the concept of zeta-potential, which is applicable for hard surfaces, loses its physical meaning for soft interfaces where applied or electrokinetically-induced flow penetrates to an extent that invalidates any *a priori* identification of slip plane location [2,3**]. Depending on the medium salinity conditions, the electric double layer may further reside deep inside soft colloids and is no longer exclusively confined to the external solution side of the colloid/electrolyte interphase. For this specific reason, Duval and collaborators [2,3**] argued that electrokinetics may be considered as a spatially-resolved technique that is suitable for deciphering the interfacial structural and electrostatic properties of soft materials with, among others, the electric Debye layer thickness as a relevant resolution length scale. Examples include the analysis of thermoresponsive and pH-

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responsive swelling of polymer film [18˙,19˙], or the evaluation of segment density distribution in surface-grafted poly(ethylene oxide) brushes with accuracy better than that reached in neutron reflectivity experiments [20˙]. The implications of the defining features of soft particles/interfaces on their AC/DC electrophoresis [1,2,21], streaming current/potential [3˙˙,22˙] or diffusiophoresis [23], have been extensively detailed both at the theoretical and experimental levels. Among the most important findings, we mention the existence of a finite non-zero plateau value reached by DC electrophoretic mobility under salinity conditions that lead to full screening of electrostatics [1,15], or the presence of maxima in the pH-dependence of streaming current of heterogeneously-swelling thin polymer films [19˙].

Beyond their intrinsic permeability and polyelectrolytic properties, an additional feature of numerous soft particles and thin polymer films is the non-uniform distribution of their anionic and cationic structural charges in the bulk phase and/or at the interphase formed with the outer aqueous solution. Polyelectrolyte multilayers [24], colloids covered with oppositely-charged polymer coatings [25˙˙], F-specific RNA bacteriophages [9], carboxylate-terminated dendrimers [26˙˙], cationic and anionic surfactant assembly [27], or polyelectrolyte–lipid membrane films [28˙˙,29] are all examples of charge-stratified systems which have a layered distribution of structural charges of opposite sign. The current review emphasizes the striking and generic electrokinetic properties of these soft colloids and polymer films. In particular, the origin of the unconventional sign reversal of their electrophoretic mobility and streaming current upon changing the concentration of *monovalent electrolyte* in solution is thoroughly discussed in terms of the key length scales involved in the electrohydrodynamic processes that come into play under lateral flow conditions. Practical cases reported in recent literature are finally discussed in detail to illustrate strategies for evaluation of data on charge-stratified systems and to emphasize the agreement between measurements and predictions from soft surface electrokinetic theory. The situations of interest in this review exclude the well-established cases where shifts of isoelectric points are obtained with changing the concentration of multivalent electrolytes or that of specifically-adsorbing ions [30].

2. Historical overview

Any quantitative interpretation of soft surface electrokinetics requires the evaluation of the equilibrium electrostatic potential profile that develops at the interface with the electrolyte solution. To the best of our knowledge, the earliest attempt to comprehensively rationalize the potential distribution $\psi(x)$ across charge-stratified soft interfaces – with x the coordinate in the direction normal to the surface – was reported by Shinagawa et al. [31˙]. The authors considered the academic situation of a (ion- and water-) planar permeable membrane consisting of an inner cationic layer supporting an outer anionic layer, carrying dissociable basic and acidic groups, respectively. On the basis of the Poisson–Boltzmann equation solved in the quasi-linearization approximation, the authors provided analytical expressions for the outer surface potential ψ^0 of the aforementioned composite membrane (note that in the context of [31˙], IUPAC electrokinetic nomenclature points to the use of the symbol ψ^d, the diffuse layer potential, rather than ψ^0). They observed a strong dependence of the pH value corresponding to $\psi^0 = 0$ (value termed isoelectric point or IEP in Ref. [31˙]) on the concentration of monovalent electrolyte. They further found that the IEP of the membrane was significantly affected upon changing the ratio between densities of acidic and basic groups, and that between the thicknesses of the two constituting soft polymer layers. These results were explained in terms of the penetration depth $1/\kappa$ of the electric double layer in the membrane. That is, Shinagawa et al. argued that the lower the electrolyte concentration, the larger is $1/\kappa$ and thus the stronger is the contribution of the fixed cationic charges embedded in the membrane to the interfacial potential distribution and to ψ^0. In turn, the IEP

increases with decreasing electrolyte concentration because it becomes significantly determined by the protolytic properties of the internal basic functional groups. As recognized by the authors, the electrophoretic mobility μ of permeable particles with charged surface layers is not directly proportional to the surface potential ψ^0. Despite this difficulty, and on the basis of their theoretical conclusions, Shinagawa et al. suggested that the measurement by electrophoresis of a monovalent electrolyte concentration-dependent IEP, viewed as the pH value where $\mu = 0$, was symptomatic of a non-uniform charge distribution at the probed particle surface. Accordingly, they attributed such a surface heterogeneity to guinea-pig polymorphonuclear leucocytes for which the electrophoretic mobility was dependent on NaCl concentration and solution pH [32] in a way similar to that computed for a cationic/anionic bilayer membrane [31˙].

Later, Langlet et al. [33˙] developed a theory for the electrophoresis of charge stratified-colloids that includes an explicit account of the electroosmotic flow. Their formalism was based on the standard set of governing equations for soft particle electrophoresis, modified to include the layered distribution of structural cationic and anionic charges as well as the friction exerted by the polymer chains on lateral flow. The conclusions derived by Langlet et al. basically support those suggested by Shinagawa et al. [31˙] on reversal of particle mobility in monovalent electrolyte solution. The authors further demonstrated that the contribution of the most internal charges to particle mobility is not only dependent on the electric double layer expansion within the particle, but also on the hydrodynamic softness of its interphase. Indeed, the latter determines the thickness of the electrokinetically-active intraparticulate region within which electroosmotic flow takes place. Within the framework of the Debye–Hückel approximation, Langlet et al. derived semi-analytical expressions for the isoelectric point of a charge-stratified colloid composed of a hard core coated by two concentric soft surface layers, both of which contain amphoteric functional groups of different natures. Results clearly highlighted the connection between the particle IEP, key electrohydrodynamic properties of the constituting particle layers (*i.e.* layers thickness, hydrodynamic softness, density and protolytic features of ionogenic groups), and the concentration of monovalent electrolyte in solution. Finally, Langlet et al. commented on the measured electrophoretic properties of (charge-stratified) F-specific RNA bacteriophages that are defined by an outer proteic layer encapsulating an internal RNA component. In particular, their theory could predict semi-quantitatively (i) the deviation between measured IEP and IEP values evaluated from the sole consideration of either the internal RNA or the external proteic phage components, and (ii) the absence of a marked dependence of phage IEP on monovalent salt concentration. The latter finding was shown to originate from the significant flow penetration within the (porous) phage and from the resulting predominant role played by internal RNA in determining particle mobility and IEP.

Very recently, Raafatnia et al. [25˙˙] reported molecular dynamics simulations of the electrophoresis of a negatively charged colloid grafted with positive polyelectrolytes. In agreement with the earlier results by Langlet et al. [33˙], the authors found particle mobility reversal in monovalent electrolyte as a consequence of the layering of positive and negative charges. A further implication is that the mobility reversal may also occur for net-neutral colloids as a consequence of the Debye-length (and flow penetration length)-dependent contribution of each layer to the electrophoretic mobility of the particle as a whole. An additional interesting feature emphasized by Raafatnia et al. [25˙˙] is the agreement between mobility predictions carried out on the basis of mean-field and molecular electrokinetic models. This comparison basically supports the relevant application of the Darcy–Brinkman equation in standard soft surface electrokinetic theories, in line with the prediction by Dukhin et al. [34].

Duval et al. [28˙˙] demonstrated the strong analogy between the electrophoresis of charge-stratified soft particles and the streaming current (I_{str}) of macroscopic soft planar polymer layers. In detail, they developed a theoretical approach for evaluating I_{str} from a proper