

Electrohydrodynamic properties of thermo-responsive thin films

Die Ladungsbildung und Quellung thermisch schaltbarer Hydrogelschichten aus Poly(N-Isopropylacrylamid-co-N-(1-phenylethyl) Acrylamid) mit einer auf Antifouling-Anwendungen in marinen Umgebungen abgestimmten Übergangstemperatur (18 °C in künstlichem Meerwasser) wurden unter Anwendung einer verallgemeinerten Theorie für die Elektrohydrodynamik an quellfähigen Polymergrenzflächen analysiert. Strömungsstrommessungen ober- und unterhalb der Übergangstemperatur (d. h. bei 22 °C bzw. 4 °C) in KCl-Lösungen mit variiertem pH-Wert und variiertes Ionenstärke haben gezeigt, dass die Ladungsbildung an der Grenzfläche aus der Adsorption von Hydroxid- und Hydroniumionen an den zur Immobilisierung des Hydrogels auf dem Substrat verwendeten Teflon®-AF-Schichten resultiert. Die Höhe des tangential zur Oberfläche verlaufenden Strömungsstroms wurde stark durch den temperaturabhängigen Quellungsgrad des Hydrogels bestimmt. Die Abhängigkeit des Strömungsstroms von der Ladung am Substrat und der Quellung der Hydrogelschichten konnte mit Hilfe der Theorie im gesamten pH-Bereich und über den Bereich von drei Größenordnungen der Ionenstärke reproduziert werden. Die umfassende Analyse der Daten hat gezeigt, dass die Polymersegmente bei beiden Temperaturen homogen in der Hydrogelschicht verteilt sind, d. h. die Schicht bei Temperaturänderung von 22 °C auf 4 °C homogen quillt.

Introduction

Hard and soft polymer coatings are used in widespread applications such as biosensors [1], tissue engineering scaffolds [2], microfluidic [3], and drug delivery systems [4]. Within the field of polymer surface engineering, stimuli-responsive polymers are of especially high interest since the properties of the polymer can be changed by an external trigger [5]. The most studied stimuli-responsive polymer is poly(*N*-isopropylacrylamide) (PNIPAAm) [6]. PNIPAAm undergoes a sharp temperature-induced coil to globule transition at 32 °C in water. The transition temperature of PNIPAAm can be tuned by various means via, e. g. copolymerization with hydrophilic or hydrophobic comonomers [7]. The structural transitions observed at the lower critical solution temperature (LCST) can be explained by the critical balance between hydrogen bonding and hydrophobic dehydration [6]. In many of the aforementioned applications, polymer films supported by a rigid substrate are in contact with aqueous solutions [1-4]. The formation of an interfacial electric charge and the occurrence of ion specific phenomena then often determine the electrostatic properties of the polymer/solution interface.

It is widely accepted that electrokinetic measurements are useful for investigating charge formation processes at interfaces between polymers and aqueous solutions [8]. The measurements are usually interpreted in terms of electric double layer (EDL) models. In principle, an appropriate EDL model should be able to link the electrostatic properties of the investigated system to a measured electrokinetic quantity in an unambiguous manner. This requires not only a relevant representation for the EDL itself, but also for the hydrodynamic flow and ion mobility along the surface.

Keywords

interfacial charge formation
electrohydrodynamics
diffuse soft interfaces
thermo-responsive hydrogel films

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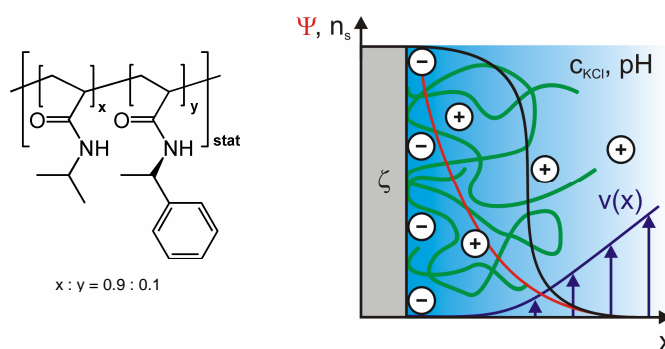
Förderer

European Union, Integrated project
AMBIO

Kooperation

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7569
(supported by the French program
PHYSICHEMBACT, ANR-07-JCJC-
0024-01)

Fig. 1: Chemical structure of the poly(*N*-isopropylacrylamide-co-*N*-(1-phenylethyl) acrylamide) copolymer (left) and schematic representation of the approach used for the numerical analysis of the electrohydrodynamic properties of the hydrogel films (right): The potential of the hard surface Ψ was assumed to be identical to the zeta potential ζ of the Teflon[®] AF film used for the immobilization of the hydrogel. The impact of the segment density n_s on the hydrodynamic flow $v(x)$ was calculated based on the Brinkman equation [9].



We have recently proposed a model for the most general situation, where a diffuse charged gel layer is supported by a charged rigid surface [9]. The theory does not suffer from any restrictions on the magnitude of (i) the volume charge density of the gel, (ii) the electrokinetic potential of the supporting rigid surface and (iii) the thickness of the gel layer (nanometer to micrometer range). It further allows to introduce any diffuse distribution of the polymer segment density from the charged supporting surface to the outer electrolyte medium. In order to evaluate the fundamentals of this model, streaming current measurements were performed at a Teflon[®] AF surface coated with a poly(*N*-isopropylacrylamide-co-*N*-(1-phenylethyl) acrylamide) (P(NIPAAm-co-PEAAm)) thermo-responsive film. The hydrogel was covalently attached to Teflon[®] AF surfaces using a low pressure plasma treatment [10]. Measurements were carried out over a large range of ionic strength and pH values (ionic strength 0.01-10 mM KCl, pH 2.5-9.5 in 1 mM KCl) at temperatures above and below the LCST of the polymer, i. e. when the gel layer was collapsed and swollen, respectively. The streaming current data were quantitatively analysed using the formalism.

Results and Discussion

Experimental results

To investigate the temperature-dependent charging process of the thermo-responsive hydrogel film supported by a Teflon[®] AF surface, streaming current measurements were performed at 4 °C and 22 °C in 1 mM KCl solution as a function of the solution pH (Fig. 2). At room temperature (22 °C), considerably higher (in magnitude) streaming current versus pressure gradients were measured as compared to the values obtained at lower temperature (4 °C) under similar pH conditions. The isoelectric point (IEP) of the interfacial system Teflon[®] AF/hydrogel/electrolyte solution was found at pH 4.4 and was independent of the temperature of the background electrolyte (KCl). As the hydrogel film bears no ionizable groups in the repeat unit [10] and the streaming current versus pressure gradient strongly depends on the pH of the solution with a resulting IEP of about 4.4, one can conclude that the charging of the interface as a whole (Teflon[®] AF surface/hydrogel film/electrolyte solution) is mainly caused by the adsorption of water ions. Unsymmetrical adsorption of hydroxide and hydronium ions was found to be the origin of surface charge for different polymeric materials without ionizable surface groups, such as fluoropolymer surfaces like Teflon[®] AF [11, 12]. Typically, isoelectric points of about 4 and an almost linear dependence of the zeta potential on the solution pH were reported [11]. In line with these results, the charging of the interface can be attributed to an excess of hydroxide ions at pH > IEP, and to an excess of hydronium ions at pH < IEP, adsorbed onto the Teflon[®] AF surface only and not at the thermo-

responsive film [10, 11]. The slightly higher IEP of pH 4.4 (as compared to 4, which is typically found for polymeric surfaces without ionisable surface groups [12]) may be attributed to the formation of a small number of amino groups during plasma immobilization of the hydrogel.

The excess surface charge caused by the adsorbed water ions at the Teflon[®] AF surface is screened by counter ions in the diffuse part of the electrical double layer that extends within and/or outside the hydrogel film. According to the Gouy-Chapman theory, the extension of the diffuse layer (as subsumed in the Debye screening length) depends on the dielectric constant, ionic strength and absolute temperature of the solution [13]. As the dielectric constant and the absolute temperature of the electrolyte do not significantly change with the experimental conditions of interest, it is verified that the extension of the diffuse layer can be considered similar at 4 °C and 22 °C for given pH and electrolyte concentration. Because the thermo-responsive hydrogel is uncharged, the significant modulation of the streaming current with decreasing temperature is then necessarily connected to different hydrodynamic accessibilities of the ions within the unswollen (22 °C) and swollen (4 °C) hydrogel films in the vicinity of the charged Teflon[®] AF surface.

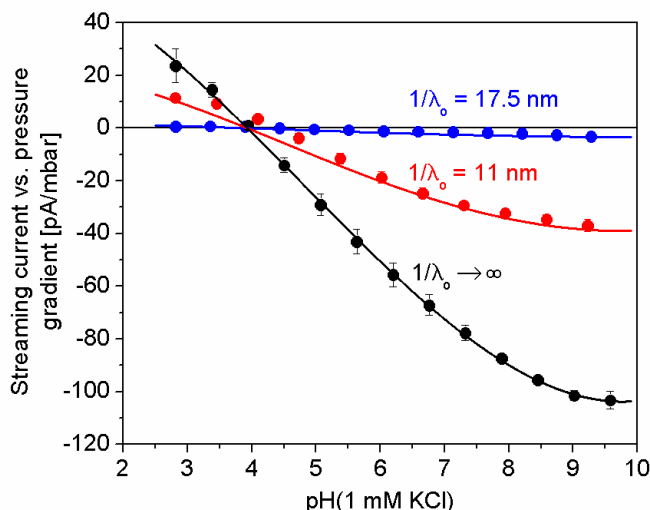
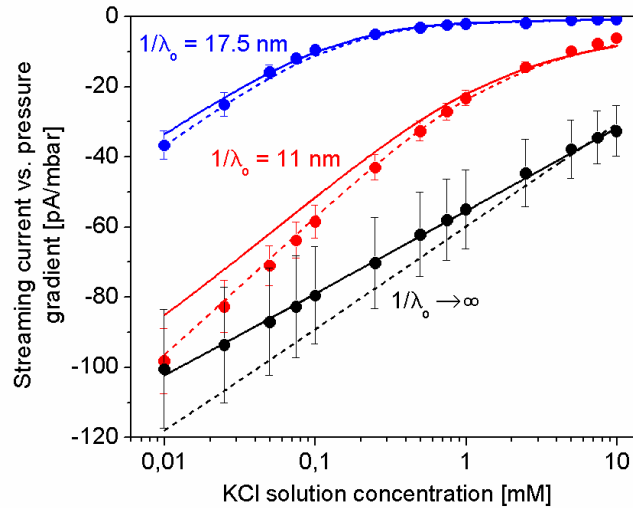


Fig. 2: Streaming current vs. pressure gradient in dependence of the solution pH in 1 mM KCl for the thermo-responsive hydrogel film at 22 °C (red) and 4 °C (blue) and the Teflon[®] AF film in absence of the hydrogel layer at 22 °C (black). The symbols pertain to the experimental data with an accompanying error bar, the solid curves represent theoretical data obtained from rigorous numerical theory. The theoretical data were evaluated with values for the hydrodynamic penetration length $1/\lambda_0$ indicated in the figure.

To further investigate the influence of the hydrogel film on the hydrodynamic ion transport along the Teflon[®] AF surface, we performed additional streaming current measurements at various KCl solution concentrations (0.1 mM-10 mM) and fixed, neutral pH (Fig. 3). For the bare Teflon[®] AF surface and the Teflon[®] AF surface coated with the thermo-responsive film at 4 °C and at 22 °C, the decrease (in magnitude) of the streaming current with increasing ionic strength is in good agreement with the screening of the Teflon[®] AF surface charge by counter ions present in the medium, as expected from the classical Gouy-Chapman theory. In line with the pH-dependent data of Fig. 2, the streaming current vs. pressure gradients measured for the hydrogel films at 4 °C are significantly lower (in magnitude) than those measured for the film at 22 °C over the whole range of KCl concentration examined. At 4 °C, the streaming current strongly decreases with increasing KCl solution concentration until reaching an asymptotic plateau at electrolyte concentrations above 0.5 mM. The presence of such plateau is not detected for the collapsed hydrogel film at 22 °C. In the next section, the electrokinetic data are quantitatively interpreted on the basis of the theoretical formalism extensively discussed in Ref. [9].

Fig. 3: Streaming current vs. pressure gradient in dependence of the KCl solution concentration at neutral pH for the thermo-responsive hydrogel film at 22 °C (red) and 4 °C (blue) and the Teflon® AF film in absence of the hydrogel layer at 22 °C (black). The symbols and solid lines have the same meaning as in Fig. 1. The dashed lines correspond to a slightly increased zeta potential of the bare Teflon® AF surface. The theoretical data were evaluated with values for the hydrodynamic penetration length $1/\lambda_0$ indicated in the figure.



Comparison of experiment with theory

Following the arguments exposed above, the presence of an electric double layer for the interfacial system Teflon® AF/hydrogel film/aqueous solution is mainly due to the presence of an excess charge at the bare Teflon® AF surface only, as a result of asymmetric adsorption of water ions. We thus consider the situation of an uncharged gel layer supported by a charged rigid surface to which we attribute a zeta potential under given pH and ionic strength conditions. In order to reconstruct the pH-dependent data of Fig. 2 ($c = 1$ mM), we first evaluated the dependence of the zeta potential on the solution pH for the bare Teflon® AF surface. To do so, we simply converted the experimental streaming current data collected for Teflon® AF in the absence of the hydrogel film into the zeta potential making appropriate use of the Smoluchowski equation [13]. Then, assuming that this dependence is not affected by the presence of the hydrogel layer, we searched for the values for the hydrodynamic penetration length $1/\lambda_0$ and the diffuseness parameter α [9] that best fit (according to least square method) the experimental data for Teflon® AF surfaces coated with unswollen and swollen hydrogel at 22 °C and 4 °C, respectively. It is stressed here that the temperature-dependent thickness, d , of the films is known from in-situ ellipsometry analysis ($d(22$ °C) = 23 nm and $d(4$ °C) = 70 nm). We found that the experimental data were very well interpreted over the whole range of pH with a homogeneous distribution of the gel layers ($\alpha/d \rightarrow 0$), $1/\lambda_0(22$ °C) = 11 nm, and $1/\lambda_0(4$ °C) = 17.5 nm. A small difference between theory and experiment was observed at pH = 4.4 (IEP) because of the impact of the hydrogel on the IEP of the bare Teflon® AF surface, as discussed above. Unsurprisingly, streaming currents for bare Teflon® AF surface are consistent with theoretical results obtained with $1/\lambda_0 \rightarrow \infty$. The dimensionless number $(\lambda_0 d)^{-1}$ reflects the hydrodynamic penetration length normalized with respect to the gel layer thickness and it may be pictured as a Darcy number for planar soft surfaces. We obtain a $(\lambda_0 d)^{-1}$ of 0.48 and of 0.25 for unswollen and swollen hydrogels, respectively, indicating that the amount of electrokinetically active ions under given pH and ionic strength conditions within the unswollen gel layer is significantly larger than that for its swollen counterpart. This effect is connected to the increased friction exerted by the swollen gel layer on the fluid flow developing in the direction parallel to the Teflon® AF surface. Stated differently, the

effective 'shear plane' is pushed further away from the Teflon[®] AF surface in the case of the swollen hydrogel film, which results in a nearly complete suppression of the streaming current for pH in the range 2.5 to 9.5. This corresponds to a situation where the hydrodynamic screening of the rigid surface by the gel is very important. Using the same strategy as adopted above we attempted a quantitative interpretation of the ionic-strength dependent data shown in Fig. 3 using the model parameters ($1/\lambda_0$, α) obtained from the analysis of the pH dependent data of Fig. 2. This procedure does not require the adjustment of any parameters and provides, within experimental error, a very satisfactory reconstruction of the data over the whole range of ionic strengths, even if 15 % deviations (at most) are observed at very low ionic strengths (0.01 mM) for unswollen hydrogels (22 °C). The remarkable fact that one is able to reproduce experimental data over 7 pH units and ionic strength varying over 3 orders of magnitude by adopting a single value of $1/\lambda_0$ for hydrogels under given temperature conditions, deserves further discussion.

We verified that the minor discrepancy between theory and experiment, particularly observed for unswollen hydrogels (22 °C) and low ionic strengths, is suppressed by considering zeta potential values for bare Teflon[®] AF surfaces slightly higher in magnitude than those given from the Smoluchowski computation (dashed lines in Fig. 3). It should however be noticed that these zeta potentials remain within the experimental error of the measurements. Taking these zeta potential values as boundaries for the electrostatic part of the problem, the reconstruction of the electrokinetic data with the same sets of ($1/\lambda_0$, α) discussed above is excellent for both hydrogels examined over the whole range of ionic strength. At a given temperature, the fit of the ionic strength-dependent data with a unique value of $1/\lambda_0$ is even more remarkable when noticing that theoretical predictions are particularly sensitive to $1/\lambda_0$ variations [9]. The comparison of the resulting fits in Fig. 3 confirms that small variations of the zeta potential do not significantly affect the streaming current, except at low ionic strength for the unswollen gel where hydrodynamic screening of the Teflon[®] AF surface charge is the least, i. e. where electrokinetics is most sensitive to details of inner potential and flow field distributions. The reasons underlying the zeta potential increase for the bare Teflon[®] AF surface following the presence of hydrogel layer are not straightforward and require detailed molecular investigations of the ordering of water molecules and of polymer segment arrangement close to the coated Teflon[®] AF surface. The slight shift of IEP discussed above suggests the presence of a small amount of positive charges at the Teflon[®] AF surface after plasma treatment and the anchoring of the hydrogel. This does not conform to the increase (in magnitude) of the zeta potential for coated Teflon[®] AF surfaces invoked in Fig. 3. We therefore suspect that the slight modification of the zeta potential of Teflon[®] AF as a result of the presence of the hydrogel actually reflects subtle modifications of the Teflon[®] AF double layer characteristics in terms of permittivity, surface charge, shear plane thickness or even propensity of water ions to adsorb onto Teflon[®] AF surface. Facing this basically unsolvable issue, we can not further discuss the physical reasons explaining the modulations of the zeta potential of Teflon[®] AF upon coating with the hydrogel. Even though the reader should be aware of these difficulties, it is important to highlight that the theory in its simplest form does underpin the basic processes explaining the variation of electrokinetic properties of bare Teflon[®] AF after deposition of hydrogels layers of different thickness at its surface.

Finally, we comment on the respective values of $1/\lambda_o$ obtained for swollen and unswollen films at 4 °C and 22 °C, respectively. Within the Debye-Bueche formulation of hydrodynamics in porous media of high water content, the ratio of the hydrodynamic penetration length $1/\lambda_o$ is expected to be equal to the square root of the segment density n_s for evenly distributed hydrogels [14]. For flat surfaces the segment density can be expressed by the layer thickness, d [9]. Using the values obtained by ellipsometry we obtain $(d(4\text{ °C})/d(22\text{ °C}))^{1/2} \sim 1.7$ in excellent agreement with the data of the electrokinetic analysis, $\lambda_o(22\text{ °C})/\lambda_o(4\text{ °C}) \sim 1.6$. This strongly confirms that the uncharged gel layers at 4 °C and 22 °C are homogeneously distributed under the pH and ionic strength conditions examined, i. e. the hydrogel undergoes a homogeneous swelling with temperature decrease. Additionally, it supports that the Debye-Bueche representation of flow within gels of high water content is highly relevant for the system of analysed here.

Conclusions

The charging and swelling of poly(*N*-isopropylacrylamide-*co-N*-(1-phenylethyl) acrylamide) thermo-responsive hydrogel films were analyzed above and below the transition temperature of the copolymer based on the rigorous numerical analysis of streaming current measurements and ellipsometry data. Streaming current measurements at varied pH and ionic strength revealed that the charging of the interface is determined by unsymmetrical adsorption of hydroxide and hydronium ions onto the Teflon[®] AF surface used for the immobilization of the films. It was shown that the recently developed theory for the electrohydrodynamics of diffuse soft interfaces reproduces the streaming current data in the entire pH range used for the measurements and over three orders of magnitude of the ionic strength. In particular, the theory allows addressing quantitatively the extent of hydrodynamic screening of the surface charge carried by the supporting substrate as a result of the presence of the hydrogel film.

It was found that this screening significantly depends on the details of the electrostatic potential profile and of the hydrodynamic flow field distribution in the vicinity of the surface, within and outside the hydrogel layer. Additionally, the ratio between the obtained Brinkman length at 4 °C and 22 °C agrees with a homogeneous distribution of polymer segments and a homogeneous swelling of the hydrogel.

As the settlement and adhesion strength of aquatic microorganisms depends on electrostatics and hydrodynamic characteristics of the interface [15-16], the results will contribute to understand the mechanisms that govern those processes [17].

Furthermore, the introduced methodology provides a versatile tool for unravelling electrohydrodynamic phenomena at composite interfaces formed between hard surfaces and soft polymer coatings in cutting edge technologies as for example in micro- and nanofluidics.

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