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Swelling dynamics of zwitterionic copolymers: The effects of concentration and type of anion and cation

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ABSTRACT

The effect of different salts and their concentration on the swelling of zwitterionic copolymers has been investigated for bulk polymer samples as well as for thin films. Relatively low ratios of the zwitterionic monomer already radically change the swelling properties of the copolymer. Increasing the NaCl concentration results in a significant increase of the swelling, which is indicative of the so-called anti-polyelectrolyte effect. The dynamic swelling experiments on the thin film show that only at high NaCl concentrations, the swelling is limited by solute diffusion. These swelling characteristics are distinctly affected by the type of ions present in the aqueous solution. The changes in maximum swelling degree are most sensitive to the type of anion, where the order of the extent of the effect of the anions follows the Hofmeister lyotropic series. For different cations, smaller changes in maximum swelling degree are found that only partially comply with the Hofmeister series. In most cases similar semi-Fickian swelling behavior is found, except in the case of LiCl concentrations above 0.8 M, where anomalous sigmoidal swelling curves are obtained. This behavior in high LiCl concentrations can be explained by the loss of interchain molecular interactions during swelling. This work provides meaningful insights on the behavior of zwitterionic copolymer films for applications such as membrane filtration that utilize different ions and ionic strengths.

1. Introduction

Zwitterionic polymers are a special class of polymers containing both positive and negative ionic charges.[1] This special characteristic makes this group of polymers an interesting candidate for a variety of applications, ranging from detergents [6], chromatographic processes and biomedical applications [7,8]. Thin layers and brushes of such polymers have been shown to reduce cell adhesion and protein adsorption, which is relevant for different biomedical coatings. Furthermore, zwitterionic layers proved to be successful as antifouling layers in different industrial applications [9–12]. Especially the latter has resulted in an increased attention for zwitterionic polymers. A particular field where zwitterionic polymers show a large potential is membrane technology, where fouling reduction is critical. In membrane systems, the operating costs and energy consumption are negatively affected by fouling. Membrane fouling results in mandatory downtime of the system and degradation of the

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[1] Different definitions (e.g. polyampholytes, polyzwitterions, polybetaines) have been used to differentiate between the nature and distribution of these charges [1–4]. Here, the IUPAC recommended definition is used where unlike polyampholytes, polyzwitterions (or zwitterionic polymers) bear the opposite charges on the same pendant group [5].

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membranes due to harsh chemical cleaning steps required. Fouling resistant membranes, based on zwitterionic polymers, may reduce or even prevent the necessity of cleaning, improving the lifetime and operating costs of membrane processes. Furthermore, in dense polymeric membranes (e.g. desalination membranes) the retention of charged low molecular weight solutes (e.g. salts) is determined by the solution–diffusion model [13,14]. As a result the retention is, amongst others, a function of the polymer charge [15]. The incorporation of both positive and negative charges via polyzwitterions affects the rejection performance of dense membranes.

Another very interesting property that polyzwitterions are known to show is the anti-polyelectrolyte effect: an increase in solubility or swelling of the polymer at increasing salt concentrations [16,17]. In addition to zwitterionic polymers, it was recently shown that cross-linked zwitterionic hydrogels also show this antipolyelectrolyte effect [18]. The reason for this effect is that the addition of ions leads to a screening of the intra- and interchain interactions of the polyzwitterions, resulting in a solubilizing effect. Similar to solubility of proteins and polyelectrolytes, this effect in zwitterionic polymers is dependent on the nature of the specific ions [16,17,19–22]. Already in 1888, Hofmeister arranged ions with respect to their ability to precipitate (salt out) egg white from aqueous solutions [23]. Since then, similar trends have been found in numerous reports, including for zwitterionic polymers. Still the mechanism behind this effect is not very well understood [24]. In the case of zwitterionic polymers, the conformation of the polymer chains was shown to be highly sensitive to the asymmetry of the counterion adsorption [25]. The anti-polyelectrolyte effect has been linked to anti-fouling behavior [26,27], and can be explained by an unfavorable entropy of conformation during protein adsorption onto swollen polymer networks [27]. Other work has also indicated the importance of electrolyte concentration and the nonspecific adsorption onto zwitterionic films [28,29].

Recently a detailed ellipsometric study was performed into the swelling of a thin copolymer film of n-butyl acrylate and SBMA. It was shown that the layer swells significantly in a 1 M NaCl aqueous solution. A key result of this investigation, was that the swelling can cause chain orientation and anisotropy in these thin zwitterionic copolymer films [30]. The focus of that work, however, was the development of an optical model to study the swelling. In this work we present the dynamic swelling behavior of zwitterionic copolymers in different aqueous electrolyte solutions. As both the separation performance in membranes and the anti-fouling properties of zwitterionic polymers are dependent on both ion type and concentration [15,31,32], we examined both the static and dynamic swelling behavior of a zwitterionic copolymer for different electrolytes and concentrations. Since the specific properties of zwitterionic polymers are mainly utilized in thin films or coatings (thickness < 500 nm), we specifically study the effects occurring in thin films using in situ spectroscopic ellipsometry (SE). SE is a precise and non-destructive measurement technique with a high acquisition rate, which allows the study of the behavior of thin films in the nano- to micrometer range [33–35]. With the appropriate experimental setup, in situ swelling experiments can also be performed. The dynamic swelling data are used as input values in the diffusion model developed by Berens and Hopfenberg [36], in order to get information on the kinetic sorption behavior of electrolytes in zwitterionic polymer films. The results presented in this study give a better insight in the dynamic interactions of zwitterionic polymers and different aqueous electrolyte solutions, which can be utilized to improve antifouling properties of coatings or enhance the separation properties of dense membranes.

2. Theory

2.1. Characterization of swelling behavior of thin polymer films

The swelling degree of a polymer film (SD) can be calculated relative to the dry sample thickness as obtained from the in situ SE experiments. This results in film thickness changes over time that yield information on the kinetics of the swelling behavior of polyzwitterions in the presence of electrolyte solutions. However, the kinetics of polymer swelling are complex. During swelling not only Fickian diffusion behavior takes place, but due to stretching of the polymer, several polymer chain relaxational phenomena will occur as well. Non-Fickian swelling dynamics can be empirically described by a model devised by Berens and Hopfenberg [36], which distinguishes between the Fickian and relaxational contributions of swelling and sorption in polymers:

$$SD(t)_{total} = SD(t)_{Fick} + SD(t)_{R} \tag{1}$$

where the ideal Fickian regime is assumed to have a constant diffusion coefficient:

$$SD(t)_{\mathrm{Fick}} = SD_{\mathrm{Fick},\infty}\left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \times e^{\left\{-\frac{D(2n+1)^2\pi^2 t}{L^2}\right\}}\right] \tag{2}$$

where $SD_{\mathrm{Fick},\infty}$ is the total swelling degree due to Fickian diffusion at infinite time, D is the diffusion coefficient (cm^2/s), L is the sample thickness (cm) and t is the time (s). The second part of the diffusion relaxation model (Eq. (1)) describes multiple relaxational contributions ($SD(t)_{\mathrm{R}i}$), and can be quantified according to Eq. (3), with the polymer relaxation time constant $k_{\mathrm{R}i}$ (min^{-1}). Often, it is sufficient to limit the number of relaxational contributions to two.

$$SD(t)_{\mathrm{R}} = \sum_{i=1}^{\infty} SD_{\mathrm{R}i}\left[1 - e^{\{-k_{\mathrm{R}i}t\}}\right] \tag{3}$$

The model is only applicable when the diffusion and relaxational contributions occur at different time scales [37,38]. Since the difference in time scale between Fickian diffusion and polymer relaxations becomes more prominent for thin films, it is assumed that in our case these processes indeed do not overlap. As already pointed out by other researchers [39], the model lacks a physicochemical