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Influence of salt on the solution dynamics of a phosphorylcholine-based polyzwitterion

Zhenyu J. Zhang [a,*], Jeppe Madsen [b], Nicholas J. Warren [b,1], Matthew Mears [a], Graham J. Leggett [b], Andrew L. Lewis [c], Mark Geoghegan [a]

[a] *Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK*
[b] *Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK*
[c] *Biocompatibles UK Ltd., Chapman House, Farnham Business Park, Weydon Lane, Farnham, Surrey GU9 8QL, UK*

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ABSTRACT

The diffusion of a polyzwitterion, poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC), in aqueous solution containing different alkali halides was studied by fluorescence correlation spectroscopy at single molecule level. It was found that the halide anion has a greater effect on the radius of zwitterionic PMPC molecules than alkali cations, which is due to the mechanism by which PMPC molecules interact with the surrounding hydrogen bond network of water molecules and adsorbed ions. With the addition of salt, the size of PMPC remains constant while its diffusion coefficient is reduced slightly, although larger cations (e.g. K^+) result in slightly increased diffusion coefficient for 1 M potassium chloride-based solutions. This enhanced diffusion coefficient is attributed to the decrease in the viscosity of the aqueous solution on the addition of salt. When the counter-ion was varied in potassium-based salts, different effects were observed for different anions, resulting a reduction in the diffusion coefficient as a function of salt concentration. This reduction was modest for KBr, but significant for KI. Overall, no discernible changes were observed as the size of the PMPC coil was varied, except in case of KI for which a significant increase was observed at higher ionic strength. Divalent cations (Ca^{2+} and Mg^{2+}), produced similar effects to those found for monovalent cations. These effects are explained by the interaction of PMPC with the hydrogen bond network of water molecules and with the adsorbed ions.

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1. Introduction

Understanding the dynamics of polyelectrolytes in aqueous solution is challenging because long-range electrostatic interactions between charged groups on the chains play an important role alongside their interactions with mobile counter-ions and solvent molecules [1,2]. The solution properties of polyzwitterions (a type of polymer that contains both positive and negative charged groups in each repeat monomer unit) have been found to exhibit the so-called antipolyelectrolyte effect [3]. In contrast to polyelectrolytes and proteins that tend to precipitate upon the addition of salt, most polyzwitterions become increasingly soluble as salt concentration increases, as attractive dipole–dipole interactions

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[*] Corresponding author at: School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.
E-mail address: z.j.zhang@bham.ac.uk (Z.J. Zhang).
[1] Present address: School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK.

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between the polyzwitterions are screened by electrostatic interactions and counter-ion adsorption. The antipolyelectrolyte effect is anticipated to be dependent upon the chemical structure and composition of the polymer as well as the solution conditions.

The phosphorylcholine (PC) group in phospholipids has inspired the development of a number of materials for the preparation of biomimetic, antifouling materials for bioscience and bioengineering applications. Of these, poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) is perhaps the most promising because it possesses characteristics that make for ideal biomaterial coatings, such as biocompatibility [4,5], colloidal stabilisation [6,7], anti-fouling [8,9], and lubrication properties [10,11]. Since biological fluids are complex solutions containing biomolecules and salts, it is crucial to understand the effect of ions on PMPC to enhance its performance. Such knowledge will also facilitate the understanding of the effect of ions on other PC-based materials, e.g. phospholipid bilayers that serve multiple functional roles in signal transduction, since these are often exposed to physiological environments [12–15].

Different views have been reported in the literature regarding the effect of ions on PMPC in aqueous solution. Both frictional properties and the swelling structure of surface-grown PMPC brushes exposed to NaCl solutions were examined as a function of salt concentration in the region of 0–5 M. It was concluded that the effect of salt on PMPC brushes was negligible [16–18]. Furthermore, the size of free PMPC molecules in aqueous solution was measured using static and dynamic light scattering techniques in concentrations from 0 to 0.5 M, and it was concluded that both the hydrodynamic radius and second virial coefficient of PMPC were independent of salt concentration [19–22]. However, in another study [23], the hydrodynamic volumes of PMPC molecules were analysed using size exclusion chromatography (SEC) in various salt solutions at concentrations from 0 to 0.3 M. It was reported that the concentration of ions has a significant effect on the size of PMPC, and a qualitative correlation between the type and concentration of salts and the solution dynamics of PMPC was established. In recent studies, the friction coefficient between two PC-functionalized surfaces was found to increase with the addition of sodium nitrate ($NaNO_3$), which was attributed to the salting-out of some PC groups at higher salt concentration [10,24].

Fluorescence correlation spectroscopy (FCS) was employed in the present work to investigate the solution dynamics of PMPC in aqueous solutions at the single molecule level to enhance the understanding of the effect of salts on the PC group. Based on a statistical analysis of the fluctuation of the fluorescence signal in a confined volume, FCS is able to observe the dynamics of molecular events, such as diffusion and conformational fluctuations of molecules. Unlike techniques such as light scattering that require relatively high concentration of solute, extremely low concentrations (a few nM) are used in FCS measurements. This eliminates interference due to intermolecular interactions that are dominant at higher concentrations. Consequently only the self-diffusion of single molecules is measured [25–27]. Previous studies have successfully demonstrated the capability and advantage of FCS in examining the solution dynamics of several polyelectrolytes in different aqueous solutions or neutral polymers in polyelectrolyte environments [28–31].

In particular, FCS is used to measure the diffusive motion of individual PMPC chains quantitatively at the single molecule level. Because the viscosities of the corresponding aqueous media in which PMPC molecules were dissolved are known, it is possible to evaluate to what extent the interaction between ions and PMPC contributes to the diffusion and consequently the size of PMPC molecules. The ion-specific effect on the PC group was then assessed resulting in a systematic knowledge of the effect of ions on the solution dynamics of PMPC. This work demonstrates that FCS is a powerful and ultrasensitive single molecule tool that can study the solution dynamics of polyzwitterions under a wide range of experimental conditions.

2. Experimental

2.1. Materials

Rhodamine 6G (99%) was obtained from Acros Organics (Geel, Belgium) and used as received. HPLC grade acetonitrile, diethyl ether, dichloromethane, methanol, tetrahydrofuran, isopropanol, *n*-heptane and regenerated cellulose dialysis membrane (1000 MWCO) were obtained from Fisher Scientific (Loughborough, UK) and used as received. 2-Methacryloyloxyethyl phosphorylcholine (MPC, 99.9%) was donated by Biocompatibles UK Ltd (Farnham, UK) and was used as received. *N*-hydroxyethyl piperazine (98%), 2-bromoisobutyryl bromide (98%), 2-bromoisobutyric acid (98%), anhydrous methanol (MeOH, 99.8%), copper bromide (CuBr, 99.999%), 2,2′-bipyridine (bpy, 99%), lithium chloride (LiCl, ACS reagent grade), sodium chloride (NaCl, ACS reagent grade), potassium chloride (KCl, ACS reagent grade), potassium bromide (KBr, ACS reagent grade), potassium iodide (KI, ACS reagent grade), calcium chloride ($CaCl_2$, ACS reagent grade), and magnesium chloride ($MgCl_2$, ACS reagent grade) were purchased from Sigma-Aldrich (Dorset, UK) and used as received. HPLC grade water (CHROMASOLV, 2.5L) purchased from Sigma-Aldrich was used to prepare polymer solutions.

2.2. Synthesis of rhodamine 6G-labelled PMPC

Rhodamine 6G was derivatized in its 2′ position by direct reaction with *N*-hydroxyethyl piperazine. Subsequent esterification of the hydroxyl-group with 2-bromoisobutyryl anhydride gave a fluorescent 2-bromoisobutyryl ester which was used as a (fluorescent) atom transfer radical polymerization (ATRP) initiator for the controlled polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC). This method of synthesis ensures that each PMPC contained precisely one rhodamine 6G molecule at the terminus of the chain. Details of this procedure can be found in a previous report [32].

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