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Influence of the Hofmeister series of anions on the molecular organization of positively ionized monolayers of a viologen derivative

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Abstract

The effects of the Hofmeister series of ions are ubiquitous in chemistry and biology. In this paper specific ion effects on the surface behavior of a viologen dication, namely 1,1′-dioctadecyl-4,4′-bipyridilium, are shown. Surface pressure and surface potential vs area isotherms were obtained on aqueous subphases containing potassium salts with several representative counterions in the Hofmeister series ($C_6H_5O_7^{3-}$, SO_4^{2-}, HPO_4^{2-}, Cl^-, Br^-, NO_3^-, I^-, and ClO_4^-). The parameters obtained from the compression isotherms (area per molecule, phase transitions, Young modulus, initial surface potential, and variation of the surface potential upon compression) are dependent on the nature of the counterion, indicating ion specificity. Aqueous subphases containing $C_6H_5O_7^{3-}$, SO_4^{2-}, and HPO_4^{2-} anions yield more expanded viologen monolayers and these anions do not effectively penetrate into the monolayer. Brewster angle microscopy was used to map the different phases of the viologen monolayers at the air–water interface. The Langmuir films were also characterized by UV–vis spectroscopy, with quantitative analysis of the reflection spectra supporting an organizational model in which the viologen chromophore undergoes a gradual transition to a more vertical position with respect to the water surface upon compression. A comparison of the tilt angles of the viologen on the different subphases indicates that anions that can more easily penetrate in the monolayer permit the viologen moieties to adopt a slightly more vertical position with respect to the water surface.

Keywords: Hofmeister series; Viologen; Molecular organization; UV–vis reflection spectroscopy; Langmuir films

1. Introduction

The Hofmeister series of ions (Scheme 1) [1,2] was established in 1888 and originates from the ranking of various ions toward their ability to precipitate a mixture of hen egg white proteins. In more recent times, the effects of the Hofmeister series have been extended to account for a wide variety of phenomena, which include protein folding, solubility of salts, electrolyte activities, pH measurements, zeta potentials, buffers, critical micellar concentrations, microemulsions, cloud point of non-ionic surfactants, ion binding to micelles, proteins and membranes, transport across membranes, gel–coagel transitions, molecular forces, colloid stability, etc. [3]. More recently, some papers have illustrated the influence of the Hofmeister series on the organization of ionized monolayers at the air–water interface [4–6]. It is noted at this point, however, that occasionally the order of anions in the series can be slightly different, depending on the phenomenon under examination, and precise details of the interactions between a substrate and ions of the Hofmeister series are not generalised. Thus, the anion series, whose effects are generally more pronounced than those for the cation series, has been ordered in terms of kosmotropes (anions on the left of the series in Scheme 1) and chaotropes (anions on the right). The first ones were believed to be “water structure makers”; they are strongly hydrated, and have stabilizing and salting out effects on proteins and macromolecules. Chaotropes, or water structure breakers, are known to destabilize folded pro-

$$C_6H_5O_7^{3-} < SO_4^{2-} < HPO_4^{2-} < Cl^- < Br^- < NO_3^- < I^- < ClO_4^-$$

Scheme 1. Hofmeister series of anions. According to the literature [7] related to this topic kosmotropic anions are drawn in green while chaotropic ones are in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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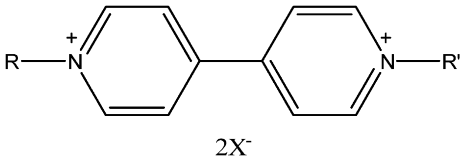
Fig. 1. Chemical structure of a 1, 1′-disubstituted-4, 4′-bipyridilium salt.

teins and give rise to salting-in behavior. Nevertheless, although the terms kosmotropes and chaotropes have been widely employed in the literature, they have been called into question by recent experiments that have shown a negligible effect of the ions on the overall hydrogen bonding of water in bulk solution [7]. Other arguments explain that the Hofmeister series effects rely on the large role played by dispersion forces. Whilst most of the work to date has been of a theoretical nature [2,8,9], new experimental evidence is also contributing to the understanding of these ion-specific effects [10,11].

Viologens, or 1,1′-disubstituted-4,4′bipyridilium salts (Fig. 1), are a source of great contemporary interest. Viologens are electroactive, being stable in at least three different oxidation states, and offer a significant electrochromic response. Viologens have found use in solar energy storage systems, as electron mediators in herbicides, and have been used to fabricate modified electrodes, bioelectronic devices, electrochromic writing paper, and molecular wires [12–19], amongst other applications [20–24]. The properties and consequently applications of viologens are sensitive to a variety of factors, including the nature of anions X^- [12]. In contrast to the large body of published work dealing with the electrochemistry of thin solid films of viologen derivatives [25–33] there is little data available for the detailed organization and properties of amphiphilic viologens arranged in thin solid films together with different counterions X^-. This has motivated us to analyze the influence of the Hofmeister series of anions on the film forming behaviors of a viologen amphiphile, and determine how these anions may affect the organization of the viologen moieties within the Langmuir monolayers. The surface behavior of a viologen derivative, with $R = R' = C_{18}H_{37}$, on several subphases (Scheme 1) has been analyzed. We have investigated the effect of different anions by measuring surface pressure and surface potential vs area per molecule isotherms as well as by Brewster Angle Microscopy. In addition, we have used reflection spectroscopy for the in situ characterization of the monolayers at the air–water interface.

2. Experimental

The films were prepared on a Nima Teflon trough with dimensions 720 × 100 mm^2, which was housed in a constant temperature (20 ± 1 °C) clean room. The surface pressure (π) of the monolayers was measured by a Wilhelmy paper plate pressure sensor. Millipore Milli-Q water (resistivity 18.2 MΩ cm) was used to dissolve the potassium salts with several anions in the Hofmeister series. The salts of highest available purity were purchased from Aldrich. Chloroform was HPLC grade, 99.9%, purchased from Aldrich and used as received, and the ethanol was HPLC grade, 99.0%, purchased from Normasolv. Aqueous solutions 2×10^{-6} M were used as subphase. A 10^{-4} M solution of 1,1′-dioctadecyl-4,4′-bipyridilium dibromide was prepared in chloroform/absolute ethanol in a ratio 4:1. A volume of 0.7 mL of the viologen solution was delivered from a syringe held very close to the surface allowing the surface pressure to return to a value as close as possible to zero between each addition. The solvent was allowed to completely evaporate over a period of at least 15 min before compression of the monolayer commenced at a constant sweeping speed of 6.6×10^{-3} nm^2/(molecule min). The uncertainty in the area per molecule obtained from the isotherms is about 5%. The ΔV–A measurements were carried out using a Kelvin Probe provided by Nanofilm Technologie GmbH, Göttingen, Germany. Each compression and surface potential isotherms were registered at least three times to ensure the reproducibility of the results. A commercial mini-Brewster Angle Microscope (mini-BAM), also from Nanofilm Technologie, was employed for the direct visualization of the monolayers at the air/water interface, and a commercial UV–vis reflection spectrophotometer, detailed described before [34], was used to obtain the reflection spectra of the Langmuir films during the compression process. The low barrier speed was chosen to minimize the relaxation phenomena of the monolayer during the recording of the reflection spectra.

3. Results and discussion

Fig. 2 shows the surface pressure–area per molecule (π–A) isotherms for the viologen derivative spread on subphases containing different potassium salts, with representative anions in the Hofmeister series. A distinct behavior due to the presence of different subphases may be taken as an evidence of the different interactions between the viologen and the anions in the subphase, which may be partially trapped by the cationic amphiphile. Thus, two different trends are observable. On the one hand, anions on the right of the Hofmeister series (Cl^-, Br^-, NO_3^-, I^-, ClO_4^-) yield isotherms very similar in shape. For these anions, the take-off in the isotherm occurs at 1.65 nm^2/molecule, and the isotherms show an overshoot at ca. 30 mN/m except for the ClO_4^- subphase, for which the isotherm overshoot takes place at ca. 20 mN/m. After the overshoot, the surface pressure increases again with decreasing area per molecule. On the other hand, anions on the left of the Hofmeister series ($C_6H_5O_7^{3-}$, SO_4^{2-}, and HPO_4^{2-}) yield Langmuir monolayers with a different behavior to that observed for anions on the right side of the Hofmeister series. Thus, for HPO_4^{2-}, SO_4^{2-}, and $C_6H_5O_7^{3-}$ aqueous subphases the surface pressure starts to increase at ca. 2.3 nm^2/molecule. These monolayers show kinks in the isotherms around 30 mN/m for the HPO_4^{2-} and SO_4^{2-} subphases, and at a slightly lower surface pressure (ca. 28 mN/m) for the $C_6H_5O_7^{3-}$ subphase. Moreover, for subphases containing $C_6H_5O_7^{3-}$, SO_4^{2-}, or HPO_4^{2-}, plateaus (regions of constant surface pressure with decreasing area per molecule) in the isotherms are observed after the kink. These observations are in good agreement with observed trends in the behavior of anions in the Hofmeister series, which strongly depend on the charge of the anions [3].