

## Adsorption of cationic polyions onto a hydrophobic surface in the presence of Hofmeister salts

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We study, using extensive Monte Carlo simulations, the behavior of cationic polyelectrolytes near hydrophobic surfaces in solutions containing Hofmeister salts. The Hofmeister anions are divided into kosmotropes and chaotropes. Near a hydrophobic surface, the chaotropes lose their solvation sheath and become partially adsorbed to the interface, while the kosmotropes remain strongly hydrated and are repelled from the interface. If the polyelectrolyte solution contains chaotropic anions, a significant adsorption of polyions onto the surface is also observed. On the other hand, the kosmotropic anions have only a small influence on polyion adsorption. These findings can have important implications for exploring the antibacterial properties of cationic polyelectrolytes.

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### Introduction

The study of electrolytes near interfaces is of great importance for science, technology, and medicine. One particularly intriguing phenomenon is the repeated appearance of the Hofmeister series of ions in various disciplines. The first observation that many physicochemical processes depend strongly on specific anions present in electrolyte solution dates back over a century ago to the pioneering work of Hofmeister.<sup>1</sup> The original lyotropic series was discovered by studying the ability of different ions to precipitate or stabilize protein solutions.<sup>2–4</sup> Following the pioneering work of Hofmeister, the same series has been observed in many other areas of science, such as electrochemistry, colloidal science,<sup>5,6</sup> surfactant micellization,<sup>7</sup> bacterial growth,<sup>8</sup> surface and interfacial tensions,<sup>9,10</sup> peptide bonds,<sup>11</sup> microemulsions, *etc.*<sup>12</sup> Recently, a theory that allows one to quantitatively predict the effect of Hofmeister ions on surface<sup>13–15</sup> and interfacial tensions<sup>16,17</sup> of electrolyte and acid solutions has been proposed. In this paper we explore the effect that Hofmeister ions have on the interaction between cationic polyelectrolytes and a hydrophobic surface. The study is motivated by the observation that *amphiphilic* cationic polyelectrolytes (with both hydrophobic and hydrophilic moieties) have been found to act as antibiotics. The electrostatic interactions between the negative charges of the membrane and the positive charges of the polyion, as well as the hydrophobic interactions between the phospholipids and the polyions, appear to be responsible for the antimicrobial behavior.<sup>18–22</sup> It is then interesting to explore how purely *hydrophilic*

polyelectrolytes (without hydrophobic parts) behave near a lipid membrane, and whether such polyions can also adsorb onto a hydrophobic surface in the presence of different electrolytes. A related property of polyelectrolytes is their ability to stabilize nanoparticles.<sup>23,24</sup> This also has some significant industrial and medical applications. In the present work, we will focus our attention on the interaction of cationic polyelectrolytes with soft hydrophobic surfaces. To perform this study, we will rely on Monte Carlo simulations in conjunction with accurate interaction potentials obtained in earlier studies of the interfacial tensions of electrolyte–oil interfaces.

### Theory

The recently developed polarizable anion theory<sup>13–17,25,26</sup> has proven to be useful in describing very accurately the experimental data for surface and interfacial tensions, as well as the electrostatic surface potential of different electrolyte solutions.<sup>9,27,28</sup> The important insight of the theory is that the chaotropic and the kosmotropic ions behave differently near a hydrophobic interface.<sup>29–31</sup> While the kosmotropes maintain their bulk hydration sheath and are repelled from a hydrophobic interface,<sup>32</sup> the strongly polarizable chaotropes lose their hydration layer and, on approaching the interface, they redistribute their electronic charge so that it remains mostly hydrated in the high dielectric environment.<sup>25</sup> To solvate an ion in water, it is first necessary to create a cavity into which the ion will be inserted. Creation of a “hole” in water costs significant entropic energy since it perturbs the structure of water hydrogen bonds and restricts the motion of water molecules. If, however, the ion moves out of water, across the interface, the perturbation to the water structure vanishes. For small cavities, the cavitation energy scales with the volume of the void.<sup>33,34</sup> For strongly hydrated kosmotropic ions, the cavitation energy

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is too small to compensate the loss of the hydration sheath and for exposing the ionic charge to the low dielectric environment of the lipid membrane. On the other hand, for weakly hydrated and highly polarizable chaotropes, the cavitation and electrostatic energies become comparable.<sup>35</sup> The theory predicts that these ions can become partially adsorbed to the interface. This prediction was confirmed by the full *ab initio* simulations, which showed that the potential of mean force (PMF) predicted by the polarizable anion theory for  $\Gamma^-$  anions agreed quantitatively with the results of the *ab initio* simulations.<sup>36,37</sup> We will first briefly discuss the interaction potentials necessary to study the behavior of Hofmeister ions near a hydrophobic interface. For more details and derivations, interested readers are referred to the original publications.

The dielectric discontinuity across the interface leads to induced charges which repel ions from the interface.<sup>14,38–41</sup> This is different from a conductor which leads to an ion–electrode attraction.<sup>42</sup> The approximate charge–image potential at a distance  $z$  from the interface was calculated to be<sup>14</sup>

$$\beta U_i(z) = \begin{cases} \beta W a \frac{e^{-2\kappa(z-a)}}{z} & \text{for } z \geq a, \\ \beta W \frac{z}{a} & \text{for } 0 \leq z \leq a, \\ 0 & \text{for } -a \leq z \leq 0, \end{cases} \quad (1)$$

where  $\kappa = \sqrt{8\pi\lambda_B c_s}$  is the inverse Debye length,  $a$  is the ionic radius,  $c_s$  is the salt concentration and  $\lambda_B = \beta q^2/\epsilon_w$  is the Bjerrum length, which for water at room temperature is 7.2 Å, and  $q$  is the proton charge. The potential at contact,  $W$ , is given by,<sup>43</sup>

$$\beta W = \frac{\lambda_B}{2} \int_0^{\infty} dk \frac{k f_1(k)}{p f_2(k)}, \quad (2)$$

where,

$$\begin{aligned} f_1(k) &= p \cosh(ka) - k \sinh(ka) \\ &\quad + \frac{\epsilon_o}{\epsilon_w} p \sinh(ka) - \frac{\epsilon_o}{\epsilon_w} k \cosh(ka), \\ f_2(k) &= p \cosh(ka) + k \sinh(ka) \\ &\quad + \frac{\epsilon_o}{\epsilon_w} p \sinh(ka) + \frac{\epsilon_o}{\epsilon_w} k \cosh(ka), \end{aligned}$$

and  $p = \sqrt{k^2 + \kappa^2}$ . The dielectric constants of water and oil are  $\epsilon_w = 80$  and  $\epsilon_o = 2$ , respectively. This potential accounts approximately for both the polarization of the ionic atmosphere around each ion and the induced charge at the dielectric interface.

In simulations, of course, it is possible to use directly the image charges of ions and monomers<sup>40,44,45</sup> to account for the induced surface charge. However, as we will see later, for monovalent ions the approximate potential (eqn (1)) provides us with a major speed up of simulations, without any significant sacrifice of accuracy.

The hydrophobic potential is proportional to the ionic volume exposed to the aqueous medium and is given by

$$\beta U_c(z) = \begin{cases} \nu a^3 & \text{for } z \geq a, \\ \frac{1}{4} \nu a^3 \left(\frac{z}{a} + 1\right)^2 \left(2 - \frac{z}{a}\right) & \text{for } -a \leq z \leq a, \end{cases} \quad (3)$$

where  $\nu = 0.3/\text{\AA}^{-3}$  is obtained using SPC/E water simulations.<sup>46</sup>

The electrostatic self-energy of a chaotropic ion at a distance  $z$  from the interface is<sup>13</sup>

$$\beta U_p(z) = \begin{cases} \frac{\lambda_B}{2a} & \text{for } z \geq a, \\ \frac{\lambda_B}{2a} \left[ \frac{\pi x^2}{\theta(z)} + \frac{\pi[1-x]^2 \epsilon_w}{[\pi - \theta(z)] \epsilon_o} \right] + \\ g \left[ x - \frac{1 - \cos[\theta(z)]}{2} \right]^2 & \text{for } -a \leq z \leq a, \end{cases} \quad (4)$$

where  $\theta(z) = \arccos[-z/a]$ ,  $g = (1 - \alpha)/\alpha$ , and  $x$  is the fraction of the ionic charge that remains hydrated. The relative polarizability is defined as  $\alpha = \gamma/a^3$ , where  $\gamma$  is the ionic polarizability. By minimizing eqn (4), we obtain the fraction of the ionic charge that remains hydrated,

$$x(z) = \frac{\frac{\lambda_B \pi \epsilon_w}{a \epsilon_o [\pi - \theta(z)]} + g[1 - \cos[\theta(z)]]}{\frac{\lambda_B \pi}{a \theta(z)} + \frac{\lambda_B \pi \epsilon_w}{a \epsilon_o [\pi - \theta(z)]} + 2g}. \quad (5)$$

Ions near a hydrophobic surface also experience dispersion interactions which are modeled by the potential<sup>16</sup>

$$\beta U_d(z) = \begin{cases} 0 & \text{for } z \geq a, \\ A_{\text{eff}} \alpha \left[ 1 - \frac{(z/a + 1)^2 (2 - z/a)}{4} \right] & \text{for } -a \leq z \leq a, \end{cases} \quad (6)$$

where  $A_{\text{eff}} = -4.4$  is the effective Hamaker constant.<sup>16</sup>

The chaotrope–interface interaction potential is the sum of all these contributions,  $U_i(z) + U_c(z) + U_p(z) + U_d(z)$ . Since the kosmotropes do not penetrate the surface, their interaction potential consists only of the ion–image contribution,  $U_i(z)$ , and the hardcore repulsion (at one hydrated radius) from the interface.

## Monte Carlo simulations

Our system consists of cations and anions, derived from a Hofmeister salt, and cationic polyions with the dissociated counterions. All the particles are confined inside a box of sides  $L_x = L_y = 182$  Å and  $L_z = 200$  Å, centered at the origin of the coordinate system. A soft hydrophobic surface (water–oil interface) is located at  $z = 0$ . The electrolyte and polyelectrolyte are restricted to the region  $0 < z < L_z/2$ . Only chaotropic ions can penetrate into the region  $-r_a < z < L_z/2$ , where  $r_a$  is the anionic radius. The aqueous medium,  $z > 0$ , is considered to be uniform with dielectric constant  $\epsilon_w$ . The uncharged lipid membrane, modeled as oil, occupies the region  $z < 0$ , and has the dielectric constant  $\epsilon_o$ . In the spirit of the primitive model, all ions are treated as hard spheres. Sodium cations have radius  $r_{\text{Na}^+}$  and charge  $q$ , anions have radius  $r_a$  and charge  $-q$ , while the polyion counterions have charge  $-q$  and a radius of  $\text{Cl}^-$ . The polyions have 10 monomers each. Each monomer is a sphere of radius

$r_{\text{Na}^+}$  and carries a positive charge  $q$ . The monomers interact between themselves by a repulsion WCA potential,<sup>47</sup>

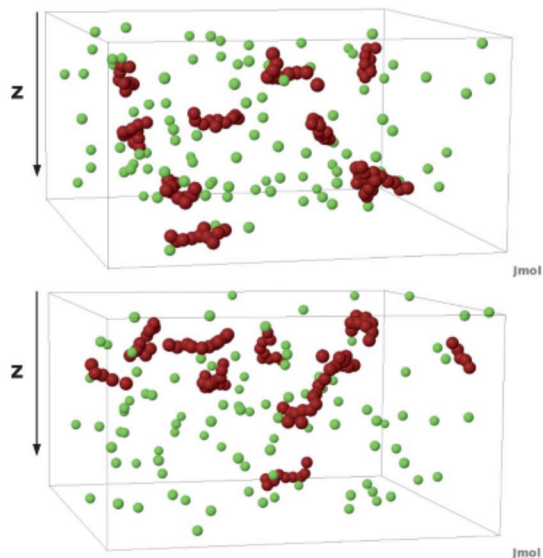
$$\beta U_{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^6 \right] \\ 0 \quad \text{for } r \geq r_c, \end{cases} \quad (7)$$

where  $r$  is the distance between the monomers,  $r_c = 2^{1/6}\sigma$ ,  $\sigma = 2r_{\text{Na}^+}$ , and  $\epsilon = 0.833$ . The adjacent monomers interact by the FENE attractive potential,<sup>47</sup>

$$\beta U_{\text{FE}}(r) = -0.5k_s R_0^2 \ln(1 - r^2/R_0^2), \quad (8)$$

where  $k_s = 7\epsilon/\sigma^2$  is the spring constant and  $R_0 = 2\sigma$  is the maximum extension. We use the same parameters as those used by Stevens and Kremer<sup>47</sup> for polyelectrolytes.

All the ions and the monomers interact between themselves by the Coulomb potential. Since in the simulations we use a slab geometry, a correction of Yeh and Berkowitz<sup>48</sup> to the standard 3d Ewald summation method is applied. The kosmotropic ions,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and the polyion monomers interact with the interface through the effective potential  $U_i(z)$ , while the chaotropic anions,  $\text{Br}^-$  and  $\text{I}^-$ , interact with the interface through the effective potential  $U_i(z) + U_c(z) + U_p(z) + U_d(z)$ . In the simulations the dielectric jump at  $z = 0$  is taken into account through the potential  $U_i(z)$ , without explicitly using the image charges. We perform regular displacements for all the microions, and reptation and rotation moves for the polyions. The equilibration is achieved after  $10^6$  MC steps. Subsequently, 10 movements per particle are used to obtain the uncorrelated configurations, and the averages are calculated using  $10^4$  equilibrated uncorrelated states. Fig. 1 shows the characteristic equilibrium configurations for the salts NaF and NaI. We can see that NaI results in an enhanced adsorption of the polyions to the interface.



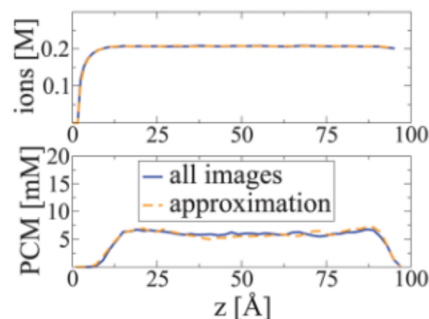
**Fig. 1** Snapshots of two equilibrium configurations for salts NaF (top panel) and NaI (bottom panel), both at a concentration of 50 mM. The concentration of polyions is 5 mM. Only anions (lighter spheres) and polyions (darker spheres) are shown. The oil–water interface is at the top of the simulation box.

## Test of the effective potential

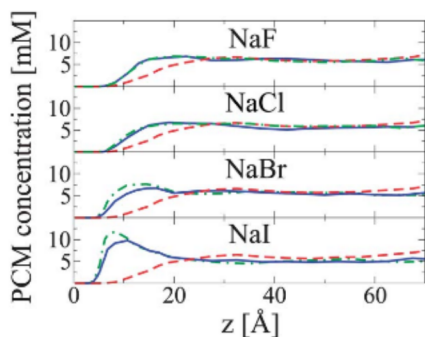
One of the difficulties in performing simulations with dielectric interfaces is the need to account for the induced surface charges (see ref. 43 for details). This makes the simulations very slow. For strongly polarizable chaotropic anions there is an additional difficulty since it is very hard to calculate exactly the electrostatic potential of an ion as it penetrates the dielectric interface. To avoid these problems, in the previous section we have used the effective charge–image interaction potential. This potential was derived by considering the solution of the linearized Poisson–Boltzmann equation. To test the reliability of this potential, we first study a polyelectrolyte solution with a kosmotropic salt, NaCl. For kosmotropic ions – which never cross the interface – it is possible to account exactly for the induced charges by including for each ion or monomer a corresponding image charge. We can then compare the results of these “exact” simulations with the “approximate” simulations in which the images are not included, but instead each ion and monomer interacts with the surface through an effective potential  $U_i(z)$ , with the inverse Debye length  $\kappa = \sqrt{8\pi\lambda_B c_s + 4\pi\lambda_B N_m c_p}$ , where  $N_m = 10$  is the number of monomers in a polyion, and  $c_p$  is the polyelectrolyte concentration. Fig. 2 shows that the simulations with the effective potential  $U_i(z)$  produce the ionic and polyelectrolyte density profiles practically indistinguishable from the exact all-image simulations. With the simulation method thus validated for kosmotropic ions, we can now proceed to study general polyelectrolyte solutions containing a full spectrum of Hofmeister ions.

## Results

In simulations, all ionic sizes and polarizabilities are the same as in the previous studies on surface and interfacial tensions of electrolyte solutions. The hydrated radii of the kosmotropic ions,  $\text{F}^-$  and  $\text{Cl}^-$ , are  $r_a = 3.54 \text{ \AA}$  and  $r_a = 2 \text{ \AA}$ , respectively.<sup>49</sup> The chaotropic ions, such as bromide and iodide, lose their



**Fig. 2** Comparison between the density profiles obtained from the “exact” simulation of ref. 43 and a simulation using the effective potential  $U_i(z)$ . In the upper panel we show the ionic profiles of the electrolyte NaCl, at a concentration of 0.2 M. The density profiles for  $\text{Na}^+$  and  $\text{Cl}^-$  are indistinguishable. In the lower panel we plot the PCM (polyelectrolyte center of mass) profile for 5 mM polyelectrolyte and NaCl at a concentration of 0.2 M. In both cases the agreement between the “exact” and the “approximate” simulations is very good.

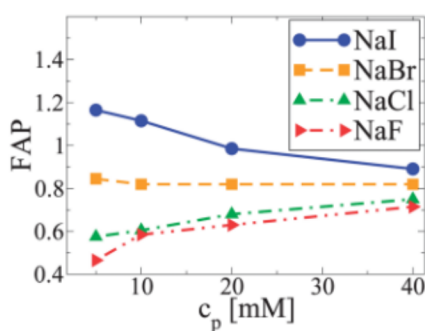


**Fig. 3** polyelectrolyte center of mass (PCM) density profile as a function of distance  $z$  from the interface, for various electrolytes and concentrations. Polyelectrolyte concentration is 5 mM. Dashed (red), solid (blue), and dashed-dotted (green) lines correspond to solutions containing salts at concentrations 0, 0.2, and 0.3 M, respectively.

hydration sheath and, as a result of their high polarizability they become partially adsorbed onto hydrophobic surfaces. The bare radius of  $\text{Br}^-$  is  $r_a = 2.05 \text{ \AA}$  and its polarizability is  $\gamma = 5.07 \text{ \AA}^3$ .<sup>50,51</sup> The bare radius of  $\text{I}^-$  is  $r_a = 2.26 \text{ \AA}$  and its polarizability is  $\gamma = 7.4 \text{ \AA}^3$ .<sup>50,51</sup> The hydrated radius<sup>52</sup> of  $\text{Na}^+$  is  $r_{\text{Na}^+} = 1.8 \text{ \AA}$ .

The simulations show that addition of kosmotropic salts such as NaF and NaCl does not have a significant influence on the interfacial adsorption of cationic polyions (see Fig. 3). The only effect of the kosmotropic salts is to increase the electrostatic screening of the monomer-image interaction, allowing the polyions to come closer to the interface. The situation is very different if the solution contains chaotropic anions. In this case, there is a significant adsorption of polyions to a hydrophobic interface (Fig. 3). The adsorption is stronger for larger chaotropic ions, such as iodide.

In Fig. 4, we plot the fraction of adsorbed polyions (FAP) as a function of the polyelectrolyte concentration. FAP is defined as the concentration of adsorbed polyions (within the distance  $z = 20 \text{ \AA}$  of the interface) divided by the average concentration of polyions in the solution. We see that if a solution contains chaotropic anions, at low concentrations of polyelectrolyte, a significant number of polyions is adsorbed to the interface. The behavior is different for electrolytes containing chaotropic and



**Fig. 4** Fraction of adsorbed polyions (FAP) as a function of polyelectrolyte concentration, at a salt concentration of 0.2 M.

kosmotropic anions. For chaotropes, the FAP decreases with the polyelectrolyte concentration. This happens because at higher concentrations of polyelectrolyte there will be more dissociated counterions, which leads to an increased screening of the electrostatic attraction between the adsorbed chaotropic anions and the polyions of the solution. On the other hand, when the polyelectrolyte solution contains only kosmotropic ions (which are repelled from the interface), increased polyelectrolyte concentration leads to stronger screening of charge-image repulsion, allowing the polyions to closely approach the hydrophobic surface, leading to an increase of FAP as a function of the polyelectrolyte concentration.

## Conclusions

We have studied the interactions of cationic polyelectrolytes with a hydrophobic surface in the presence of Hofmeister salts. Ionic interactions with the interface were modeled using the effective potentials derived in earlier studies regarding the interfacial tension of electrolyte-oil interfaces. For salts containing kosmotropic anions, the simulation methodology was verified against the explicit all-atom simulations. This opens up the possibility of using the effective potentials to significantly speed up the simulations for systems containing monovalent ions. The agreement between the “approximate” and the “exact” simulations also suggests that the effective potentials should be sufficient to study polyelectrolyte solutions containing chaotropic anions. In this case, the direct implementation of the “exact” simulations is further complicated by the difficulty in accounting for electrostatic boundary conditions when strongly polarizable chaotropic ions penetrate the dielectric interface. The method presented in this paper allows us to overcome this problem by using the effective potentials. At this point, however, our results for chaotropic ions are predictions based on the effective potentials developed in earlier studies of the oil water interface<sup>16</sup> and should be verified by more detailed atomistic simulations.<sup>53</sup> Unfortunately, the state of the art force fields for atomistic simulations lead to too much adsorption of chaotropic ions, resulting in surface tensions which deviate strongly from the experimental measurements.<sup>17,35</sup> On the other hand, the effective potentials used in the present work result in a lower adsorption and produce surface and interfacial tensions in excellent agreement with the experimental measurements.<sup>13,14,16</sup> This makes it difficult for us to compare our methodology with the classical atomistic simulations.

An important conclusion of the present work is that chaotropic anions can significantly increase the adsorption of cationic hydrophilic polyions to an uncharged lipid membrane. The simulations presented here allow us to make quantitative estimates on the amount of adsorption. Since the antibacterial effect of a polyelectrolyte is related to the polyion adsorption, this can prove to be important for the development of antibacterial applications involving hydrophilic cationic polyelectrolytes — the amphiphilic polyions used for this purpose often show high toxicity. However, since the bacterial membranes are partially composed of negatively charged phospholipids, it will also be

important to explore the role of surface charge in polyion adsorption.

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