SUPPORTING INFORMATION FOR

Electrostatic Interactions and Physisorption: Mechanisms of Passive Cesium Adsorption on Prussian Blue

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Supplementary Section 1 – Non-Linear Isotherm Fitting

This section shows a nonlinear fitting procedure for extracting the three unknown parameters the in EL model. The challenge with extracting these parameters is that the expression is highly nonlinear. Mainly, there is exponential dependency on the k_q fitting parameter and the adsorption q though $\exp(k_q)$. Another challenge is that the fitting parameters appear as a product. Also, the K_L and k_q factors have similar effects on the predicted adsorption, which could lead to instability in the fitting method.

To improve the stability of the fitting method, we first normalize the input parameters. Thus, $\bar{q} = q/q_0$, $\bar{c} = c/c_0$. Here, q_0 and c_0 are taken as the largest values of the corresponding parameter in the data set, such that the normalized data takes on values between 0 and 1. The equations show the fitting parameters with bars too to show that they correspond to the normalized equations. Finally, the parameter $\bar{K}_q$ is introduced as $\bar{K}_q = \exp(\bar{k}_q)$ to reduce the clutter in the equations. This yields the corrected normalized form in Equation (S1).

$$\frac{\bar{c}}{\bar{q}} = \frac{\bar{K}_q^{\bar{q}}}{\bar{q}_m \bar{K}_L} + \frac{\bar{c}}{\bar{q}_m} \tag{S1}$$

This normalized form can be expressed as a matrix equation (Equation (S2)) with multiple components (Equations (S3)-(S5)). We are introducing bold font to indicate parameters that are vectors or matrices. Column vectors are assumed as default. Here, q is the vector of observed equilibrium adsorption for experiments with concentrations listed in c (Nx1 vector corresponding to N experiments). Also, "./" (with a dot) indicates elementwise division and "." (dot) in an exponent indicates elementwise raised-to-power.

$$y = X\beta \tag{S2}$$

$$y \equiv \bar{c}./\bar{q} \tag{S3}$$

$$X \equiv \left[\bar{K}_q^{\bar{q}} \; \bar{c}\right] \tag{S4}$$

$$\beta \equiv \left[1/(\bar{q}_m \bar{K}_L) \; 1/\bar{q}_m\right]^T \tag{S5}$$

Now, β can be expressed as the standard solution to the least-squares problem, $\hat{\beta} = (X^T X)^{-1} X^T y$. Here, $\hat{\beta}$ is the fitted value of β. The system parameters $\bar{q}_m$ and $\bar{K}_L$ can then be calculated based on the entries in $\hat{\beta}$. This is enough to solve the system if K_q is known, such as in the classical Langmuir wherein $K_q = 1$ because $k_q = 0$. Otherwise, we can reinsert the expression for $\hat{\beta}$ into Equation (S2) to get Equation (S6). This is equivalent to Equation (S7). The only unknown parameter in this equation is K_q (which appears in X). As usual, there is no guarantee that a parameter value exists that fulfills the equation exactly. However, the equation can be solved in the least-squares sense using a nonlinear solver (Equation (S8)). Knowing the value of K_q, the other parameters can then be derived from β as described above.

$$y = X(X^T X)^{-1} X^T y \tag{S6}$$

$$(I - X(X^T X)^{-1} X^T)y = 0 \tag{S7}$$

$$\bar{K}_q = argmin_{\bar{K}_q} \left\|(I - X(X^T X)^{-1} X^T)y\right\| \tag{S8}$$

Supplementary Section 2 – Time-Series Data

Figure S1 shows the time-series data for the MD simulation in the main manuscript. The Gibbs-free energy was calculated at each ps of simulation time for a total of 2000 ps. Also, the Gibbs-free energies shown here were averaged to produce the data points in Figure 4, giving the trend of energy for increasing numbers of excess cesium. Taking the average energy can reduce the noise in the model, especially relating to the configuration of the solvating water molecules. Notably, the time-series data here demonstrate that the average free energy is stable over time, which suggests that the adsorption sites are stable.

a) 1 Cs$^+$
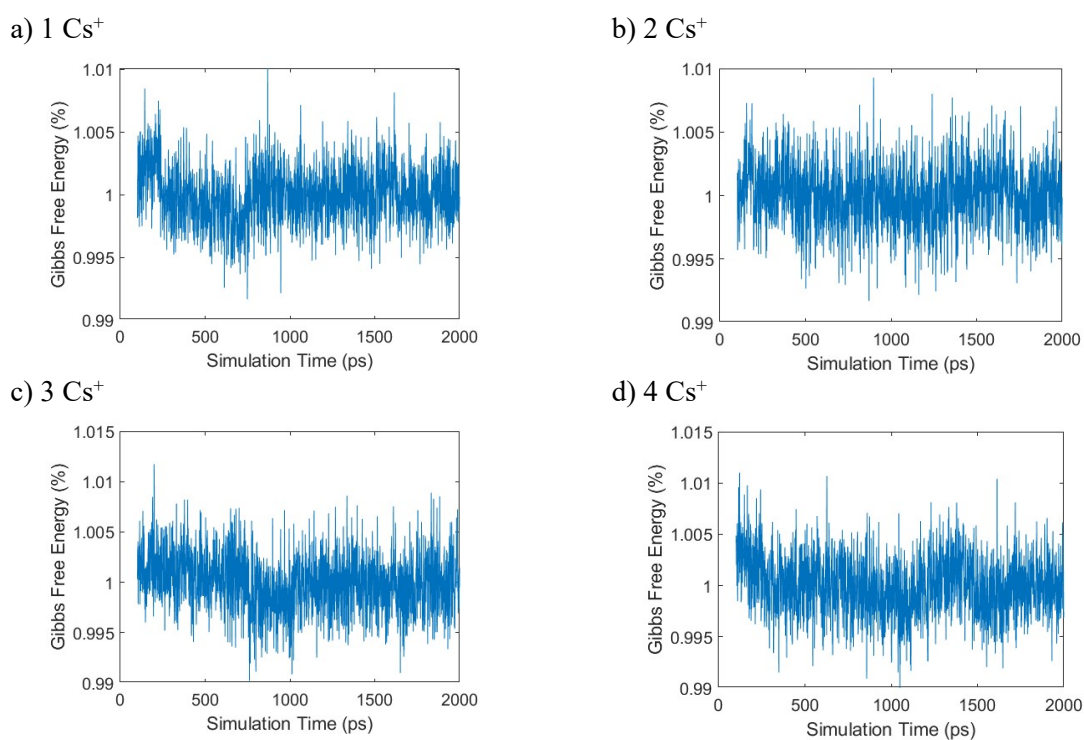
b) 2 Cs$^+$

c) 3 Cs$^+$

d) 4 Cs$^+$

Figure S1. The Gibbs free energy as estimated from the Hessian. The abscissa shows the simulation time, and one snapshot was extracted every ps. The snapshots were then used to generate a statistical average of the Gibbs free energy of the system. The ordinate shows the Gibbs free energy normalized by the average Gibbs energy in the time series. Notably, the mean energies are essentially independent of simulation time; that is, the period of simulation used to extract information can be regarded as well equilibrated. (a-d) The time series for N=1-4 cesium ions in excess.

Supplementary Section 3 – Principles of Electrostatics in Adsorption

How should electrostatic properties affect adsorption? Let us begin by considering the Coulombic interactions in a simplified model (Figure S2). In this model, an ion approaches a large flat surface. The surface pulls the ions by dielectric forces, but already adsorbed ions are repelling incoming new ions.

For the sake of illustration, suppose an ion with charge q approaches a surface at a distance r. The surface can generate a dipole moment in response to the approaching ion. The dipole moment can be represented with a charge q_d separated by a distance r_0 that is rather long at an atomic scale. In addition, there is already a collective repulsive charge q_A from adsorbed charge (cations) in the way ($q_A < q_d$). If the charge at the surface and one end of the dipole charge are in the same place, Equation (S9) gives an expression for the net pulling force F. This expression can be rewritten into a criterium for a net attractive force (Equations (S10) and (S11)). Interestingly, the results show that the net force can be attractive if the ion gets close enough, even if there is overall a more repelling charge than attracting charge. This means the example surface can provide net adsorption at equilibrium only based on Coulombic interactions.
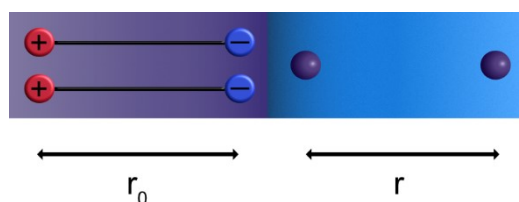

Figure S2. A toy model of dielectric forces. The left-hand side (violet) shows the solid and the right-hand side shows the solution. An ion is approaching the surface at a distance r. If the dielectric forces are strong enough, they can overcome the repulsion from ions that are already adsorbed. In a real system, PB has a molecular surface structure and flexible cyanide ligands, and therefore we should expect some dielectric adaptation with respect to approaching ions.

$$F = Kq\left(\frac{q_d - q_A}{r^2} - \frac{q_d}{(r + r_0)^2}\right) \tag{S9}$$

$$F > 0: \quad \frac{q_d - q_A}{r^2} > \frac{q_d}{(r + r_0)^2} \tag{S10}$$

$$F > 0: \quad r < r_0\frac{\sqrt{1 - q_A/q_d}}{1 - \sqrt{1 - q_A/q_d}} \tag{S11}$$

Alternatively, we can also use the same model but with the charge smeared out over a large flat surface. Gauss law gives the electric field E of a surface charge σ, as shown in Equation (S12). Here, ϵ_0 is the permittivity of free space. In this case, there is no fall-off in the field as a function of the distance. Any internal dipole moment will thus always yield a zero field. Consequently, an adsorbed surface charge σ_A will always yield a net repulsive force towards incoming ions of the same charge. While the previous example argued that Coulombic interaction can contribute to localized adsorption, this model instead suggests that there cannot be full monolayer adsorption.

$$E = \frac{\sigma}{2\epsilon_0} \tag{S12}$$

Despite these expected results from the two models, one could argue that non-Coulombic interactions still could make adsorption favorable. We should also bear in mind that the dipole moments of water will contribute to shielding any electrostatic interaction. However, the main point made is that the adsorption energy will depend on the number of adsorbed ions. This invalidates the fundamental presumptions of the Langmuir isotherm. It is important to highlight these fundamental differences in the models employed.