We consider the primitive model of electrolytes between hard, planar, charged surfaces. The solvent is described by a uniform dielectric constant. The ions are modeled as charged, hard spheres with a point charge in their center. Diameter of the anion: d = 0.425 nm. Valence of the anion: z = 1. Diameter of the small and large cations are 0.2 and 0.425 nm. Monovalent and divalent cations are considered. The distance between the charged walls was varied from 0.06 to 0.09 nm.

The electrical double layer is formed at the interface of the solid phase (electrode) and the electrolyte. We study the effect of the charge and/or size asymmetry on the electrode potential, and the competition of two cations of different size and valence near a highly charged electrode. If the ions have different diameters and/or valences, the electrode potential is nonzero even if the electrode charge is zero (PZC potential) [1]. Size and valence asymmetries are two competing effects regarding the sign and magnitude of the PZC potential [2,3]. Grand canonical simulations are used to study the ion selectivity of electrolyte mixtures into slit-like pores.

**MODEL**

**STUDY OF THE SELECTIVE ADSORPTION OF DIFFERENT TYPE OF CATIONS ON THE SURFACE OF THE ELECTRODE**

At positive surface charges anions are preferred at the electrode, while at negative surface charges the two cations compete space near the interface. No wonder that the smaller ions come out of the competition as a winner. Their preference is more pronounced at higher surface charges. For mixtures of small and large divalent ions this preference is even more obvious. At large negative surface charges the large cations even surpass the anions. Its explanation is that the association of a divalent cation with two anions has a higher probability. This association is more probable in the case of small ions. At high surface charges, the small cations tend to bring the anions with themselves to the interface to maintain electroneutrality and minimum free energy just to the degree entropy allows. A layering structure is formed at the electrode charge inversion.

**COMPETITION BETWEEN SIZE AND VALENCE**

The adsorption as a function of the electrode charge for small and large divalent cations. The concentration of either cations is 1 M, the concentration of the anion is 2 M.

<table>
<thead>
<tr>
<th>Concentration Profile</th>
<th>Electrode Charge (mC/m2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

At positive surface charges anions are preferred at the electrode, while at negative surface charges the two cations compete space near the interface. No wonder that the smaller ions come out of the competition as a winner. Their preference is more pronounced at higher surface charges. For mixtures of small and large divalent ions this preference is even more obvious. At large negative surface charges the large cations even surpass the anions. Its explanation is that the association of a divalent cation with two anions has a higher probability. This association is more probable in the case of small ions. At high surface charges, the small cations tend to bring the anions with themselves to the interface to maintain electroneutrality and minimum free energy just to the degree entropy allows. A layering structure is formed at the electrode charge inversion.

**MC: MOLECULAR COMPUTER SIMULATION**

The chemical potentials corresponding to prescribed concentrations were determined with the method of Malasics et al. [4]. The process converges fast, needed just a few iterations. We computed the terms of the chemical potential profiles using Widom’s particle insertion method.

**ION SELECTIVITY IN A SLIT**

Here we studied the competitive case, where the small monovalent cation compete with the large divalent cation in case of different electrode charge and width of the slit. The concentrations of the two cations are the same. We studied 4 different cases: 0.05, 0.1, 0.5 and 1 M cation concentrations. Ion selectivity is defined as the ratio of the number of the small monovalent and large divalent cations in the slit.

**ENERGETICS IN THE SLIT**

The competition of the repulsive entropic (hard spheres exclusion) and the attractive electrostatic forces can be demonstrated by the separation of the total chemical potential in profiles in the following way:

$$\mu^{TOT}(x) = kT \log \frac{c(x)}{c_{bulk}} + \mu^{ES}(x) + \mu^{HS}(x)$$

where $c(x)$ is the concentration at a distance $x$ from the electrode, $c_{bulk}$ is the bulk concentration, $k$ is the Boltzmann constant, $T$ is the temperature, and $\mu^{ES}$ and $\mu^{HS}$ are the electrostatic and entropic contributions, respectively.

The total chemical potential was calculated with an iterative method of Malasics et al. [4]. We are interested in the accumulation of the ion at the interface or in the slit from an electrolyte of fixed concentrations. So, we related our terms of the chemical potential to the bulk values.

**REFERENCES AND ACKNOWLEDGEMENT**


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