

Ion selectivity in capacitive deionization with functionalized electrode: theory and experimental validation

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Abstract

This supporting information document provides additional descriptions of our model's treatment of ion adsorption. Included are a discussion of pH effects, the moderate pH assumption in model, and parameters used in numerical simulations.

1. Electric double-layer model with pH effects

A generalized formulation of micropores concentration includes chloride, nitrate, hydroxide, sodium, and hydronium ions. Using a modified Donnan (mD) model, we relate micropore to macropore concentrations as

$$c_{m,i,j} = c_i \exp(-z_i \Delta \phi_{D,j} / V_T) \quad (1)$$

$$i = \text{Cl}^-, \text{NO}_3^-, \text{OH}^-, \text{Na}^+, \text{H}^+$$

$$j = \text{A}, \text{C}$$

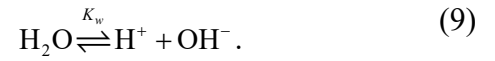
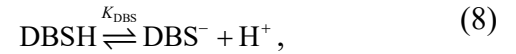
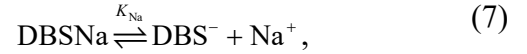
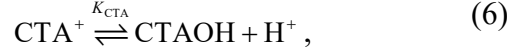
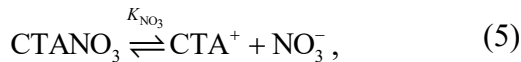
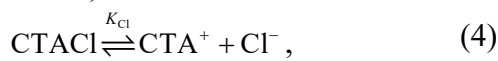
where A and C correspond to anode and cathode electrodes. The ionic charge and electroneutrality conditions can be written as

$$\sigma_{\text{ionic},j} = F \sum_i z_i c_{m,i,j} \quad (2)$$

$$c_{\text{Na}^+} = c_{\text{Cl}^-} + c_{\text{NO}_3^-} + c_{\text{OH}^-} + c_{\text{H}^+} \quad (3)$$

2. Equilibrium model for ion selectivity with pH effects

We here present the equilibrium reaction of the quaternary ammonium surfactant CTAB, and sodium dodecyl benzenesulfonate surfactant SDBS. Equilibrium equations are presented for chloride, nitrate, hydroxyl, sodium and hydronium (represented as H⁺) as



Dissociation constants for the equilibrium reaction can be written as

$$K_{\text{Cl}} = c_{\text{CTA}^+} c_{m,\text{Cl}^-,\text{A}} / c_{\text{CTACl}}, \quad (10)$$

$$K_{\text{NO}_3} = c_{\text{CTA}^+} c_{m,\text{NO}_3^-,\text{A}} / c_{\text{CTANO}_3}, \quad (11)$$

$$K_{\text{CTA}} = c_{\text{CTAOH}} c_{\text{H}^+} / c_{\text{CTA}^+}, \quad (12)$$

$$K_{\text{Na}} = c_{\text{DBS}^-} c_{m,\text{Na}^+,\text{C}} / c_{\text{DBSNa}}, \quad (13)$$

$$K_{\text{DBS}} = c_{\text{DBSH}} / c_{\text{DBS}^-} c_{m,\text{H}^+,\text{C}}, \quad (14)$$

$$K_w = c_{\text{H}^+} c_{\text{OH}^-}. \quad (15)$$

Note the usual formulation wherein the equilibrium constant for the autoprotolysis of water (eq. 15) has units different than the other second-order, reversible reaction equilibrium expressions. (Persat et al., 2009)

Moderate pH assumption

By definition of pH, the concentration of hydronium and hydroxyl ions is each less than 0.1 mM for a pH range of 4-10. This range was termed the “moderate pH” regime by Persat et al. (Persat et al., 2009) who discuss its implication on approximations of the electroneutrality condition eq. (3).

It is useful to compare this 0.1 mM limit to relevant concentrations in our i-CDI system. For example, in this work, the concentration of chloride and

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nitrate ions is around 2 mM. Neglecting Faradaic reactions and assuming moderate pH implies that $c_{\text{NO}_3^-}, c_{\text{Cl}^-} \gg c_{\text{OH}^-}$ and $c_{\text{Na}^+} \gg c_{\text{H}^+}$. Under these two assumptions, electroneutrality condition can be reduced to $c_{\text{Na}^+} \approx c_{\text{Cl}^-} + c_{\text{NO}_3^-}$ (i.e. moderate pH).

Dissociation constant of quaternary ammoniums exhibits less affinity for hydroxide ions such as nitrate or chloride (Wheaton and Bauman, 1951) as described by the following inequalities

$$K_{\text{NO}_3} > K_{\text{Cl}} \gg 1 / K_{\text{CTA}} \quad (16)$$

With this in mind, we take the ratio of chemically adsorbed chloride and hydroxide ions (eqs. (10) and (12)), respectively, and use eq. (1) to relate micropore to macropore concentration to arrive at

$$\frac{c_{\text{CTACl}}}{c_{\text{CTAOH}}} = \frac{c_{\text{Cl}^-}}{K_{\text{Cl}}} \frac{c_{\text{H}^+}}{K_{\text{CTA}}} \quad (17)$$

$1/(K_{\text{Cl}}K_{\text{CTA}})$ is on the order of 10^{-13} for quaternary ammonium.(Wheaton and Bauman, 1951) We relate c_{OH^-} to c_{H^+} and pH using water autoprotolysis eq. 15. We then use 2 mM for c_{Cl^-} and represent ratios of dissociation constants in terms of pH to arrive at

$$\frac{c_{\text{CTACl}}}{c_{\text{CTAOH}}} \approx 2 \cdot 10^{10-\text{pH}} \quad (18)$$

As a result, $c_{\text{CTACl}} \gg c_{\text{CTAOH}}$ for $\text{pH} < 9$. Comparing chemically-adsorbed nitrate and hydroxyl, c_{CTANa} and c_{CTAOH} results in the same range for pH. So, $\text{pH} \approx 9$ is the upper limit for our analysis to be valid. Further, using a similar argument for SDBS surfactant,

$$\frac{c_{\text{DBSNa}}}{c_{\text{DBSH}}} = \frac{c_{\text{Na}^+}}{c_{\text{H}^+}} \frac{1}{K_{\text{Na}}} \frac{1}{K_{\text{DBS}}} \quad (19)$$

Here $1/(K_{\text{Na}}K_{\text{DBS}}) \sim 0.1$, $\text{pH} > 5$ satisfies the $c_{\text{DBSNa}} \gg c_{\text{DBSH}}$ inequality. This is thus the lower applicability limit for pH. Combining the two limits discussed above, the final pH range is about $5 < \text{pH} < 9$. For this pH range, we neglect the contribution of equation 12 in our dynamic model

and transport equations can be simplified to those presented in the main text.

We note that a full accounting of pH in iCDI cells with functionalized electrodes may be required in situations where pH varies well outside the aforementioned range of $5 < \text{pH} < 9$. We hypothesize this may be the case Faraday reactions significantly influence the acid/base equilibrium in the system. Including such details requires detailed knowledge of Faraday reaction species and rates relative to both electrostatic conditions in double layers and to transport rates through the system—making the problem much more complex. In such systems, detailed accounting of Faraday reaction(s) and pH are likely required for a more generalized multispecies model of CDI cells.

Lastly, Table S1 lists the key parameters used in our model.

Table S1. Parameters used in our model

Parameter	Description	Value	Unit
v_{cell}	Cell volume	3.0	mL
k_{int}	Intrinsic selectivity coefficient	7.7	-
$N_{\text{CTA},0}$	Amount of surfactant on CTA-AC	1000	mmole
$N_{\text{DBS},0}$	Amount of surfactant on DBS-AC	1000	mmole
C_m	Micropore capacitance	130	F cm ⁻³

References

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