

Structure of the electrical double layer at the ice-water interface

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Abstract

The surface of ice in contact with water contains sites that undergo deprotonation and protonation, and can act as adsorption sites for aqueous ions. Therefore, an electrical double layer should form at this interface, and existing models for describing the electrical double layer at metal oxide-water interfaces should be able to be modified to describe the surface charge, surface potential, and ionic occupancy at the ice-water interface. I used a surface complexation model along with literature measurements of zeta potential of ice in brines of various strength and pH to constrain equilibrium constants. I then made predictions of ion site occupancy, surface charge density, and partitioning of counterions between the Stern and diffuse layers. The equilibrium constant for cation adsorption is more than 5 orders of magnitude larger than the other constants, indicating that this reaction dominates even at low salinity. Deprotonated OH sites are predicted to be slightly more abundant than dangling O sites, consistent with previous work. Surface charge densities are on the order of $\pm 0.001 \text{ C/m}^2$ and are always negative at the moderate pH values of interest to atmospheric and geophysical applications (6-9). In this pH range, over 99% of the counterions are contained in the Stern layer. This suggests that diffuse layer polarization will not occur because the ionic concentrations in the diffuse layer are nearly identical to those in the bulk electrolyte, and that electrical conduction and polarization in the Stern layer will be negligible due to reduced ion mobility.

1 **Structure of the electrical double layer at the ice-water interface**

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25 I. INTRODUCTION

26 Ice occurs in contact with water in many natural systems, including glaciers, permafrost,
27 sea, lake, and river ice, snow, and atmospheric ice crystals¹. The properties of the ice-
28 water interface, including chemistry and surface forces, control many natural processes like
29 frost heave, glacier motion, sea ice growth, destruction of stratospheric ozone, and possibly
30 charge buildup in thunderstorms². Similarly, ice-water interfacial properties are impor-
31 tant for geophysical techniques like electromagnetic surveys, which are used to monitor
32 both permafrost³⁻⁶ and glaciers^{7,8}. Of particular importance is understanding adsorption
33 of impurities at the ice-water interface, as this affects surface electrical conductivity⁹, pre-
34 melted layer thickness¹⁰, ice rheology¹¹, and atmospheric chemical processes including ozone
35 depletion¹²⁻¹⁴.

36 The present work focuses on ice Ih, the hexagonal structure that is stable at ambient
37 conditions¹ and relevant to geophysical and atmospheric applications. The surface chemical
38 structure of pristine ice Ih remains an area of active research due partly to experimental
39 difficulties in probing the surface, and partly to the nature of the surface itself, which may
40 not be homogeneous in terms of atom location and in fact can change over time due to
41 residual entropy^{15,16}. As discussed by Petrenko¹⁷, the simple model of Fletcher^{18,19} has
42 proven particularly durable in terms of predicting various observed properties of the ice-air
43 interface. In this model, the oxygen atoms at the surface are preferentially oriented with
44 their protons facing out. This should give the surface a net positive charge, and indeed
45 experiments by Petrenko and Colbeck²⁰ showed that metal and dielectric sliders picked up a
46 positive charge from the surface of pure, polycrystalline ice at temperatures between -5 and
47 -35°C. Dosch et al.²¹ similarly demonstrated the presence of a positive surface charge on ice
48 at -12.8°C by measuring the abundance of Bjerrum defects with x-ray diffraction. Although
49 the Fletcher model describes the ice-air interface, it is relevant to the ice-water interface as
50 well due to the existence of a premelted layer at temperatures above about 200 K²².

51 However, there are situations in which the ice surface attains a negative surface charge.
52 For instance, in thunderstorms, the surface charge of ice crystals and graupel can be positive
53 or negative depending on temperature, cloud water content, and the presence of airborne
54 impurities like smoke²³⁻²⁵. This is not necessarily inconsistent with the Fletcher model.
55 Pedersen et al.²⁶ used long-timescale kinetic Monte Carlo simulations to show that molecular

56 reordering can occur on the basal plane of ice Ih, which might suggest that even pure ice
57 does not always have a positive surface charge. Dash et al.²⁷ showed that the rate of
58 ice crystal growth can also influence the surface charge when ice is grown from vapor, as
59 in thunderstorms. In particular, when crystal growth occurs at a sufficiently large free
60 energy difference between the liquid or vapor phase and the solid phase (above the so-called
61 roughening transition), the ice surface is rough and disordered, with OH⁻ ions preferentially
62 present at asperities^{2,27}. The presence of a thin premelted film of water between ice and
63 negatively charged silicate minerals typical of soils also points to a negative surface charge
64 on the ice since the existence of the premelted film relies on a balance between attractive
65 van der Waals forces and repulsive electrostatic forces^{2,28}. Finally, when a thin premelted
66 layer separates the bulk ice from air, the charge on the ice-water interface may be affected by
67 protonation and deprotonation reactions on the nearby air-water interface, which assumes a
68 negative charge at pH greater than about 4^{29,30}. Zeta potential measurements of the interface
69 between bulk ice and bulk water phases have demonstrated that the interface always has a
70 negative charge at neutral pH³¹⁻³⁵.

71 Dangling valences in the form of H and O atoms and are known to exist on the ice surface
72 from theoretical computation and experimental observation³⁶⁻⁴². As Buch et al.³⁹ note, these
73 dangling valences provide important surface sites for adsorbates. When the ice surface is
74 in contact with water containing dissolved ions, the ions will be attracted to unbalanced
75 charges at the ice-water interface, resulting in the formation of an electrical double layer.
76 Petrenko and Ryzhkin⁴³ theoretically predicted the existence of an electrical double layer
77 on the surface of pure ice whose thickness corresponded roughly to the thickness of the
78 premelted layer. Kallay et al.⁴⁴ and Inagawa et al.³⁵ showed that the zeta potential of the
79 ice surface in contact with brines could be described with the Guoy-Chapman model for the
80 electrical double layer in a manner analogous to metal oxide-brine interfaces. While previous
81 work has analyzed surface charge and electrical conduction at the ice-water interface, the
82 links between surface reactions with the charge and more importantly the structure of the
83 electrical double layer has not been presented. Here, I extend an existing model for surface
84 reactions at the ice-water interface, compare the model with data from the literature, and
85 make some predictions of charge distribution within the electrical double layer.

86 II. SURFACE REACTION AND CHARGE MODEL

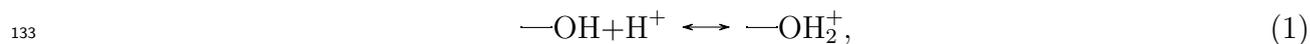
87 A. Model development

88 In hexagonal ice Ih, water molecules are arranged in a tetrahedral lattice in which most
89 of the lattice energy comes from hydrogen bonds¹. The arrangement of atoms in the ice
90 lattice should conform to the Bernal-Fowler-Pauling ice rules, which state that (1) every
91 oxygen atom is bonded covalently to 2 hydrogen atoms, and (2) every O–O vertex contains
92 1 hydrogen atom^{15,45}. These rules are sometimes violated, resulting in point defects. Ionic
93 defects arise from violations of the first rule, resulting in the presence of H_3O^+ or OH^-
94 ions. Bjerrum defects are the result of violating the second rule, with L- and D-defects
95 corresponding to O–O vertices with 0 or 2 hydrogen atoms^{1,46}. On the surface of an ice
96 crystal, the first rule is violated because of a lack of available bonds⁴⁷, so the surface has
97 dangling H and O atoms^{36,39}. The ordering and spatial arrangement of these dangling bonds
98 on pristine ice surfaces is an area of active research (e.g.,^{39,40,47,48}.

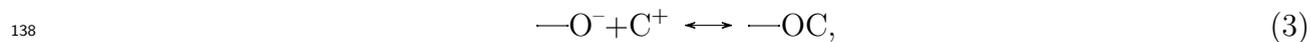
99 In the present work, I am concerned with reactions that occur on the surface of ice
100 in equilibrium with a bulk aqueous phase. This situation arises in many natural systems,
101 including saline permafrost and glaciers and snow that are close enough to the melting point
102 to have an interconnected network of premelted layers through a polycrystalline structure.
103 At a molecular level, the ice-water interface is not a discrete interface but a zone about 1
104 nm thick across which the molecular ordering changes from that of crystalline ice to liquid
105 water^{49–51}. The behavior of ions at this interface has been investigated in a few studies^{42,51,52},
106 which have demonstrated that Na^+ cations exhibit a strong affinity for the ice-water interface
107 through interactions with O atoms, while anions, particularly Cl^- and F^- , tend to bind with
108 positively charged dangling H^+ atoms and can also penetrate into the ice crystal lattice by
109 replacing O atoms and creating Bjerrum L-defects^{1,53,54}. Because the ice-water interface is
110 the interface between a solid and its melt, ionic association occurs not on a 2-dimensional
111 surface but on a surface where the ions can penetrate at least partially into the surface. This
112 has been demonstrated through molecular dynamics simulations both of salt ions^{42,51,52} and
113 metal cations⁵⁵. In the limit of complete penetration of the interface by dissolved ions, no
114 charge separation between the aqueous phase and the ice surface can exist, and the surface
115 would lack a zeta (electrokinetic) potential⁵⁶. The presence of a measurable zeta potential,

116 and its variation with salinity and pH, suggests that the ice-water interface can be treated as
117 a quasi-2-dimensional surface insofar as ionic association and electrical charge are concerned.

118 The amphoteric nature of water suggests that the dangling H and O atoms on the ice
119 surface can undergo protonation and deprotonation in equilibrium with an aqueous phase,
120 and further can act as Lewis acids and bases and serve as sorption sites for dissolved ions.
121 In light of this, it should be expected that surface reactions at the ice-water interface can be
122 described in a manner analogous to existing models for metal oxides in aqueous solutions.
123 Kallay et al.⁴⁴ and Inagawa et al.³⁵ both demonstrated that such models could explain
124 the variation of zeta potential at the ice-water interface as a function of salinity and pH.
125 Here I show the development of such a model to describe the distribution of charge within
126 the electrical double layer at the ice-water interface. I consider six reactions: protonation
127 and deprotonation of surface hydroxyls, sorption of H^+ and dissolved cations on dangling
128 O atoms, and adsorption and desorption of dissolved ions at charged surface sites. Water
129 molecules in the ice crystal structure at the ice-water interface can be oriented either with
130 a hydrogen atom or a lone pair pointing towards the water phase. The dangling hydrogen
131 atoms can undergo protonation or deprotonation. Following Schindler and Stumm⁵⁷, the
132 protonation and deprotonation reactions are

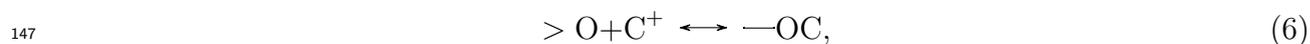
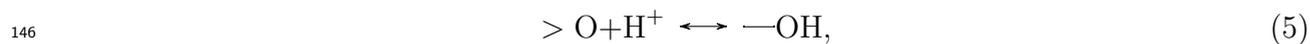


135 with equilibrium constants K_p and K_d . The deprotonated and protonation sites can act as
136 sorption sites for dissolved ions in the aqueous phase. Considering a simple 1:1 electrolyte,
137 the ion association reactions on deprotonated and protonated sites are



140 where C^+ and A^- represent the electrolyte cations and anions. The equilibrium constants for
141 Eqs. 3 and 4 are K_C and K_A . Water molecules at the ice-water interface oriented with lone
142 pairs on oxygen atoms pointing toward the liquid phase represent negatively charged surface

143 sites that can adsorb H^+ and C^+ ions. Assuming that these oxygen atoms are hydrogen-
144 bonded to one H atom of a neighboring water molecule in the ice lattice, these sites have a
145 single negative charge and the ion association reactions are



148 with equilibrium constants K_{HO} and K_{CO} .

149 The reactions in Eqs. 3, 4, and 6 represent surface charge neutralization, and the ions
150 involved are referred to as counterions. The interaction of counterions with the ice surface
151 gives rise to an electrical double layer: the Stern layer, which contains the counterions,
152 and the diffuse layer, within which the ionic concentrations vary with distance from their
153 concentration at the Stern plane to their concentrations in the bulk electrolyte (Fig. 1). For
154 simplicity, I assume that the Stern layer is immediately adjacent to the ice-water interface
155 and ignore any possible counterion penetration into the ice surface. Such penetration would
156 increase the capacitance of the Stern layer and result in a smaller potential difference between
157 the ice-water interface and the Stern plane⁵⁶. However, since the degree of penetration, if any,
158 is difficult to constrain, I will proceed with the understanding that Stern layer capacitances
159 may be underestimated from this model. In the model of Grahame⁵⁸, the Stern layer is
160 divided into the inner and outer Helmholtz layers by the β plane, which is located along
161 the centers of cations or anions that are adsorbed directly to the ice surface. Hydrated ions
162 do not approach the surface as closely, and the Stern plane is located along the centers of
163 hydrated ions that associate with the surface.

164 Following Revil and Glover⁵⁹, the equilibrium conditions for Eqs. 1–6 are expressed in
165 terms of electrochemical potentials μ_i^0 as

$$166 \quad \mu_{s,OH}^0 + \mu_{H^+}^0 = \mu_{s,OH_2^+}^0, \quad (7)$$

$$167 \quad \mu_{s,OH}^0 = \mu_{s,O^-}^0 + \mu_{H^+}^0, \quad (8)$$

$$168 \quad \mu_{s,O^-}^0 + \mu_{C^+}^0 = \mu_{s,OC}^0, \quad (9)$$

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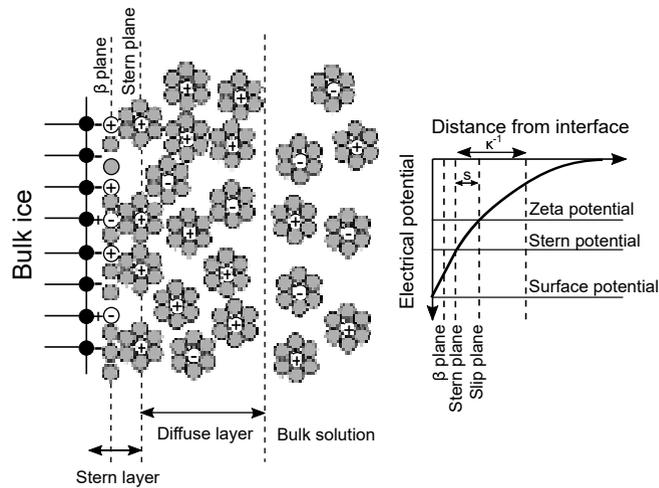


FIG. 1. Electrical double layer at the ice-water interface. Left: configuration of the Stern and diffuse layers at moderate pH. The Stern and β planes are labeled. O atoms on the ice surface (black circles) are protonated or deprotonated, and counterions (white circles) are arranged in the Stern layer where they neutralize the unbalanced charge. Gray circles represent water molecules at the ice surface and as hydration shells around aqueous ions. Right: electrical potential as a function of distance from the ice-water interface with important potentials noted. From the Debye-Hückel approximation, the Debye length κ^{-1} is the length over which the potential decreases by a factor of $1/e$ from its value at the Stern plane and the diffuse layer extends a distance $2\kappa^{-1}$ from the Stern plane.

$$169 \quad \mu_{s,\text{OH}_2^+}^0 + \mu_{\text{A}^-}^0 = \mu_{s,\text{OH}_2\text{A}}^0, \quad (10)$$

$$170 \quad \mu_{s,>\text{O}}^0 + \mu_{\text{H}^+}^0 = \mu_{s,\text{OH}}^0, \quad (11)$$

$$171 \quad \mu_{s,>\text{O}}^0 + \mu_{\text{C}^+}^0 = \mu_{s,\text{OC}}^0, \quad (12)$$

172 where the subscript s denotes a surface site (all nomenclature is defined in Table 1). The
173 electrochemical potentials are related to the standard chemical potentials by $\mu_i^0 = \mu_i^{(\circ)} +$
174 $kT \ln \Gamma_i^0$ for surface sites, where Γ_i^0 is the number density of surface site species i ; and
175 $\mu_i^0 = \mu_i^{(\circ)} + kT \ln 1000 N_A a_i - e z_i \varphi_\beta$ for ions in solution and $\mu_i^0 = \mu_i^{(\circ)} + kT \ln 1000 N_A a_i - e z_i \varphi_0$
176 for H^+ , where a_i is the activity of ionic species i in the bulk aqueous phase, N_A is Avogadro's

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177 number, e is the elementary charge, z_i is the charge number of the ion (positive or negative),
178 φ_0 is the surface potential, and φ_β is the potential on the β plane. Here, surface sites
179 are defined as dangling OH and O associated with water molecules in the outermost layer
180 of the ordered structure of ice. In the case of surface sites, the difference between the
181 electrochemical and standard chemical potentials is due to the entropy associated with the
182 different arrangements of the surface sites, while in the case of ions the difference is due to
183 entropy as well as the change in potential energy that results from bringing the ion from a
184 reference state at infinite distance to the surface.

Variable	Description	Dimensions
A	Debye-Hückel function A	$(\text{M}/\text{mol})^{\frac{1}{2}}$
a	Debye-Hückel constant	L
a_i	Activity of species i	mol/L^3
B	Debye-Hückel function B	$(1/\text{L})(\text{M}/\text{mol})^{\frac{1}{2}}$
b	Debye-Hückel constant	L^3/mol
C	Stern layer capacitance	$\text{T}^4\text{I}^2/\text{ML}^2$
C_f	Molar concentration of electrolyte in bulk aqueous phase	mol/L^3
C_i^f	Molar concentration of ionic species i in bulk aqueous phase	mol/L^3
e	Elementary charge	$\text{M}^{\frac{1}{2}}\text{L}^{\frac{3}{2}}\text{T}$
f	Counterion partition coefficient	-
I	Ionic strength	mol/L^3
I_m	Ionic strength in molality	mol/M
k	Boltzmann's constant	$\text{ML}^2/\text{T}^2\theta$
K_A	Equilibrium constant for anion sorption on protonated sites	-
K_C	Equilibrium constant for cation sorption on deprotonated sites	-
K_{CO}	Equilibrium constant for cation sorption on dangling O	-
K_d	Equilibrium constant for deprotonation	-

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K_{HO}	Equilibrium constant for H^+ sorption on dangling O	-
K_p	Equilibrium constant for protonation	-
N_A	Avogadro's number	1/mol
pK_w	Water dissociation constant	-
Q_s	Charge density in the diffuse layer	$M^{1/2}/L^{1/2}T$
Q_s^0	Surface charge density	$M^{1/2}/L^{1/2}T$
R	Universal gas constant	$ML^2/2mol$
T	Temperature	θ
z_i	Charge number of ionic species i	$1/L^2$
α	Inverse surface site density of OH groups	-
γ_i	Activity coefficient	-
Γ_i^0	Number density of surface site species i	$1/L^2$
Γ_i^d	Equivalent surface site density of species i in the diffuse layer	$1/L^2$
Γ_s^0	Total surface site density	$1/L^2$
ε	Relative dielectric permittivity	-
ε_0	Vacuum dielectric permittivity	L/L
ε_w	Water relative dielectric permittivity	-
ζ	Zeta potential	$M^{1/2}L^{1/2}T$
κ	Inverse Debye length	$1/L$
$\mu_i^{(o)}$	Standard chemical potential of species i	ML^2/T^2
μ_i^0	Electrochemical potential of species i	ML^2/T^2
ρ	Water density	M/L^3
φ	Potential	$M^{1/2}L^{1/2}T$
$\tilde{\varphi}_d$	Dimensionless reduced Stern potential	-
φ_0	Surface potential	$M^{1/2}L^{1/2}T$
φ_d	Stern potential	$M^{1/2}L^{1/2}T$
φ_β	Potential on the β -plane	$M^{1/2}L^{1/2}T$

Ω_i^0	Fractional surface site occupancy of species i
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TABLE I: Nomenclature

185 The equilibrium constants are defined in terms of the standard chemical potentials of the
186 species involved in Eqs. 1–6:

$$187 \quad \ln K_p = \frac{1}{kT}(\mu_{\text{OH}}^{(\circ)} + \mu_{\text{H}^+}^{(\circ)} - \mu_{\text{OH}_2^+}^{(\circ)}), \quad (13)$$

$$188 \quad \ln K_d = \frac{1}{kT}(\mu_{\text{OH}}^{(\circ)} - \mu_{\text{O}^-}^{(\circ)} - \mu_{\text{H}^+}^{(\circ)}), \quad (14)$$

$$189 \quad \ln K_C = \frac{1}{kT}(\mu_{\text{O}^-}^{(\circ)} + \mu_{\text{C}^+}^{(\circ)} - \mu_{\text{OC}}^{(\circ)}), \quad (15)$$

$$190 \quad \ln K_A = \frac{1}{kT}(\mu_{\text{OH}_2^+}^{(\circ)} + \mu_{\text{A}^-}^{(\circ)} - \mu_{\text{OH}_2\text{A}}^{(\circ)}), \quad (16)$$

$$191 \quad \ln K_{\text{HO}} = \frac{1}{kT}(\mu_{>\text{O}}^{(\circ)} + \mu_{\text{H}^+}^{(\circ)} - \mu_{\text{OH}}^{(\circ)}), \quad (17)$$

$$192 \quad \ln K_{\text{CO}} = \frac{1}{kT}(\mu_{>\text{O}}^{(\circ)} + \mu_{\text{C}^+}^{(\circ)} - \mu_{\text{OC}}^{(\circ)}), \quad (18)$$

193 where k is Boltmann's constant, T is absolute temperature, and $\mu_i^{(\circ)}$ is the standard chemical
194 potential of species i .

195 Combining these relationships with Eqs. 7–12 yields

$$196 \quad K_p = \frac{\Gamma_{\text{OH}_2^+}^0}{\Gamma_{\text{OH}}^0 a_{\text{H}^+}} e^{\frac{e\varphi_0}{kT}}, \quad (19)$$

$$197 \quad K_d = \frac{\Gamma_{\text{O}^-}^0 a_{\text{H}^+}}{\Gamma_{\text{OH}}^0} e^{-\frac{e\varphi_0}{kT}}, \quad (20)$$

$$198 \quad K_C = \frac{\Gamma_{\text{OC}}^0}{\Gamma_{\text{O}^-}^0 a_{\text{C}^+}} e^{\frac{e\varphi_\beta}{kT}}, \quad (21)$$

$$199 \quad K_A = \frac{\Gamma_{\text{OH}_2\text{A}}^0}{\Gamma_{\text{OH}_2^+}^0 a_{\text{A}^-}} e^{-\frac{e\varphi_\beta}{kT}}, \quad (22)$$

$$K_{HO} = \frac{\Gamma_{OH}^0}{\Gamma_{>O}^0 a_{H^+}} e^{\frac{e\varphi_0}{kT}}, \quad (23)$$

$$K_{CO} = \frac{\Gamma_{OC}^0}{\Gamma_{>O}^0 a_{C^+}} e^{\frac{e\varphi_\beta}{kT}}. \quad (24)$$

It should be noted that only 5 of these constants are independent because no distinction is made between surface OH and OC sites formed by association with deprotonated hydroxyls and dangling O atoms. Therefore,

$$K_{CO} = K_d K_C K_{HO}. \quad (25)$$

The surface charge density Q_s^0 is simply the sum of the charge densities of each surface site:

$$Q_s^0 = \sum_{i=1} e z_i \Gamma_i^0. \quad (26)$$

Since $z = 0$ for the neutral surface sites,

$$Q_s^0 = e(\Gamma_{OH_2^+}^0 - \Gamma_{O^-}^0 - \Gamma_{>O}^0). \quad (27)$$

Let the fractional surface site occupancies for positive sites Ω_+ and for negative sites Ω_- be defined as

$$\Omega_+ = \frac{\Gamma_{OH_2^+}^0}{\Gamma_s^0} = \frac{\Gamma_{OH}^0 a_{H^+} K_p}{\Gamma_s^0} e^{-\frac{e\varphi_0}{kT}}, \quad (28)$$

$$\Omega_- = \frac{\Gamma_{O^-}^0 + \Gamma_{>O}^0}{\Gamma_s^0} = \frac{\Gamma_{OH}^0}{\Gamma_s^0 a_{H^+}} \left(K_d + \frac{1}{K_{HO}} \right) e^{\frac{e\varphi_0}{kT}}, \quad (29)$$

where the total surface site density Γ_s^0 is

$$\Gamma_s^0 = \Gamma_{OH}^0 + \Gamma_{OH_2^+}^0 + \Gamma_{O^-}^0 + \Gamma_{>O}^0 + \Gamma_{OC}^0 + \Gamma_{OH_2A}^0. \quad (30)$$

From Eqs. 19–25 and 30, the ratio $\frac{\Gamma_s^0}{\Gamma_{OH}^0}$ can be expressed as

$$\frac{\Gamma_s^0}{\Gamma_{OH}^0} = 1 + \left[K_d + \frac{1}{K_{HO}} + \frac{K_{CO} a_{C^+}}{K_{HO}} e^{-\frac{e\varphi_\beta}{kT}} \right] \frac{e^{\frac{e\varphi_0}{kT}}}{a_{H^+}} + \left[1 + K_A a_A e^{\frac{e\varphi_\beta}{kT}} \right] K_p a_{H^+} e^{-\frac{e\varphi_0}{kT}} = \alpha. \quad (31)$$

219 Combining Eq. 31 with Eqs. 28 and 29 yields

$$220 \quad \Omega_+^0 = \frac{a_{\text{H}^+} K_p}{\alpha} e^{-\frac{e\varphi_0}{kT}}, \quad (32)$$

$$221 \quad \Omega_-^0 = \frac{1}{\alpha a_{\text{H}^+}} \left(K_d + \frac{1}{K_{\text{HO}}} \right) e^{\frac{e\varphi_0}{kT}}, \quad (33)$$

222 so Eq. 27 becomes

$$223 \quad Q_s^0 = e\Gamma_s^0(\Omega_+^0 - \Omega_-^0) = \frac{e\Gamma_s^0}{\alpha} \left(a_{\text{H}^+} K_p e^{-\frac{e\varphi_0}{kT}} - \frac{K_d + \frac{1}{K_{\text{HO}}}}{a_{\text{H}^+}} e^{\frac{e\varphi_0}{kT}} \right). \quad (34)$$

224 Electroneutrality requires that the surface charge be balanced by the charge in the diffuse
225 layer Q_s such that $Q_s^0 + Q_s = 0$. Assuming the Debye-Hückel approximation of low surface
226 potential (expressed for a 1:1 electrolyte as $|\frac{e\varphi_d}{2kT}| \ll 1$, where φ_d is the potential at the Stern
227 plane), from Pride⁶⁰ and Revil and Glover⁵⁹ Q_s may be expressed as

$$228 \quad Q_s = 2000\kappa^{-1} \sum_{i=1} e z_i N_A C_i^f e^{\frac{z_i \tilde{\varphi}_d}{2}}, \quad (35)$$

229 where $\tilde{\varphi}_d = -\frac{e\varphi_d}{kT}$ is the dimensionless reduced Stern potential and κ^{-1} is the Debye length
230 given by

$$231 \quad \kappa^{-1} = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{2000 N_A e^2 I}}, \quad (36)$$

232 where ε is the relative dielectric permittivity of the electrolyte, ε_0 is the vacuum permittivity,
233 and I is the ionic strength in mol/l. While the Debye-Hückel approximation is strictly
234 valid for $|\varphi_d| \ll 47$ mV at $T = 0^\circ\text{C}$, Pride⁶⁰ suggested it could be valid at even larger
235 potentials, though the upper limit is not defined. Available data in the literature suggest
236 that $|\varphi_d| < 47$ mV at the ice-water interface^{33,35,44}, so the Debye-Hückel approximation is
237 probably valid here.

238 Eqs. 35 and 36 may be combined with the electroneutrality condition for the electrolyte
239 ($C_{\text{A}}^f + C_{\text{OH}^-}^f = C_{\text{C}}^f + C_{\text{H}^+}^f$), where C_i^f is the molar concentration of species i in the aqueous
240 phase, to arrive at the Grahame equation in terms of salinity and pH^{44,59}:

$$241 \quad Q_s = \sqrt{8000\varepsilon\varepsilon_0 kT N_A I} \sinh \frac{\tilde{\varphi}_d}{2}, \quad (37)$$

242 where C_f is the electrolyte concentration in mol/l. Assuming that changes in pH are brought
 243 about by the addition of either HA or COH, where again A stands for a monovalent anion
 244 and C stands for a monovalent cation, let $C_{\text{H}^+}^f = 10^{-\text{pH}} = C_{\text{acid}}$ and $C_{\text{OH}^-}^f = 10^{\text{pH} + \text{pK}_w} = C_{\text{base}}$
 245 where pK_w is the dissociation constant for water (13.8). Under acidic conditions $C_f = C_C^f$
 246 and $C_A^f = C_f + C_{\text{acid}}$. while under basic conditions $C_A^f = C_f$ and $C_C^f = C_f + C_{\text{base}}$. Combining
 247 Eqs. 34 and 37, the behavior of the surface and Stern potentials as a function of pH, salinity,
 248 and temperature is described by

$$249 \quad \sqrt{8000\epsilon\epsilon_0kTN_AI} \sinh \frac{\tilde{\varphi}_d}{2} + \frac{e\Gamma_s^0}{\alpha} (a_{\text{H}^+} K_p e^{-\frac{e\varphi_0}{kT}} - \frac{K_d + \frac{1}{K_{\text{HO}}}}{a_{\text{H}^+}} e^{\frac{e\varphi_0}{kT}}) = 0. \quad (38)$$

250 B. Method of solution

251 The potentials and equilibrium constants in Eq. 38 can be determined through compar-
 252 ison with laboratory data. Typically what is known in laboratory measurements is pH,
 253 salinity, temperature, and zeta potential. The zeta potential ζ is the potential at the slip
 254 plane, which is located within the diffuse layer some distance from the Stern plane (Fig. 1).
 255 Estimates of this distance vary: Kallay et al.⁴⁴ assumed a value of 15 Å, which they selected
 256 based on previous work on adsorption of alcohols and organic molecules on hematite^{61,62}.
 257 Revil and Glover⁵⁹ found a value of 2.4 Å for quartz in contact with KCl solution based
 258 on a fit of experimental data. Other studies assume that the slip plane coincides with the
 259 Stern plane^{60,63}, which is probably reasonable in the absence of macromolecule or polymer
 260 adsorption⁶⁴. Therefore I assumed that $\zeta = \varphi_d$. Next, I assumed following Kallay et al.⁴⁴
 261 that the β - and Stern planes are collocated and that $\varphi_\beta = \varphi_d$. This is consistent with the
 262 reactions in Eqs. 1–4 in which only electrostatic interactions are assumed between electrolyte
 263 ions and the ice surface and there is no specific adsorption⁶⁵. In this case, the capacitance
 264 C of the Stern layer is

$$265 \quad C = \frac{Q_s^0}{\varphi_0 - \varphi_d}. \quad (39)$$

266 I assumed $C = 1 \text{ F/m}^2$, which is consistent with estimates from metal oxide-water
 267 interfaces^{66,67}.

268 The activities of ions in solution are determined from the molar concentrations C_i^f as
 269 $a_i = \gamma_i C_i^f$, where γ_i is the activity coefficient. The activity coefficient is calculated from

270 Debye-Hückel theory extended to high salinity⁶⁸:

$$271 \quad \log_{10} \gamma_i = -\frac{Az_i^2 \sqrt{I_m}}{1 + Ba\sqrt{I_m}} + bI_m, \quad (40)$$

272 where I_m is the ionic strength in molality and a and b are constants. The functions A and
273 B are given by

$$274 \quad A = \frac{N_A^2 e^3 \sqrt{2\rho}}{8\pi \ln 10 (\varepsilon_w \varepsilon_0 RT)^{\frac{3}{2}}}, \quad (41)$$

$$275 \quad B = \frac{N_A e \sqrt{2\rho}}{\sqrt{\varepsilon_w \varepsilon_0 RT}}, \quad (42)$$

276 where R is the universal gas constant and ρ and ε_w are the density and relative dielectric
277 permittivity of water. Eq. 40 is valid up to ionic strengths of about 2 molal or slightly less
278 than 2000 mM for NaCl and HCl⁶⁹. Here, for simplicity I assumed $\rho = 1000 \text{ kg/m}^3$, and
279 used $a = 4.78 \text{ \AA}$ and $b = 0.24 \text{ L/mol}$ for H^+ , $a = 4.32 \text{ \AA}$ and $b = 0.06 \text{ L/mol}$ for Na^+ , and
280 $a = 3.71 \text{ \AA}$ and $b = 0.01 \text{ L/mol}$ for both Cl^- and NO_3^- ^{69,70}.

281 Finally, I assumed Γ_s^0 had a constant value of 5.7 sites/ nm^2 . This is based on a assumption
282 of hexagonal ice Ih with an a -axis length of 0.45 nm^2 ⁷¹. With these assumptions and the
283 relationship expressed in Eq. 25, fitting zeta potential versus salinity or pH using Eq. 38
284 requires optimizing for K_p , K_d , K_C , K_A , and K_{HO} .

285 III. RESULTS AND DISCUSSION

286 A. Model predictions

287 In this section I compare the surface charge model to results in the literature. This
288 comparison involves using measurements of zeta potential as a function of pH and salinity
289 to determine the equilibrium constants and surface charge density by optimizing Eq. 38. In
290 this comparison I assume that the zeta potential is equal to the Stern potential φ_d . While
291 this is not always necessarily the case, in the absence of macromolecule adsorption the two
292 should be very close to each other^{60,64}. The literature results I used for this comparison are
293 from Drzymala et al.³³, Kallay et al.⁴⁴, and Inagawa et al.³⁵. I note here that measuring
294 the zeta potential of the surface of ice in contact with water is difficult. Drzymala et
295 al.³³ used conventional electrophoretic mobility measurements on crushed ice particles in

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296 low-salinity brine, but used D_2O as the ice phase (melting temperature $3.8^\circ C$) to allow a
297 working temperature range within which the ice would remain frozen and the brine would
298 remain liquid. Kallay et al.⁴⁴ reported the results of Kallay and Čakara³⁴, who used a
299 specially constructed ice electrode to measure the potential between the ice-coated electrode
300 and the brine solution. Inagawa et al.³⁵ measured the electrophoretic mobility of tracer
301 particles (polystyrene) in brine through a microchannel in ice and added glycerol to the
302 brine to prevent freezing. The difficulty of making these measurements and the necessity for
303 custom-built equipment means that there are few published results, and that those results
304 can sometimes have large uncertainties (e.g.,³³).

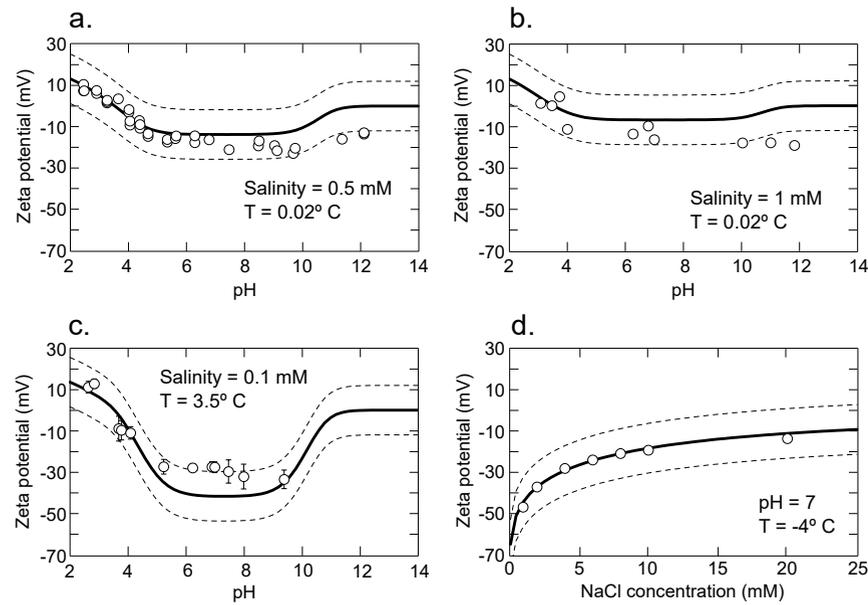


FIG. 2. Comparison of predicted zeta potential from Eq. 38 with literature results. Circles are measured data points, dark black lines are model predictions, and dashed lines are ± 2 standard deviations. Salinities and temperatures are noted on each subplot. (a) Data from Kallay and Čakara³⁴ using water and $NaNO_3$. Zeta potential was measured with an ice electrode. (b) Data from Kallay and Čakara³⁴ using water and $NaNO_3$. Zeta potential was measured with an ice electrode. (c) Data from Drzymala et al.³³ using frozen D_2O and liquid H_2O with $NaCl$. Zeta potential was determined from electrophoretic mobility of crushed ice particles in brine solution. (d) Data from Inagawa et al.³⁵ using water and $NaCl$ with glycerol to prevent freezing. Zeta potential was determined from electrophoretic mobility of polystyrene tracer particles through a microchannel in ice.

305 The comparison between measurements and predictions from Eq. 38 are shown in Fig. 2.
306 The corresponding equilibrium constants are given in Table 2 with uncertainties determined
307 using the bootstrap method described in Hu et al.⁷².

Constant	Value ± 1 standard deviation
$\log_{10}K_p$	-0.0617 ± 0.0137
$\log_{10}K_d$	-7.44 ± 1.80
$\log_{10}K_C$	6.45 ± 1.94
$\log_{10}K_A$ (for Cl^-)	0.205 ± 0.0273
$\log_{10}K_A$ (for NO_3^-)	0.160 ± 0.0313
$\log_{10}K_{HO}$	7.60 ± 1.83

TABLE II. Equilibrium constants derived from reported experimental data

308 Zeta potential values are positive under strongly acidic conditions and negative over the
309 rest of the pH range represented in the data. The pH corresponding to a zeta potential of
310 zero, known as the pH at the point of zero charge or pH(pzc), is the pH value at which
311 $\Gamma_{>O}^0 + \Gamma_{O^-}^0 = \Gamma_{\text{OH}_2^+}^0$. From Eqs. 19, 20, and 23,

$$312 \quad \text{pH(pzc)} = -\frac{1}{2} \log_{10} \left[\frac{1}{K_p} \left(\frac{1}{K_{HO}} + K_d \right) \right]. \quad (43)$$

313 Using the average values for K_p , K_d , and K_{HO} from Table 2, I obtain $\text{pH(pzc)} = 3.69$. This
314 is consistent with the results of Drzymala et al.³³ and Kallay et al.⁴⁴.

315 B. Surface site occupancies and surface reactions

316 The model fits in Fig. 2 all predict that the zeta potential reaches a plateau at pH between
317 about 5 and 10 and decreases to near neutral at $\text{pH} < 11$. This behavior can be understood
318 in terms of the number of sites with a given charge present at the ice-water interface. The
319 fractional surface site occupancies are defined in a manner analogous to Eqs. 32 and 33 as

$$320 \quad \Omega_{>O}^0 = \frac{1}{\alpha K_{HO} a_{\text{H}^+}} e^{\frac{e\varphi_0}{kT}}, \quad (44)$$

$$321 \quad \Omega_{O^-}^0 = \frac{K_d}{\alpha a_{\text{H}^+}} e^{\frac{e\varphi_0}{kT}}, \quad (45)$$

322
$$\Omega_{\text{OH}}^0 = \frac{1}{\alpha}, \quad (46)$$

323
$$\Omega_{\text{OH}_2^+}^0 = \frac{a_{\text{H}^+} K_p}{\alpha} e^{-\frac{e\varphi_0}{kT}}, \quad (47)$$

324
$$\Omega_{\text{OH}_2\text{A}}^0 = \Omega_{\text{OH}_2^+}^0 K_A a_A e^{\frac{e\varphi_d}{kT}}, \quad (48)$$

325
$$\Omega_{\text{OC}}^0 = 1 - \Omega_{>\text{O}}^0 - \Omega_{\text{O}^-}^0 - \Omega_{\text{OH}}^0 - \Omega_{\text{OH}_2^+}^0 - \Omega_{\text{OH}_2\text{A}}^0. \quad (49)$$

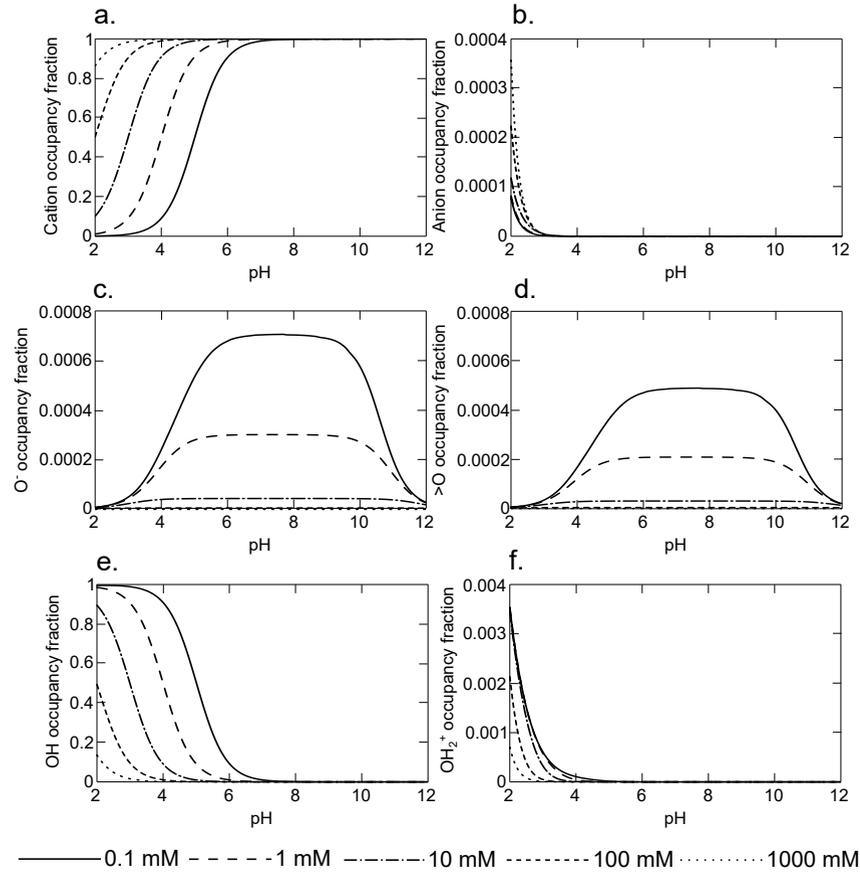


FIG. 3. Fractional site occupancies at different NaCl concentrations at $T = 0^\circ\text{C}$ for cations (a), anions (b), O^- (c), $>\text{O}$ (d), OH (e), and OH_2^+ (f).

326 Fig. 3 shows $\Omega_{>\text{O}}^0$, $\Omega_{\text{O}^-}^0$, Ω_{OH}^0 , $\Omega_{\text{OH}_2^+}^0$, $\Omega_{\text{OH}_2\text{A}}^0$, and Ω_{OC}^0 as a function of pH at various salinities
 327 and $T = 0^\circ\text{C}$ using the average equilibrium constant values from Table 2 (K_A was taken
 328 as the value corresponding to Cl^-). While it is not physically possible for ice to exist in

329 equilibrium with anything except pure water at this temperature, it is useful to perform all
330 the calculations at a consistent temperature. Since adsorption of dissolved ions neutralizes
331 surface charge in the modeled reactions (Eqs. 1–4), any nonzero zeta potential values are due
332 to excess charge that is not neutralized. Therefore, zeta potential should follow the trend of
333 available O^- , $> \text{O}$, or OH_2^+ sites. Figs. 3a and 3b show that cations occupy nearly all surface
334 sites above a pH value that decreases as salinity increases, and that anions occupy a small
335 amount of surface sites below $\text{pH}(\text{pzc})$. Despite the cation occupancy being so large, some
336 O^- and $> \text{O}$ sites are exposed at pH between about 4 and 12, and occupancy of these sites
337 follows the trend of zeta potential (Figs. 3c and 3d). Interestingly, the surface occupancies
338 of cations and OH nearly mirror each other (Fig. 3e).

339 These features can be explained in terms of the surface reactions assumed in the model
340 (Eqs. 1–6). O^- and $> \text{O}$ occupancy are predicted overall to be very small even at low salinity.
341 This suggests that at most only a small fraction of OH sites remain deprotonated, and that
342 $> \text{O}$ readily adsorbs cations. On the other hand, the reduction in H^+ concentration in the
343 aqueous phase at elevated pH should drive towards the aqueous phase, so one might expect
344 that O^- and $> \text{O}$ should be more abundant on the surface at higher pH. The decrease
345 in O^- and $> \text{O}$ surface occupancy at $\text{pH} > 10$ appears inconsistent with this, but it is
346 important here to remember my assumption that basic pH is the result of addition of a
347 hydroxide of the aqueous cation (in this case NaOH), which causes the cation concentration
348 in the aqueous phase to increase along with the hydroxide concentration. This would inhibit
349 the preservation of a net negative charge at high pH as any aqueous Na^+ would segregate
350 towards the ice-water interface. The high surface occupancy of Na^+ appears to suggest
351 that nearly all the OH sites deprotonate and that Na^+ replaces the missing H^+ at nearly
352 all of them. This is supported by the complementary relationship between cation and OH
353 occupancies (Figs. 3a and 3e). Inagawa et al.³⁵ suggested that only about 1.4% of OH
354 sites were deprotonated above pH of 5, which they ascribed to proton disorder of the ice
355 surface inhibiting deprotonation of neighboring OH sites through fast reorientation of water
356 molecules. It is important to note that surface occupancy represents the net concentration
357 on the surface, so these two facts are not necessarily inconsistent. Indeed, the opposite
358 trends of Na^+ and OH occupancy indicate that Na^+ is taking the place of OH on the surface
359 as pH increases, which requires the latter first to be deprotonated. Additional cations
360 are taken up by the $> \text{O}$ sites. The small negative zeta potential observed on the ice-water

361 interface at moderate pH indicates that nearly all of the negative surface sites are neutralized
362 by cations, but the remaining negative surface sites consist of both deprotonated OH and
363 dangling O. It is important to note here that this model does not consider bonding of Na^+
364 ions with multiple O atoms on the ice surface as suggested, for instance, by the simulations
365 of Shoaib and Choi⁴². This would reduce the number of Na^+ ions required to occupy all
366 available surface sites, but is also inconsistent with the Guoy-Chapman model. A different
367 description of the electrical double layer at the ice-water interface could be developed, but
368 that is beyond the scope of this work.

369 The computed surface site occupancies in Fig. 3 provide some insight into the relative
370 proportions of dangling OH and dangling O on the ice-water interface. Fletcher³⁶ suggested
371 that, at low temperatures (<70 K) the ice-air interface contains roughly equal amounts of
372 dangling OH and dangling O. This was supported by Buch et al.³⁹ using molecular dynam-
373 ics simulations. On the other hand, Nojima et al.⁷³ showed that the ice-air interface has
374 predominantly dangling OH at 100 K. Ishiyama and Kitanaka⁷⁴ found using molecular dy-
375 namics simulations that the ice-water interface contains nearly equal numbers of dangling
376 OH and dangling O, with a slight preference for dangling OH. In Figs. 3c and 3d, the present
377 model predicts that deprotonated OH groups are indeed favored over dangling O, but not by
378 much. From Eqs. 44 and 45, $\frac{\Omega_{\text{O}^-}^0}{\Omega_{>\text{O}}^0} = \frac{\Gamma_{\text{O}^-}^0}{\Gamma_{>\text{O}}^0} = K_d K_{HO}$, which means that there are about 1.4
379 times as many deprotonated OH as there are dangling O, even in pure water. Ishiyama and
380 Kitanaka⁷⁴ ascribe this to the fact that more hydrogen bonds exist on average in ice than
381 in water, creating a slight imbalance at the interface. Similar molecular dynamics results
382 were reported by Bryk and Haymet⁷⁵. Overall, my results support these previous results
383 and indicate that the ice-water interface slightly favors dangling OH groups.

384 C. Surface charge density

385 The surface charge density Q_s^0 is the sum of the number of each surface site per unit
386 area times its charge (Eq. 26), and is determined as a function of salinity and pH from
387 Eq. 34. The maximum value of Q_s^0 corresponds to complete occupancy of all surface sites
388 either by positive or negative charges and is equal to $\pm e\Gamma_s^0$. Using $\Gamma_s^0 = 5.7$ sites/nm²
389 yields a maximum Q_s^0 of ± 0.91 C/m². However, because the fractional surface occupancy
390 of different ionic species varies with salinity and pH (Fig. 3), the maximum Q_s^0 may not

necessarily be reached. The value of Q_s^0 is important to constrain as it determines the electrostatic potential of the ice-water interface and electrostatic forces between adjacent ice crystals separated by water, which are significant parameters affecting processes from lightning generation to atmospheric chemistry to frost heave and glacier motion^{2,24}.

Fig. 4 shows Q_s^0 calculated from Eq. 34 as a function of pH and salinity at 0°C. The average equilibrium constants from Table 2 were used for calculation. For salinities greater than about 100 mM, $Q_s^0 \approx 0$ for pH greater than the point of zero charge (3.69). Q_s^0 is always positive for pH < 3.69, and negative for pH > 3.69 at lower salinities. However, Q_s^0 remains well below the maximum value in the range of pH and salinity I considered. This broadly follows the trends of the unoccupied positive and negative surface sites (Fig. 3), driven by the strong affinity of Na⁺ for the surface at alkaline pH and the abundance of exposed neutral surface sites at acidic pH.

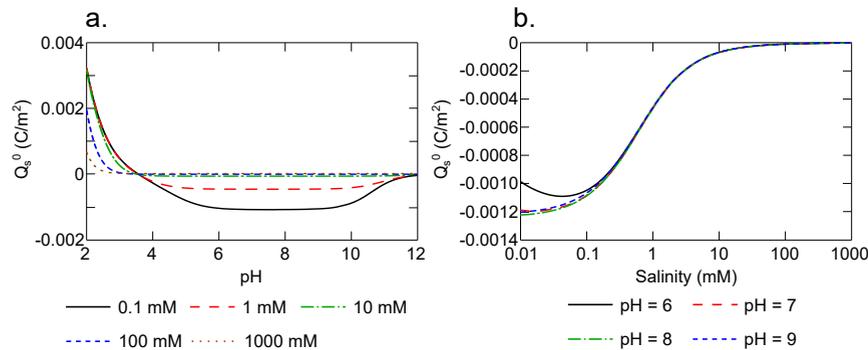


FIG. 4. Surface charge density at $T = 0^\circ\text{C}$ as a function of pH (a) and salinity (b).

These surface charge density values have implications for the thickness of a premelted layer that can exist between ice grains or between ice and air. Wettlaufer¹⁰ presented an analysis of the equilibrium premelted layer thickness by minimizing the total system free energy, including excess surface energy contributed by van der Waals and electrostatic interactions. The equilibrium premelted layer thickness therefore depends on a balance of colligative, van der Waals, and electrostatic energies. Thomson et al.⁷⁶ compared this theory with optical measurements of premelted layer thickness at ice grain boundaries in equilibrium with brines of varying salinity, and showed that the results could be explained by the limit in which electrostatic repulsion was insignificant (i.e., small Q_s^0), though they also showed that the data could equally be explained by assuming a very large Q_s^0 . For $|Q_s^0| \sim \mathcal{O}(10^{-3})$ C/m², model-based calculations of premelted layer thickness indicate that

414 the thickness scales inversely with undercooling for NaCl concentrations above about 1
415 mM⁷⁷, which suggests that electrostatic repulsion is negligible above this salinity with the
416 surface charge densities I predicted. The calculated layer thicknesses are < 10 nm for
417 undercoolings larger than about 0.1 K. That being said, model calculations are sensitive to
418 input parameters that may have considerable uncertainty, for example Hamaker constants.
419 In their recent review on premelting, Slater and Michaelides⁷⁸ present a summary of physical
420 measurements of premelted layer thickness as a function of temperature, which indicates that
421 the layer is generally thinner than 10 nm, and persist to temperatures as low as about 248
422 K. This is consistent with the simulation results of Llombart et al.²². Since larger surface
423 charge densities tend to cause the premelted layer to collapse at larger temperatures⁷⁷, my
424 results are consistent with the general idea of the ice-water interface having a sufficiently low
425 surface charge density that premelted layer thickness is governed mainly by van der Waals
426 and colligative energies.

427 **D. Partitioning of cations in the electrical double layer and induced** 428 **polarization**

429 The cations in the electrical double layer will be partitioned between the diffuse and
430 Stern layers. Understanding the degree of this partitioning is important for predicting the
431 electrical properties of the ice-water interface, and particularly the frequency dependence of
432 those properties. In the presence of an alternating electrical field, the complex conductivity
433 of porous media such as sand packs and glass beads exhibit an increase in the
434 imaginary (quadrature) component of conductivity at low frequencies (< 100 Hz). This
435 relaxation is generally attributed to polarization of the Stern and/or diffuse layers, which
436 occurs as charges move within the electrical double layer in response to the applied external
437 field. Stern and diffuse layer polarization has been studied extensively by many authors⁷⁹⁻⁸⁷,
438 and it is not relevant here for me to describe the phenomena in detail. I note here that I
439 focus in this section on induced polarization due to ionic mobility in the electrical double
440 layer. Several other polarization mechanisms operate at the ice-water interface, including
441 rotational relaxations in the ice and water near the ice surface caused by the intrinsic dipole
442 of water^{88,89}. These effects at higher frequency could be accounted for through consideration
443 of the orientation of water molecules that associate with the OH and dangling O surface

444 sites, but that is beyond the scope of the present study.

445 Generally speaking, the amount of polarization that occurs in the Stern and diffuse lay-
446 ers and the corresponding imaginary conductivity response depends on the concentration
447 of ions within each layer and their mobilities^{85,87}. Complex conductivity measurements of
448 sand packs, glass beads, and clays show evidence of this polarization, even in materials with
449 low surface area⁹⁰. In contrast, when complex conductivity measurements are performed on
450 mixtures of sediments, ice, and brine, there is no apparent contribution from polarization of
451 the electrical double layer at the ice-water interface, with only the electrical double layer on
452 the mineral grains affecting the response^{8,89,91}. A large body of literature on the electrical
453 conductivity of ice (both low-frequency and high-frequency) similarly suggests that the elec-
454 trical double layer at the ice-water interface plays little to no role in electrical conduction,
455 and that the conductivity of brine channels at grain boundaries follows Archie's law with no
456 contribution from conduction in the electrical double layer^{53,88,89,92-95}. These measurements
457 suggest instead that Jaccard theory⁹⁶ best describes electrical conductivity of ice, whereby
458 current flows via migration of proton point defects, even at the ice-water interface⁸⁹.

459 The apparent lack of Stern and diffuse layer polarization and contribution of the electrical
460 double layer to ice conductivity can be explained in terms of the charge distribution within
461 the electrical double layer. Following Leroy et al.^{85,97}, I define a partition coefficient f for
462 the counterions, which is the fraction of counterions in the electrical double layer that are
463 contained in the Stern layer:

$$464 \quad f = \frac{\Gamma_i^0}{\Gamma_i^0 + \Gamma_i^d}, \quad (50)$$

465 where Γ_i^d is the equivalent surface site density in the diffuse layer. Since the counterions are
466 cations at $\text{pH} > \text{pH}(\text{pzc})$ and anions at $\text{pH} < \text{pH}(\text{pzc})$, the subscript i can refer either to
467 cations or anions depending on pH. The equivalent site densities are defined as

$$468 \quad \Gamma_i^d \equiv 1000 N_A C_i^f \int_0^{\frac{2}{\kappa}} \left(\exp\left[-\frac{z_i e \varphi(x)}{kT}\right] - 1 \right) dx, \quad (51)$$

469 where $\varphi(x)$ is the local potential at a distance x from the ice-water interface^{59,97}. Using the
470 Debye-Hückel approximation,

$$471 \quad \varphi(x) \approx \varphi_d \exp(-\kappa x). \quad (52)$$

472 The surface site densities are $\Gamma_{\text{OH}_2\text{A}}^0 = \Gamma_s^0 \Omega_{\text{OH}_2\text{A}}^0$ and $\Gamma_{\text{OC}}^0 = \Gamma_s^0 \Omega_{\text{OC}}^0$, where Ω_{OC}^0 and $\Omega_{\text{OH}_2\text{A}}^0$
473 are given by Eqs. 48 and 49.

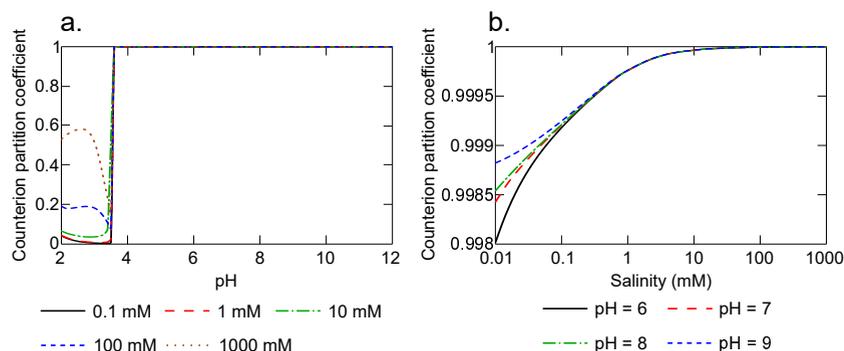


FIG. 5. Counterion partition coefficient as a function of pH (a) and salinity (b) at $T = 0^\circ\text{C}$. Note that for $\text{pH} < \text{pH}(\text{pzc})$, the counterions are anions, while for $\text{pH} > \text{pH}(\text{pzc})$ the counterions are cations.

474 Fig. 5 shows the partition coefficient as a function of pH and salinity at 0°C . For
475 $\text{pH} > \text{pH}(\text{pzc})$, almost all the counterions are contained in the Stern layer, while at
476 $\text{pH} < \text{pH}(\text{pzc})$ partitioning is more variable. In the pH range of 6–9, which is of great
477 interest for geophysical and atmospheric applications, $f > 0.998$ over the entire salinity
478 range I considered. This indicates that nearly all the counterions are contained in the Stern
479 layer and that the ion concentration in the diffuse layer is nearly identical to that of the
480 bulk aqueous phase. There are two main implications arising from this result. First, there
481 is very little excess conductivity in the diffuse layer with respect to the bulk electrolyte, and
482 regardless of salinity the electrical double layer will behave as if the diffuse layer had negli-
483 gible thickness. Overall this means that no diffuse layer polarization will occur and that the
484 diffuse layer does not contribute to excess surface conductivity. This is consistent with ob-
485 servations. Second, the high concentration of counterions in the Stern layer is likely related
486 to the observed lack of Stern layer conductivity and polarization due to reduced counterion
487 mobility. Some clays, particularly kaolinite, have similarly large proportions of counterions
488 in their Stern layers ($f > 0.95$)⁹⁸ and the dense packing of counterions appears to result in
489 a drastically reduced mobility within the Stern layer (at least 100 times smaller)⁸⁶. It is not
490 surprising therefore that the ice-water interface has a negligible conductivity contribution
491 from the electrical double layer and exhibits little low-frequency relaxation response. The
492 fact that counterions can penetrate partially into the ice surface will additionally restrict

493 their mobility.

494 IV. CONCLUSIONS

495 The hypothesis underlying this work was that existing models for describing the electrical
496 double layer at metal oxide-water interfaces should be able to be modified to describe the
497 surface charge, surface potential, and ionic occupancy at the ice-water interface. To test
498 this, I used an existing model for the electrical double layer at metal oxide-brine interfaces
499 to describe the surface charge and ion occupancy at the ice-water interface. The model
500 considers protonation and deprotonation on the ice surface as well as adsorption of aqueous
501 ions. I compared the model to measurements of ice zeta potential in brines of various
502 strengths and pH to determine the equilibrium constants for each of the surface reactions.
503 The results indicated a consistent pH at the point of zero charge of 3.69. Aqueous cation
504 adsorption is by far the dominant surface reaction, even at very low salinities, with an
505 equilibrium constant at least 5 orders of magnitude larger than the others. These cations
506 occupy nearly all the available surface sites at $\text{pH} > 7$ in fresh water (0.1 mM salinity) and at
507 $\text{pH} > 3$ in brines of seawater salinity or higher. Deprotonated OH groups are slightly favored
508 over dangling O sites, which is consistent with previous work^{74,75}. At moderate pH (between
509 6 and 9), the surface charge density varies from around -0.001 C/m^2 at salinity $< 1 \text{ mM}$ to
510 near 0 at higher salinity.

511 The surface complexation model allowed me to make predictions about the partitioning
512 of counterions between the Stern and diffuse layers. For $\text{pH} < 3.69$, the counterions are
513 anions and are preferentially located in the diffuse layer. However, when $\text{pH} > 3.69$ and
514 the counterions are cations, the partition coefficient is > 0.998 , indicating that the vast
515 majority of the counterions are located in the Stern layer. This has important implications
516 for electrical conductivity and the induced polarization response of the ice-water interface
517 at the moderate pH values of interest to atmospheric and geophysical applications. In
518 particular, diffuse layer polarization will not occur since the ionic concentration in the diffuse
519 layer is nearly identical to that of the bulk electrolyte, and Stern layer polarization and
520 electrical conduction will tend not to occur because the high cation concentration and partial
521 penetration into the ice surface will drastically reduce cation mobility. This is consistent
522 with observations.

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533 **DATA AVAILABILITY STATEMENT**

534 Data sharing is not applicable to this article as no new data were created or analyzed in
535 this study.

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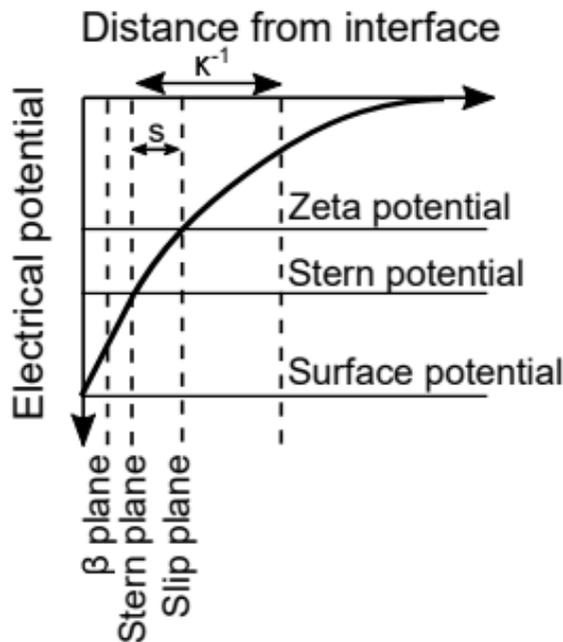
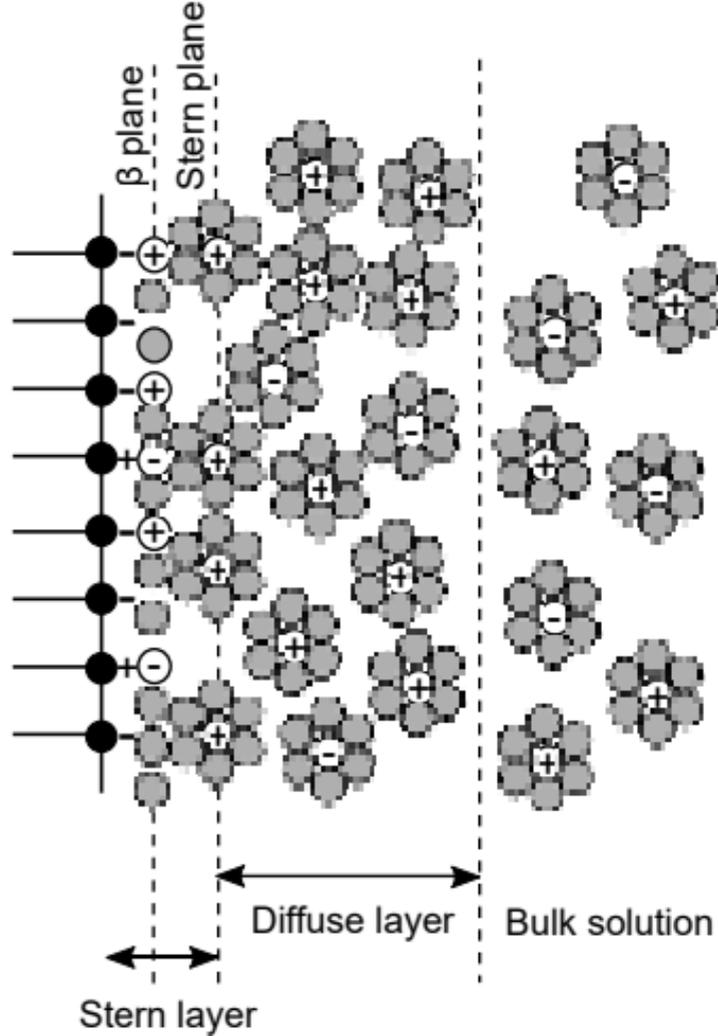
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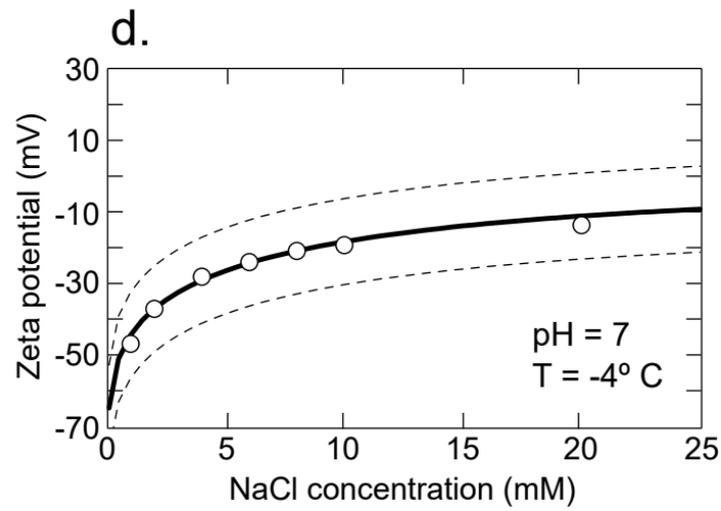
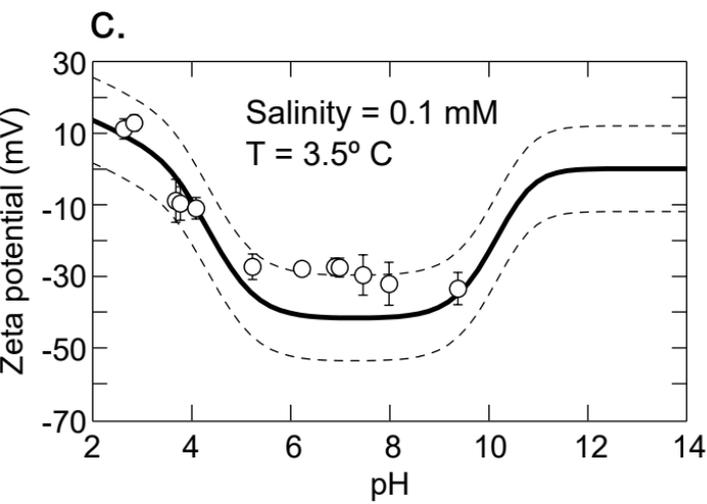
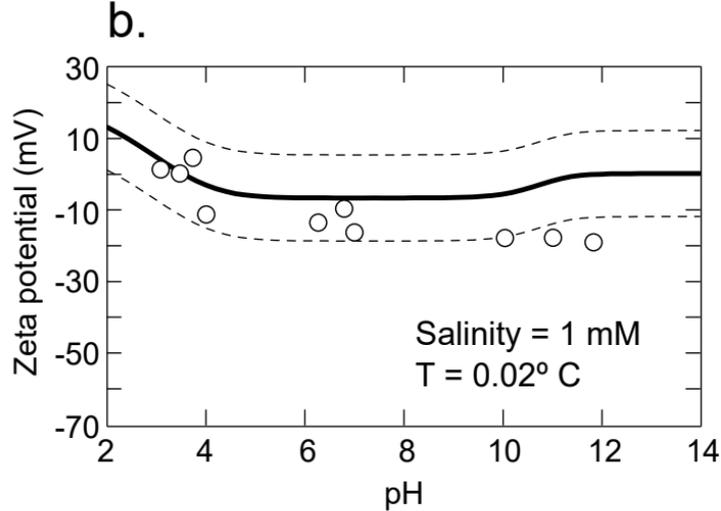
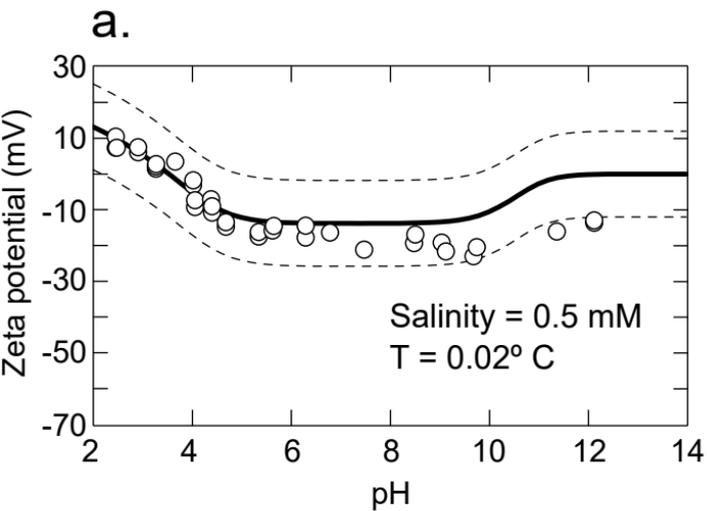
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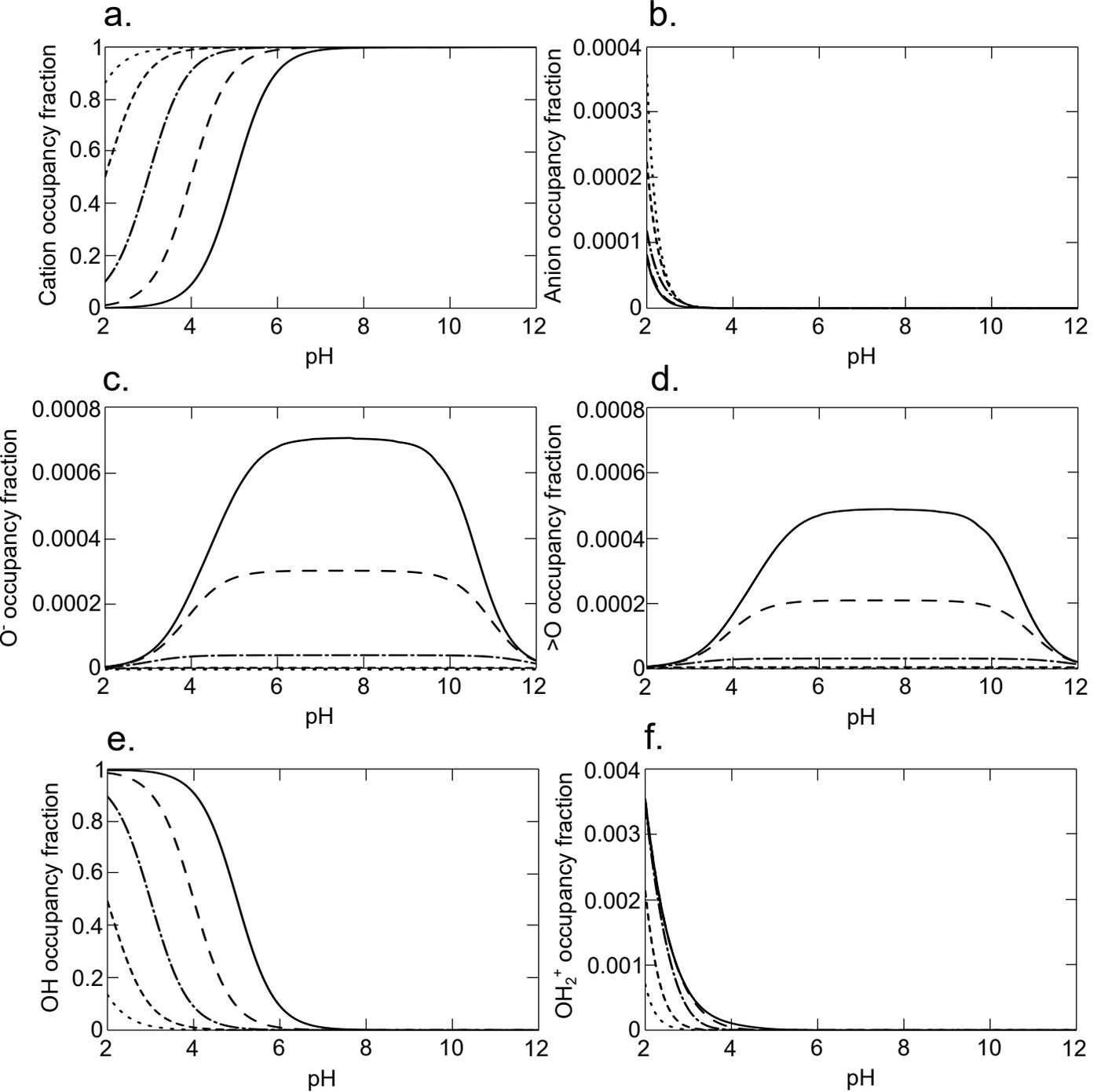
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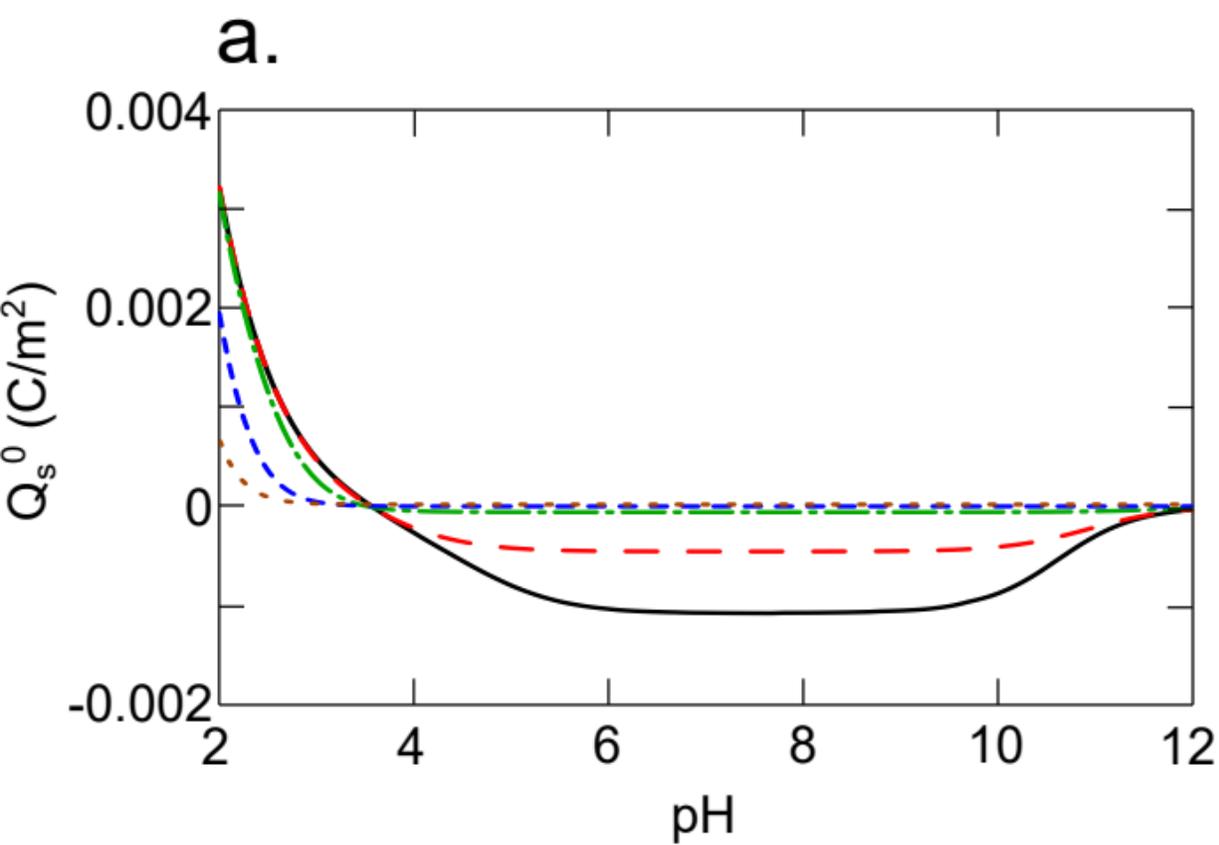
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Bulk ice

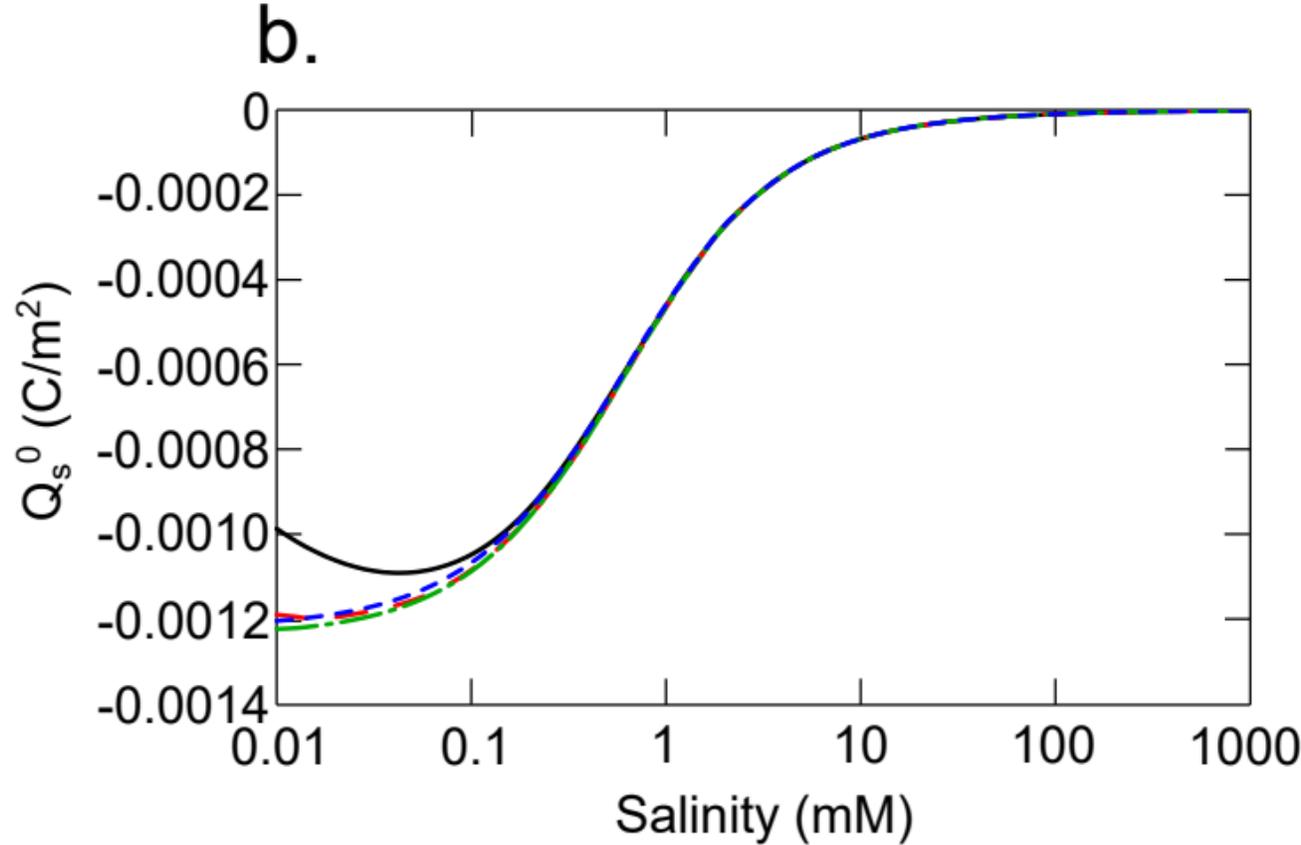








— 0.1 mM - - - 1 mM - · - · - 10 mM
- - - 100 mM · · · · 1000 mM



— pH = 6 - - - pH = 7
- · - · - pH = 8 · · · · pH = 9

