Liquid-like Layers on Ice in the Environment: Bridging the Quasi-liquid and Brine Layer Paradigms

SUPPLEMENTARY MATERIAL

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A. Derivation of BL Model (eqs. 1 and 2)

List of symbols

Symbol	***Quantity***
T	System temperature
T_m	Bulk melting temperature of ice
P	System pressure
f_w^{ice}	Fugacity of pure ice
$\hat{f}_w^{brine}$	Fugacity of water in brine layer
x_w	Mole fraction of water in brine layer
$x_{w,0}$	Mole fraction of water in unfrozen solution
H_w^{ice}	Enthalpy of ice at T, P
$H_w^{ice,0}$	Enthalpy of ice at reference state
$\overline{H}_w^{brine}$	Partial molar enthalpy of water in brine layer
$H_w^{liq,0}$	Enthalpy of water in unfrozen liquid solution
$\overline{V}_w^{brine}$	Partial molar volume of water in brine layer
ΔH_w^{fus}	Enthalpy change of fusion
$\Delta\overline{H}_w^{brine}$	Enthalpy change upon formation of brine layer
ΔV_w^{fus}	Volume change of fusion
$\Delta\overline{V}_w^{brine}$	Volume change upon formation of brine layer
γ_w	Activity coefficient of water in brine

f_w^{vap}	Fugacity of water in vapor space above ice
ΔH_w^{vap}	Enthalpy change upon vaporization
ΔV_w^{vap}	Volume change upon vaporization
φ	Liquid water fraction
n_w^{brine}	Moles of water in brine layer
n_w	Total number of moles of water
n_s	Number of moles of solute
d	Thickness of liquid layer
V	Volume of ice sample
A	Surface area of ice sample
ρ_w	Density of water
ρ_{ice}	Density of ice

At equilibrium (Tester and Modell, 1996),

$$d\ln f_w^{ice} = d\ln \hat{f}_w^{brine} \qquad \text{(S1)}$$

Expanding,

$$\left(\frac{\partial \ln f_w^{ice}}{\partial T}\right)_P dT + \left(\frac{\partial \ln f_w^{ice}}{\partial P}\right)_T dP = \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial T}\right)_{P,x_w} dT + \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial P}\right)_{T,x_w} dP + \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} dx_w \quad \text{(S2)}$$

Substituting for the partial derivatives of fugacity,

$$-\left(\frac{H_w^{ice}-H_w^{ice,0}}{RT^2}\right) dT + \frac{V_w^{ice}}{RT} dP = -\left(\frac{\bar{H}_w^{brine}-H_w^{liq,0}}{RT^2}\right) dT + \frac{\bar{V}_w^{brine}}{RT} dP + \left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x}\right)_{T,P} dx_w \qquad \text{(S3)}$$

Collecting terms,

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} \frac{dx_w}{dT} = -\left(\frac{H_w^{ice}-\bar{H}_w^{brine}}{RT^2}\right) + \frac{V_w^{ice}-\bar{V}_w^{brine}}{RT}\frac{dP}{dT} \qquad \text{(S4)}$$

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} \frac{dx_w}{dT} = -\left(\frac{\Delta H_w^{fus}-\Delta\bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{fus}-\Delta\bar{V}_w^{brine}}{RT}\right)\frac{dP}{dT} \qquad \text{(S5)}$$

we know

$$\hat{f}_w^{brine} = \gamma_w f_w x_w \qquad \text{(S6)}$$

therefore,

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P} = \frac{1}{\gamma_w f_w x_w}\gamma_w f_w = \frac{1}{x_w} \quad \text{(S7)}$$

and

$$\frac{1}{x_w}\frac{dx_w}{dT} = \frac{d\ln x_w}{dT} = -\left(\frac{\Delta H_w^{fus} - \Delta\bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{fus} - \Delta\bar{V}_w^{brine}}{RT}\right)\frac{dP}{dT} \quad \text{(S8)}$$

Also,

$$d\ln f_w^{vap} = d\ln \hat{f}_w^{brine} \qquad \text{(S9)}$$

$$\left(\frac{\partial \ln \hat{f}_w^{brine}}{\partial x_w}\right)_{T,P}\frac{dx_w}{dT} = -\left(\frac{\Delta H_w^{vap} - \Delta\bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{vap} - \Delta\bar{V}_w^{brine}}{RT}\right)\frac{dP}{dT} \qquad \text{(S10)}$$

Equating eqs (S5) and (S10),

$$\frac{dP}{dT} = \left(\frac{\Delta H_w^{vap} - \Delta H_w^{fus}}{T\left(\Delta V_w^{vap} - \Delta V_w^{fus}\right)}\right) \qquad \text{(S11)}$$

Substituting eq (S11) into eq (S5),

$$\frac{d\ln x_w}{dT} = -\left(\frac{\Delta H_w^{fus} - \Delta\bar{H}_w^{brine}}{RT^2}\right) + \left(\frac{\Delta V_w^{fus} - \Delta\bar{V}_w^{brine}}{RT}\right)\left(\frac{\Delta H_w^{vap} - \Delta H_w^{fus}}{T\left(\Delta V_w^{vap} - \Delta V_w^{fus}\right)}\right) \qquad \text{(S12)}$$

Neglect the partial molar enthalpy and volume of mixing, and simplify.

$$\frac{d\ln x_w}{dT} = \frac{\Delta V_w^{fus}\Delta H_w^{vap} - \Delta H_w^{fus}\Delta V_w^{vap}}{RT^2\left(\Delta V_w^{vap} - \Delta V_w^{fus}\right)} \qquad \text{(S13)}$$

Dividing through on top & bottom by ΔV_w^{vap} and using the fact that $\Delta V_w^{fus} << \Delta V_w^{vap}$, eq (S13) simplifies to:

$$\frac{d\ln x_w}{dT} = \frac{-\Delta H_w^{fus}}{RT^2} \qquad \text{(S14)}$$

Integrating,

$$x_w = x_{w,0}\exp\left[-\frac{\Delta H_w^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad \text{(S15)}$$

In order to calculate layer thickness we first relate x_w to the liquid water fraction, φ

$$\varphi = \frac{n_w^{brine}}{n_w} = \frac{dA}{V}\frac{\rho_{ice}}{\rho_w} \qquad \text{(S16)}$$

Where *d* is BL thickness, *A* and *V* are dimensions of the sample, and ρ is density.

From the definition of x_w, we get

$$x_{w,0} = \frac{n_w}{n_w+n_s} \qquad x_w = \frac{n_w^{brine}}{n_w^{brine}+n_s} \qquad \text{(S17)}$$

Rearranging and substituting, we get

$$d = \frac{V}{A}\frac{\rho_w}{\rho_{ice}}\left(\frac{x_w}{x_{w,0}}\frac{(1-x_{w,0})}{(1-x_w)}\right) \qquad \text{(S18)}$$

B. Derivation of Semi-Empirical Models for the QLL

Table 1: The semi-empirical models ($d_{QLL,ln}$, $d_{QLL,-1/2}$, $d_{QLL,-1/3}$) presented in section 3 of the manuscript obtained based on the fit parameter data.

	$\lvert\ln((T_m - T)/T_m))\rvert$			$(T_m - T)^{-1/2}$			$(T_m - T)^{-1/3}$		
	Slope	Intercept	R^2	Slope	Intercept	R^2	Slope	Intercept	R^2
Dosch	16.371	-51.919	0.8218	66.855	-19.83	0.9341	80.95	-36.155	0.9037
Doppenschmidt	10.262	-17.72	0.8208	45.757	0.0502	0.8572	53.9	10.051	0.8521
Mazzega	1.1	-2.4711	1	0.8906	0.9297	0.6744	2.2058	0.1019	0.8231
Bluhm	0.8423	-2.1323	0.9165	3.7415	-0.6945	0.9547	4.4728	-1.5471	0.9596
Pittenger	0.3151	-0.8009	0.8919	1.2272	-0.1601	0.9819	1.512	-0.4723	0.9613
Sadtchenko	2.4478	-8.231	0.9786	2.7037	0.8935	0.974	5.3146	-1.3638	0.9931
R^2-weighted avg	4.866871	-12.9671		20.40124	-3.31141		24.01679	-4.97332	

REFERENCES

Bluhm, H., Ogletree, D. F., Fadley, C. S., Hussain, Z., and Salmeron, M.: The Premelting of Ice Studied With Photoelectron Spectroscopy, *J. Phys.: Cond. Matter*, *14* (8), L227-L233, 2002.

Doppenschmidt, A. and Butt, H.-J.: Measuring the Thickness of the Liquid-like Layer on Ice Surfaces with Atomic Force Microscopy, *Langmuir*, *16* (16), 6709-6714, 2000.

Dosch, H., Lied, A., and Bilgram, J. H.: Disruption of the Hydrogen-bonding Network at the Surface of Ih Ice Near Surface Premelting, *Surf. Sci.*, *366* (1), 43-50, 1996.

Mazzega, E., Pennino, U. D., Loria, A., and Mantovani, S.: Volta Effect and Liquid-Like Layer at Ice Surface, *J. Chem. Phys.*, *64* (3), 1028-1031, 1976.

Pittenger, B., Fain, S. C., Cochran, M. J., Donev, J. M. K., Robertson, B. E., Szuchmacher, A., and Overney, R. M.: Premelting at Ice-Solid Interfaces Studied via Velocity-Dependent Indentation with Force Microscope Tips, *Phys. Rev. B*, *6313* (13), 134102, 2001.

Sadtchenko, V. and Ewing, G. E.: Interfacial Melting of Thin Ice Films: An Infrared Study, *J. Chem. Phys.*, *116* (11), 4686-4697, 2002.

Tester, J.W. and Modell, M. Thermodynamics and its Applications, 3rd Ed. Prentice Hall, Upper Saddle River, N.J. (1996)