

Supporting information: Adsorption properties of triethylene glycol on a hydrated {10 $\bar{1}$ 4} calcite surface and its effect on adsorbed water

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Table S1. Lennard-Jones parameters σ and ϵ , masses m and charges q for the OPLS-AA TEG molecule.

Atom	σ [Å]	ϵ [kJ/mol]	m [u]	q [e]
HO	0.000	0.000	1.0008	0.435
OH	3.070	0.711	15.9994	-0.700
CT1	3.500	0.276	12.0107	0.145
CT2	3.500	0.276	12.0107	0.140
HC1	2.500	0.126	1.0008	0.060
HC2	2.500	0.126	1.0008	0.030
OS	2.900	0.586	15.9994	-0.400

Table S2. Bond stretching parameters for the OPLS-AA TEG molecule.

Bond	K^r [kJ·Å ⁻² /mol]	r_0 [Å]
HO-OH	2313.752	0.945
OH-CT	1338.880	1.410
CT-HC	1422.560	1.090
CT-CT	1121.312	1.529
CT-OS	1338.880	1.410

Table S3. Covalent angle parameters for the OPLS-AA TEG molecule.

Angle	K^θ [kJ·rad ⁻² /mol]	θ_0 [°]
HO-OH-CT	230.120	108.5
HC-CT-OH	146.440	109.5
HC-CT-HC	138.072	107.8
HC-CT-CT	156.900	110.7
HC-CT-OS	146.440	109.5
CT-CT-OS	209.200	109.5
CT-CT-OH	209.200	109.5
CT-OS-CT	251.040	109.5

Table S4. Dihedral angle parameters for the OPLS-AA TEG molecule ($V_4 = 0$, Cx can be replaced by any carbon atom type).

Dihedral	V_1 [kJ/mol]	V_2 [kJ/mol]	V_3 [kJ/mol]
HO-OH-CT-HC	0.0000	0.0000	1.4744
HO-OH-CT-CT	-1.4895	-0.7280	2.0585
HC-CT-CT-HC	0.0000	0.0000	1.2552
HC-CT-CT-OS	0.0000	0.0000	1.9581
HC-CT-CT-OH	0.0000	0.0000	1.9581
HC-CT-OS-Cx	0.0000	0.0000	3.1798
CT-CT-OS-CT	2.7196	-1.0460	2.8033
OH-CT-CT-OS	18.0707	0.0000	0.0000
OS-CT-CT-OS	-2.3012	0.0000	0.0000

Table S5. Parameters of the flexible SPC water model ($r_{1,0}$, $r_{2,0}$ and $r_{3,0}$ are equilibrium bond lengths and atomic separations).

Parameter	Value	Unit
H-O $r_{1,0}$ and $r_{2,0}$	1.000	Å
H-H $r_{3,0}$	1.633	Å
Dissociation energy D_m	426.702	kJ/mol
Coefficient ρ_m	2.566	Å ⁻¹
Coefficient c	-884.630	kJ·Å ⁻² /mol
Coefficient b	687.410	kJ·Å ⁻² /mol
Coefficient d	467.310	kJ·Å ⁻² /mol

Force-field parameters

In the following subsections we have listed force-field parameters used in our work. OPLS¹⁻¹¹ was used to model TEG-TEG and TEG-water interactions. Calcite Buckingham parameters¹² were fitted to Lennard-Jones potentials and mixing rules were applied to find Lennard-Jones pair parameters for TEG-calcite interactions. Water-water and water-TEG interactions were modelled using the fSPC¹³ force-field while water-calcite interactions were modelled using Buckingham parameters from the literature.

TEG force-field

Lennard-Jones parameters and charges of the TEG model are shown in Tab. S1, while bond-stretching parameters are shown in Tab. S2. A TEG molecule has 40 covalent angles and 45 dihedral angles. The types of covalent angles and dihedral angles that occur in the TEG model are shown in Tab. S3 and Tab. S4 together with the assigned force-field parameters. See Fig. 1 in paper for naming convention of atomic types.

Water force-field

The flexible SPC parameters used for water are shown in Tab. S5. Oxygen Lennard-Jones parameters are $\sigma_O = 3.1656$ Å, and $\epsilon_O = 0.6502$ kJ/mol. Hydrogen atoms are not

involved in short range interactions. As such, $\epsilon_H = 0$ and $\sigma_H = 0$. Partial charges, responsible for long range Coulomb interactions, are $q_H = +0.41$ and $q_O = -0.82$ for hydrogen and oxygen atoms, respectively.

Calcite force-field

Buckingham parameters for calcite are shown in Tab. S6. Partial charges used in long range Coulomb interactions towards H₂O and TEG were set to $q_{Ca} = +1.881$, $q_C = +1.482$ and $q_O = -1.118$.

Table S6. Buckingham parameters A and ρ , used in calcite-calcite and calcite-water interactions.

Atom	A [kJ/mol]	ρ [Å]	C [kJ·Å ⁶ /mol]
Ca	82942.86	0.455	55686.70
O	230230.10	0.253	1123.56
C	369822.70	0.278	2432.71

Table S7. Buckingham parameters A and ρ , used in calcite-water interactions.

Interaction	A [kJ/mol]	ρ [Å]	C [kJ·Å ⁶ /mol]
O	2196380.310	0.1490	2894.402
H	665.539	0.4195	0.000

Water-calcite force-field

Pure Buckingham parameters for water are listed in Tab. S7. These were used to obtain cross interactions towards calcite from the geometric mixing rules $A_{ij} = \sqrt{A_i A_j}$, $\rho_{ij} = \sqrt{\rho_i \rho_j}$ and $C_{ij} = \sqrt{C_i C_j}$.

Non-bonded energy distributions

In addition to investigating geometric positioning of TEG hydroxyls towards calcite we looked at the distribution of non-bonded energies (described by Eq. (1) of paper) towards calcite (in the system containing a single TEG molecule adsorbed to the hydrated surface). Fig. S1 shows energy distributions (normalized to unity) of contributions from interactions between hydroxyl hydrogens of TEG and closest carbon of carbonate, hydroxyl hydrogen of TEG and closest oxygen of carbonate, hydroxyl oxygen of TEG and closest carbon of carbonate, as well as between hydroxyl oxygen of TEG and closest calcium of calcite. These energies separately have large magnitudes (for comparison, O-H bond energies of water are in the order of 427kJ/mol, while hydrogen bonds between water is in order of 25kJ/mol.¹⁴). However, it can be seen that the energies were centred around both positive and negative energies and, as is discussed in paper, adsorption energies were found to be sensible.

Effect of calcite slab reduction

Equivalent simulations were also performed on systems where the calcite slab was replaced by a slab of dimension 40Å×44Å×7.6Å. We observed no change in the first and second water density peaks. For no TEG and one TEG, the water density profiles were identical to those of the large calcite slab. Since for more than 16 TEG the final adsorbed amount of TEG differed from the amounts seen on the larger calcite slab the third and fourth water density peaks were different, but within the same range. The overall behaviour of TEG, as seen in Fig. 5 in paper, did not change with the reduced calcite slab. Furthermore, distances and angles

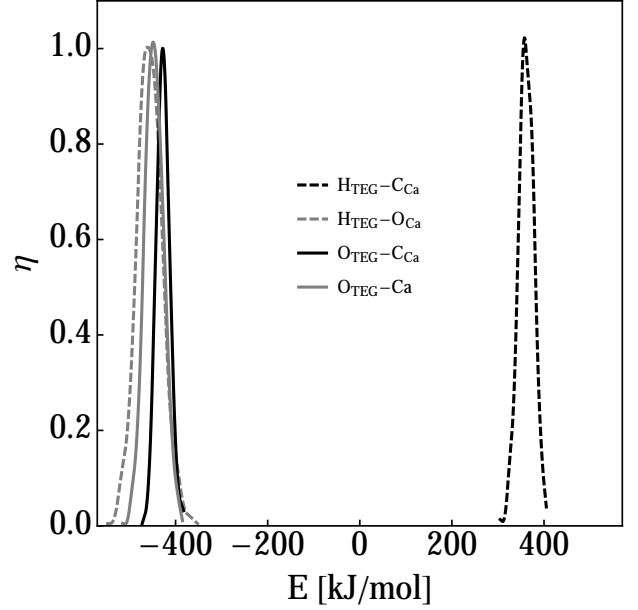


Figure S1. Normalized distribution for system with one TEG at 298K of hydroxyl hydrogen - calcite carbon ($H_{\text{TEG-C}_{\text{Ca}}}$) non-bonded energy, hydroxyl hydrogen - calcite oxygen ($H_{\text{TEG-O}_{\text{Ca}}}$) non-bonded energy, hydroxyl oxygen - calcite carbon ($O_{\text{TEG-C}_{\text{Ca}}}$) non-bonded energy and hydroxyl oxygen - calcite calcium ($O_{\text{TEG-Ca}}$) non-bonded energy. Also see d_1 , d_2 , d_3 and d_4 of Fig. 6(b) in paper, respectively.

listed in Tab. 1(I) and Tab. 1(II) in paper overlapped, within given standard deviations, with those found using a thinner calcite slab (i.e. $\{v_1 \pm \sigma_1\} \cap \{v_2 \pm \sigma_2\} \neq \emptyset$).

Free energy based on density

Let \mathcal{A} be a system consisting of a hydrated calcite slab with ρ_{ads} adsorbed TEG, and let z denote the distance from a calcium atom at the $\{10\bar{1}4\}$ calcite surface to water molecule index M , in the water phase, projected along the z -axis (normal to the calcite surface). The partition function describing all possible states in phase-space where water molecule M is located at z is

$$Q_{\mathcal{A}}(z, \rho_{\text{ads}}) = C \int \prod_{i=1}^{N_w} d\mathbf{r}_i^w \prod_{j=1}^{N_t} d\mathbf{r}_j^t \prod_{k=1}^{N_{\text{cal}}} d\mathbf{r}_k^{\text{cal}} \times \prod_{\mu=3M+1}^{3M+3} \delta(\mathbf{r}_\mu^w - \mathbf{r}_\mu^{w,0}(z)) e^{-\beta \Phi(\rho_{\text{ads}}, \mathbf{r}_1^w, \dots, \mathbf{r}_{N_{\text{cal}}}^{\text{cal}})},$$

where w, t, and cal denote water, TEG, and calcite, respectively, N_n is number of atoms, $\mathbf{r}_\mu^{w,0}(z)$ is constrained position of water atom μ to z , and Φ is the potential part of complete system Hamiltonian. C is the standard normalization due to kinetic part of Hamiltonian, adjustment of over-counting (i.e. indistinguishability of particles) and due to quantum correction coming from the Heisenberg uncertainty relation.

A free energy difference between water M at z and water

M at z_0 is now described by

$$\begin{aligned}\Delta A_{\text{H}_2\text{O}}(z, \rho_{\text{ads}}) &= -RT \ln \left[\frac{Q_{\mathcal{A}}(z, \rho_{\text{ads}})}{Q_{\mathcal{A}}(z_0, \rho_{\text{ads}})} \right] \\ &= -RT \ln \left[\frac{\langle \delta(\mathbf{r}_{\mu}^{\text{w}} - \mathbf{r}_{\mu}^{\text{w},0}(z)) \rangle}{\langle \delta(\mathbf{r}_{\mu}^{\text{w}} - \mathbf{r}_{\mu}^{\text{w},0}(z_0)) \rangle} \right] \\ &= -RT \ln \left[\frac{P(z, \rho_{\text{ads}})}{P(z_0, \rho_{\text{ads}})} \right],\end{aligned}$$

where $P(z, \rho_{\text{ads}})$ is the probability of water M being present at z with adsorbed TEG density ρ_{ads} . Since this probability is also proportional to the density $\rho_{\text{H}_2\text{O}}(z, \rho_{\text{ads}})$ we can find the free energy difference, $\Delta A_{\text{H}_2\text{O}}$, between water at z and water in bulk by¹⁵

$$\Delta A_{\text{H}_2\text{O}}(z, \rho_{\text{ads}}) = -RT \ln \left[\frac{\rho_{\text{H}_2\text{O}}(z, \rho_{\text{ads}})}{\rho_{\text{H}_2\text{O}}^{\text{bulk}}} \right].$$

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