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Supplementary Information

Ion-specific Interactions at Calcite-Brine Interfaces: A Nano-Scale Study of the Surface Charge Development and Preferential Binding of Polar Hydrocarbons

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Table S1 Force-field parameters for calcite, water and ions utilized in the current study. For relevant formulations refer to eqs. 1-4 in the main text.

Atomwise LJ parameters and partial atomic charges for $CaCO_3$			
Atom type	*Partial charge*	$\epsilon\ (kcal.mol^{-1})$	σ (Å)
$Ca_{calcite}$	+1.668	0.478	2.370
$O_{calcite}$	+0.999	0.139	3.090
$C_{calcite}$	-0.889	0.088	3.823
Atomwise LJ parameters and partial atomic charges for water (TIP3P model)			
O_w	-0.834	0.1521	3.1507
H_w	0.417	0.0000	0.0000
Interatomic LJ parameters for $CaCO_3$ and water			
$C_{calcite}$	$O_{calcite}$	6.270	1.197
$O_{calcite}$	$O_{calcite}$	0.000273	4.744
$Ca_{calcite}$	O_w	0.270056	2.760
$C_{calcite}$	O_w	0.116185	3.469
$O_{calcite}$	O_w	0.146128	3.118
$O_{calcite}$	H_w	6.97252e-6	4.497
Atomwise LJ parameters for ions			
Na^+	+1.000	0.0028	3.33
Cl^-	-1.000	0.1178	4.42
Mg^{2+}	+2.000	0.0621	2.11
$S_{sulfate}$	+2.300	0.2000	3.55
$O_{sulfate}$	-1.075	0.1553	3.25
Atomwise LJ parameters and partial atomic charges for benzoic acid[1]			
C_{phenyl}	-0.1150	0.070	3.550
H_{phenyl}	+0.1150	0.030	2.420
$C_{phenyl,\ carboxylic}$	-0.1150	0.070	3.550
$C_{carboxylic}$	+0.6350	0.105	3.750
$OH_{carboxylic}$	-0.5300	0.170	3.000
$O_{carboxylic}$	-0.4400	0.210	2.960
$HO_{carboxylic}$	+0.4500	0.000	0.000
Bond stretching parameters			
Bond type		*Stiffness,* $K_b\ (kcal.Å^{-2}mol^{-1})$	*Bond length,* (Å)
$C_{calcite}$	$O_{calcite}$	314.5	1.294
O_w	H_w	450.0	0.9572
C_{phenyl}	H_{phenyl}	367.0	1.080
C_{phenyl}	C_{phenyl}	469.0	1.400
C_{phenyl}	$C_{phenyl,\ carboxylic}$	469.0	1.400
$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	469.0	1.409
$C_{carboxylic}$	$O_{carboxylic}$	656.0	1.250
$C_{carboxylic}$	$OH_{carboxylic}$	450.0	1.364
$OH_{carboxylic}$	$HO_{carboxylic}$	553.0	0.960
$S_{sulfate}$	$O_{sulfate}$	525.5	1.487
Angle bending parameters			
Angle type		*Stiffness,*	*Angle,* (deg)

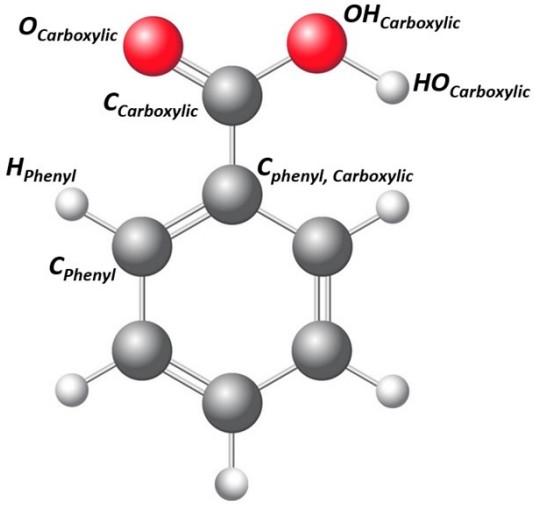
			$K_b\ (kcal.deg^{-2}mol^{-1})$	
C_{phenyl}	$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	63.0	120.0
$C_{carboxylic}$	$OH_{carboxylic}$	$HO_{carboxylic}$	35.0	113.0
H_{phenyl}	C_{phenyl}	C_{phenyl}	35.0	120.0
H_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	35.0	120.0
H_w	O_w	H_w	55.0	104.52
C_{phenyl}	C_{phenyl}	C_{phenyl}	63.0	120.0
C_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	63.0	120.0
$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	$O_{carboxylic}$	80.0	120.4
$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	$OH_{carboxylic}$	70.0	120.0
$O_{carboxylic}$	$C_{carboxylic}$	$OH_{carboxylic}$	80.0	121.0
$O_{calcite}$	$C_{calcite}$	$O_{calcite}$	221.3	120.0
$O_{sulfate}$	$S_{sulfate}$	$O_{sulfate}$	140.0	109.47

Dihedral torsion parameters[2]

Dihedral type				K_1	K_2	K_3	K_4
H_{phenyl}	C_{phenyl}	C_{phenyl}	H_{phenyl}	0.0	7.25	0.0	0.0
H_{phenyl}	C_{phenyl}	C_{phenyl}	C_{phenyl}	0.0	7.25	0.0	0.0
H_{phenyl}	C_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	0.0	7.25	0.0	0.0
H_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	0.0	7.25	0.0	0.0
H_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	C_{phenyl}	0.0	7.25	0.0	0.0
C_{phenyl}	C_{phenyl}	C_{phenyl}	C_{phenyl}	0.0	7.25	0.0	0.0
C_{phenyl}	C_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	0.0	7.25	0.0	0.0
C_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	0.0	7.25	0.0	0.0
C_{phenyl}	C_{phenyl}	$C_{phenyl,\ carboxylic}$	C_{phenyl}	0.0	7.25	0.0	0.0
$C_{phenyl,\ carboxylic}$	$C_{carboxylic}$	$OH_{carboxylic}$	$HO_{carboxylic}$	4.0	5.00	0.0	0.0
$O_{carboxylic}$	$C_{carboxylic}$	$OH_{carboxylic}$	$HO_{carboxylic}$	0.0	5.00	0.0	0.0
$OH_{carboxylic}$	$C_{carboxylic}$	$C_{phenyl,\ carboxylic}$	C_{phenyl}	0.0	5.00	0.0	0.0

[1] Atom types for a benzoic molecules are defined in the sketch below.

[2] Dihedral potential is calculated by LAMMPS through the expression: $E = \frac{1}{2}K_1(1 + cos\emptyset) + \frac{1}{2}K_2(1 - cos2\emptyset) + \frac{1}{2}K_3(1 + cos3\emptyset) + \frac{1}{2}K_4(1 - cos4\emptyset)$



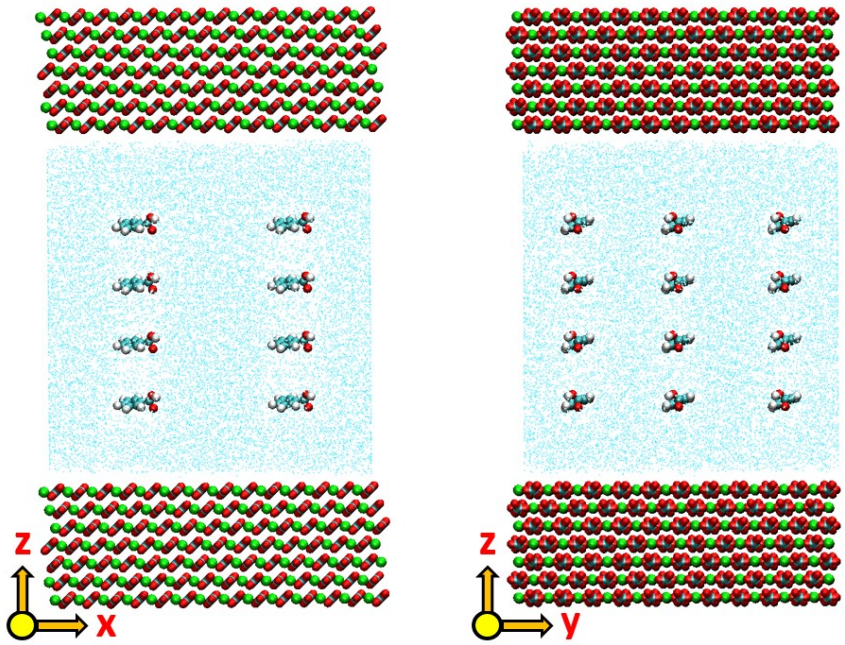


Figure S1 Initial configuration of the simulation ensemble from (left) XZ and (right) YZ views.

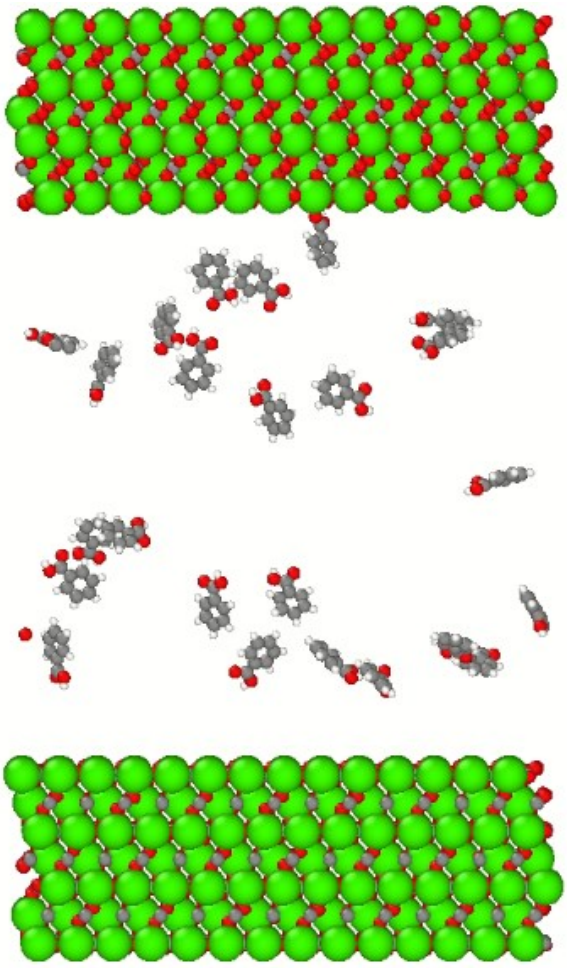


Figure S2 Final configuration of BA molecules in deionized water (DW) confined within the calcite slit.

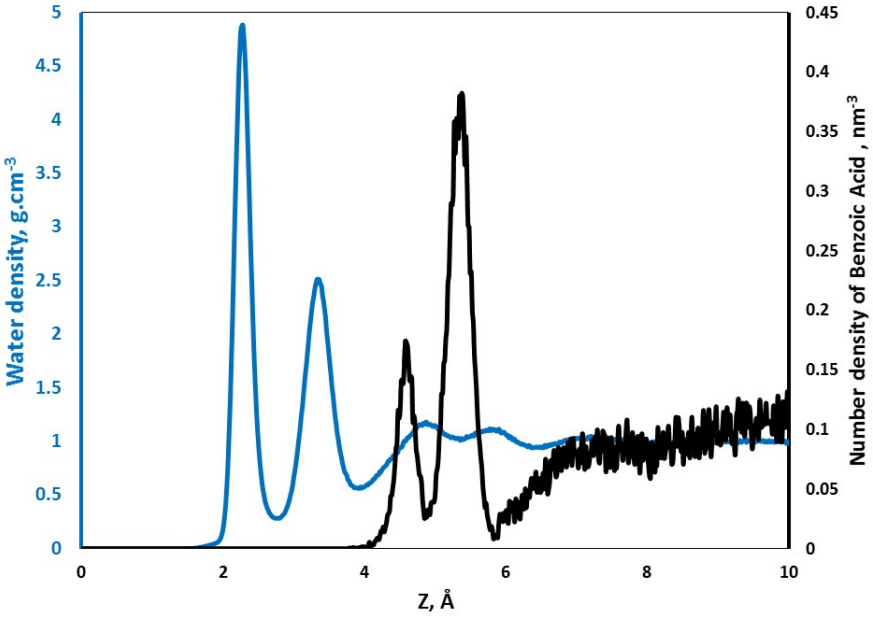


Figure S3 Density profile of water and BA at the interface of calcite-DW.