Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information of

Salinity and pH effect on water-oil-calcite interfaces by molecular dynamics

Authors

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Table S1. Individual parameters.

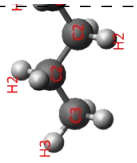
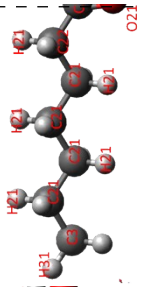
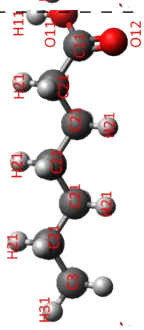
Phase	Atom type	Charge (e)	A12 (kcal/mol)	B6 (kcal/mol)
Carbonate	C_calcite	-0.999	3441682.6004	1101.8164
	Ca_calcite	+1.668	60229.4455	339.3881
	O_calcite	-0.889	423040.1530	485.1816
Salts	Na_ion	+1	20648.4015	15.1310
	Ca_ion	+2	69748.1484	354.1901
	Mg_ion	+2	1368.9918	69.2222
	Cl_ion	-1	26000401.2760	3500.0486
	O_sulfate_ion	-1.1	954391.6818	976.9297
	S_sulfate_ion	+2.4	4006270.2004	2001.5669
Water	H_water	+0.417	0.0000	0.0000
	O_water	-0.834	582202.1981	595.1570
Heptane 	C2	-0.12	892114.2141	485.3021
	C3	-0.18	892114.2141	485.3021
	H2	+0.06	7152.5574	29.2969
	H3	+0.06	7152.5574	29.2969
Heptanoate 	C11	+0.7	3248063.4400	1167.9840
	C21	-0.12	892114.2141	485.3021
	C22	-0.12	892114.2141	485.3021
	C31	-0.18	811012.9219	441.1838
	H21	+0.06	7152.5574	29.2969
	H31	+0.06	7152.5574	29.2969
	O21	-0.8	379996.6945	564.9754
Heptanoic acid 	C11	+0.52	3248063.4400	1167.9840
	C21	-0.12	892114.2141	485.3021
	C31	-0.18	892114.2141	485.3021
	H11	+0.45	0.0000	0.0000
	H21	+0.06	7152.5574	29.2969
	H31	+0.06	7152.5574	29.2969
	O11	-0.53	578580.8310	627.2439
	O12	-0.44	379996.6945	564.9754

Tabla S2. Combinated parameters.

Atom type 1	Atom type 2	A12 (kcal/mol)	B6 (kcal/mol)
C_calcite	C_calcite	1101816.44359	3417.78203
C_calcite	Ca_calcite	0.00000	0.00000
C_calcite	O_calcite	216.06119	73.61377
Ca_calcite	Ca_calcite	0.00000	0.00000
Ca_calcite	O_calcite	226816.44359	0.00000
O_calcite	O_calcite	141969.40727	12.45220
C_calcite	H_water	0.00000	0.00000
C_calcite	O_water	1412523.90057	810.22945
Ca_calcite	H_water	0.00000	0.00000
Ca_calcite	O_water	211520.07648	478.01147
O_calcite	H_water	1907.26577	0.23064
O_calcite	O_water	494741.87380	537.76291

Table S3. Systems evaluated on the surface affinity of surface *(104)* of calcite to crude oil models in the SW models at different conditions.

	Crude oil model composition (disperse phase)/Smart water composition (continues phase)	Molecules numbers	Polar compounds concentration (ppm)/Salt concentration (ppm)	pH
Non-polar crude oil model	Water/heptane	1453 / 1264	----/----	----
	Heptane/water	156 / 11777	----/----	
	Heptane/NaCl – water	156 / (11^{+} 11^{-}) – 11777	---- / 3000	
		156 / (112^{+} 112^{-}) – 11777	---- / 30000	
	Heptane/$CaCl_2$ – water	156 / (6^{+} 12^{-}) – 11777	---- / 3000	
		156 / (59^{+} 118^{-}) – 11777	---- / 30000	
	Heptane/$CaSO_4$ – water	156 / (4^{+} 4^{-}) – 11777	---- / 2600	
		156 / (42^{+} 42^{-}) – 11777	---- / 26000	
	Heptane/$MgSO_4$ – water	156 / (5^{+} 5^{-}) – 11777	---- / 3000	
		156 / (55^{+} 55^{-}) – 11777	---- / 30000	
Polar crude oil model	Heptanoate – heptane/Na^{+} – water	30 – 156 / 30 – 11777	198652 / ----	>> 4.4
	Heptanoate – heptane/Ca^{2+} – water	30 – 156 / 15 – 11777	198652 / ----	
	Heptanoate – heptane/Mg^{2+} – water	30 – 156 / 15 – 11777	198652 / ----	
	Heptanoate – heptane/NaCl – water	30 – 156 / (11^{+} 11^{-}) – 11777	198652 / 3000	
		30 – 156 / (112^{+} 112^{-}) – 11777	198652 / 30000	
	Heptanoate – heptane/Na_2SO_4 – water	30 – 156 / (38^{+} 4^{-}) – 11777	198652 / 3000	
		30 – 156 / (122^{+} 46^{-}) – 11777	198652 / 30000	
	Heptanoate – heptane/$CaCl_2$ – water	30 – 156 / (6^{+} 12^{-}) – 11777	198652 / 3000	
		30 – 156 / (59^{+} 118^{-}) – 11777	198652 / 30000	
	Heptanoate – heptane/$CaSO_4$ – water	30 – 156 / (4^{+} 4^{-}) – 11777	198652 / 2600	

	30 – 156 / (42^{+} 42^{-}) – 11777	198652 / 26000	
Heptanoate – heptane/$MgCl_2$ – water	30 – 156 / (22^{+} 14^{-}) – 11777	198652 / 3000	
	30 – 156 / (83^{+} 136^{-}) – 11777	198652 / 30000	
Heptanoate – heptane/$MgSO_4$ – water	30 – 156 / (5^{+} 5^{-}) – 11777	198652 / 3000	
	30 – 156 / (55^{+} 55^{-}) – 11777	198652 / 30000	
Heptanoic acid – heptanoate – heptane/Na^{+} – water	15 – 15 – 156 / 15 – 11777	100023 – 99249 / ----	
Heptanoic acid – heptanoate – heptane/NaCl – water	15 – 15 – 156 / (26^{+} 11^{-}) – 11777	100023 – 99249 / 3000	= 4.4
	15 – 15 – 156 / (127^{+} 112^{-}) – 11777	100023 – 99249 / 30000	
Heptanoic acid – heptane/water	15 – 156 / 11777	199892 / ----	
Heptanoic acid – heptane/NaCl – water	15 – 156 / (11^{+} 11^{-}) – 11777	199892 / 3000	<< 4.4
	15 – 156 / (112^{+} 112^{-}) – 11777	199892 / 30000	

Note: $^{+}$ and $^{-}$ above the numbers correspond to the number of cations and anions in water, respectively. The concentrations in the crude oil models correspond to polar molecules in heptane. “=” equal to, “<<” much less than, and “>>” much greater than.

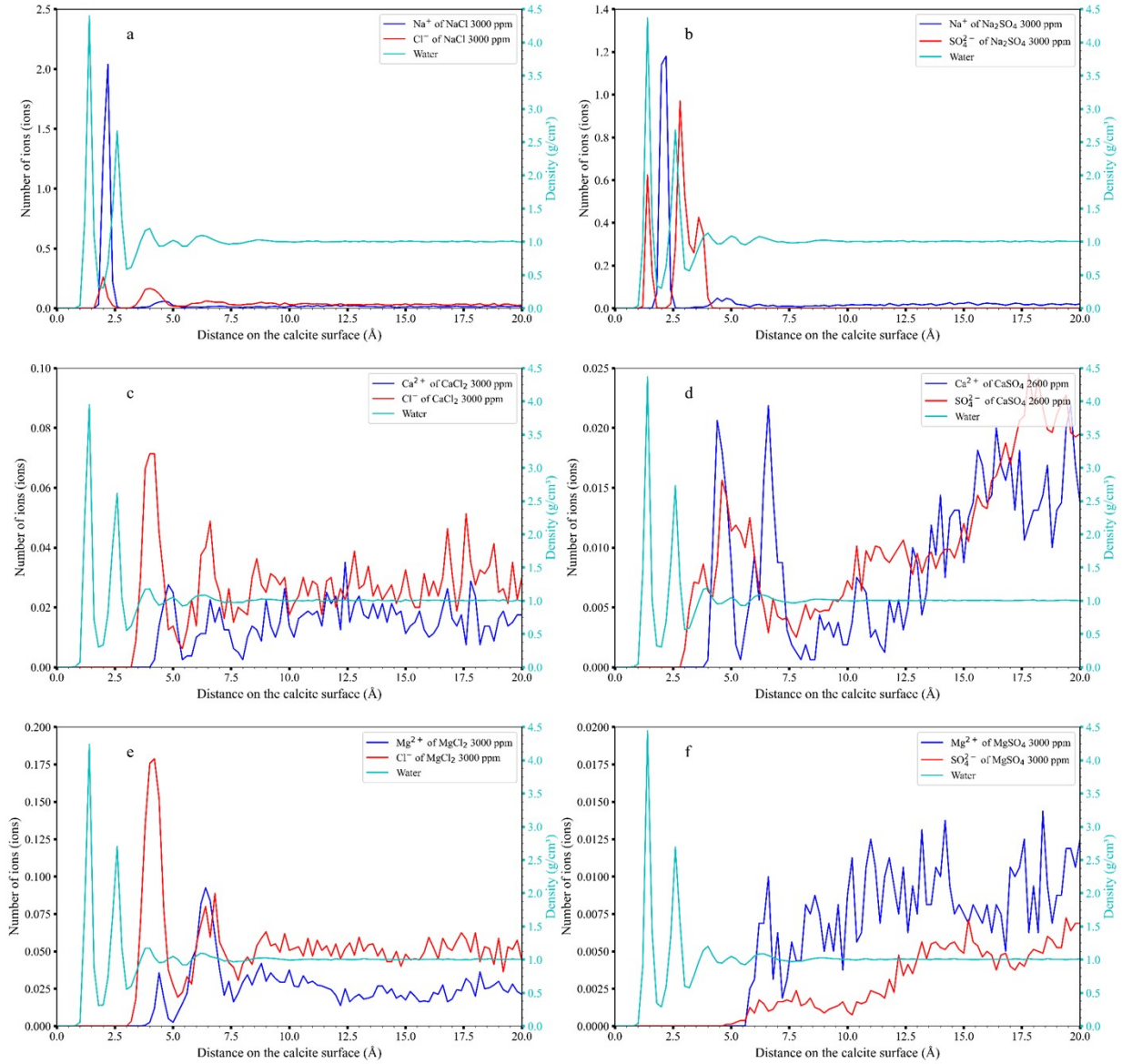


Figure S1. Distribution of cations, distribution of anions, and the one-dimensional mass water density profile of SW models on the calcite surface at LSCC. a) NaCl SW. b) Na_2SO_4 SW. c) $CaCl_2$ SW. d) $CaSO_4$ SW. e) $MgCl_2$ SW. f) $MgSO_4$ SW. These profiles were averaged for 8 ns.

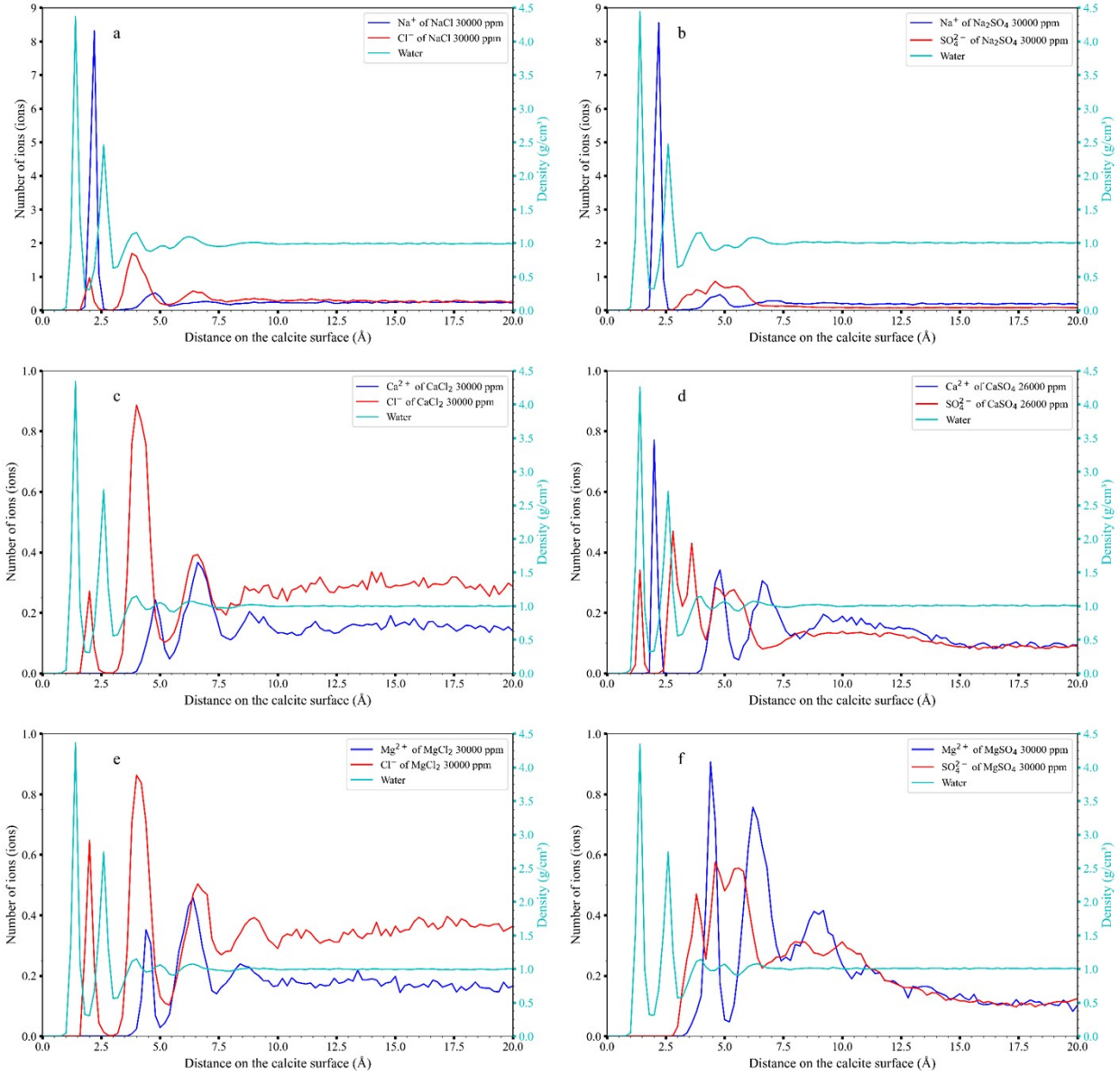


Figure S2. Distribution of cations, distribution of anions, and the one-dimensional mass water density profile of SW models on the calcite surface at HSCC. a) NaCl SW. b) Na_2SO_4 SW. c) $CaCl_2$ SW. d) $CaSO_4$ SW. e) $MgCl_2$ SW. f) $MgSO_4$ SW. These profiles were averaged for 8 ns.

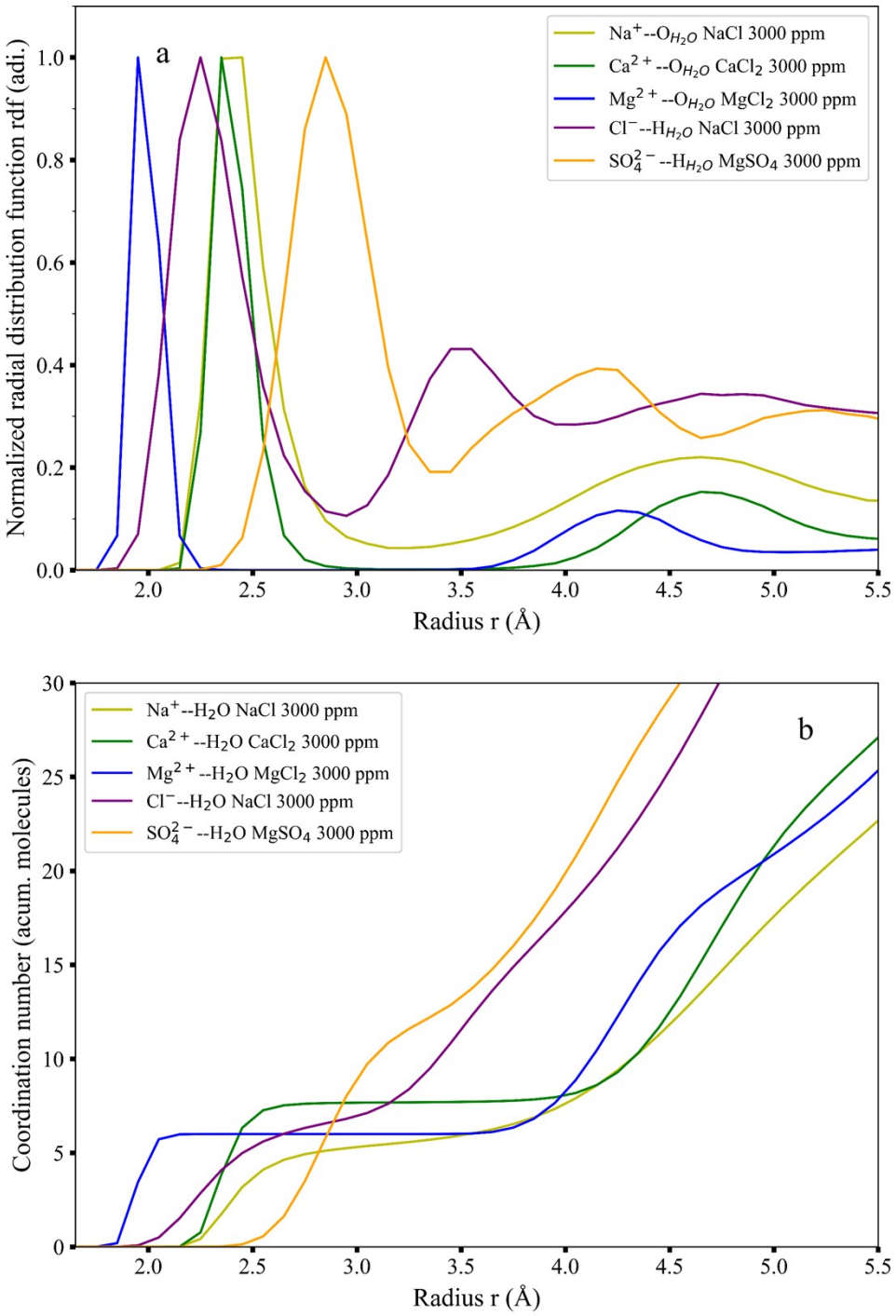


Figure S3. a) Normalized *rdf* of $Na^+ -- O_{H_2O}$, $Ca^{2+} -- O_{H_2O}$, $Mg^{2+} -- O_{H_2O}$, $SO^{2-}_4 -- H_{H_2O}$ and $Cl^- -- H_{H_2O}$ at LSCC. b) Coordination number of $Na^+ -- O_{H_2O}$, $Ca^{2+} -- O_{H_2O}$, $Mg^{2+} -- O_{H_2O}$, $SO^{2-}_4 -- H_{H_2O}$ and $Cl^- -- H_{H_2O}$ at LSCC. Theses profiles were averaged for 8 ns.

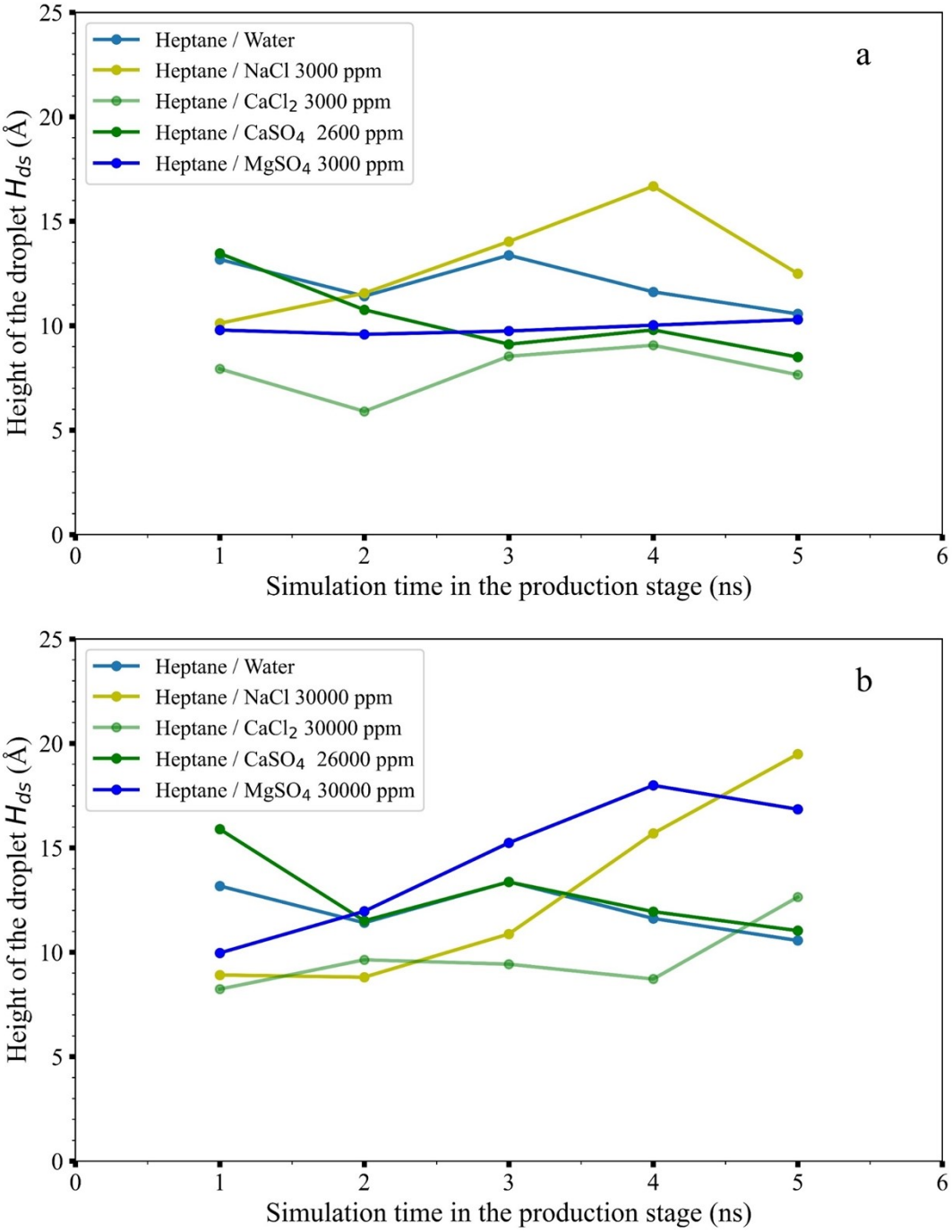


Figure S4. Height of droplet Hds of non-polar crude oil model (non-polar or heptane) in the SW models at pH ==7 and 298.15 K versus simulations time in the production stage. a) At LSCC. b) At HSCC.

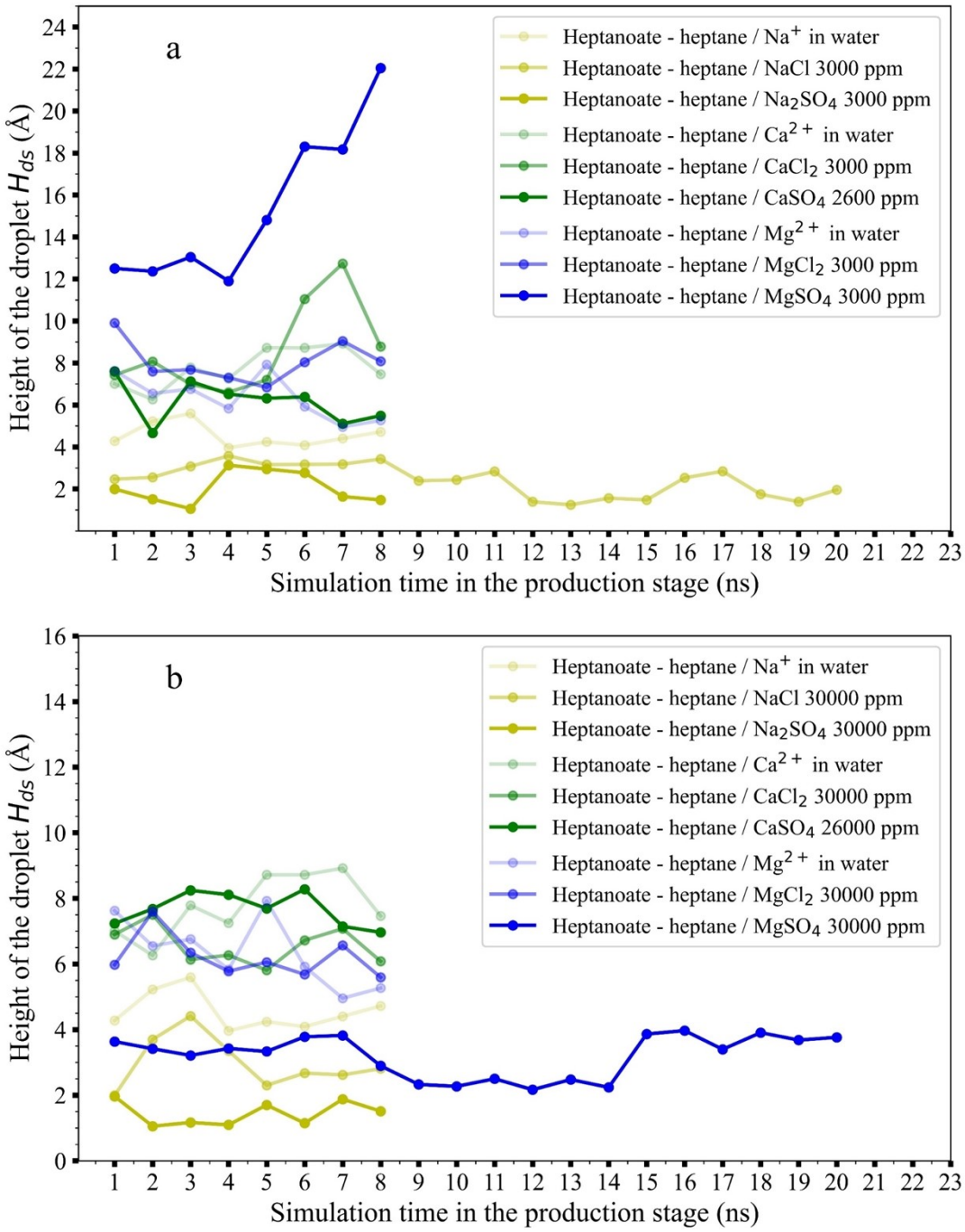


Figure S5. Height of droplet Hds of polar crude oil model (heptanoate – heptane) in the SW models at pH >> 4.4 versus simulations time in the production stage. a) At LSCC. b) At HSCC.

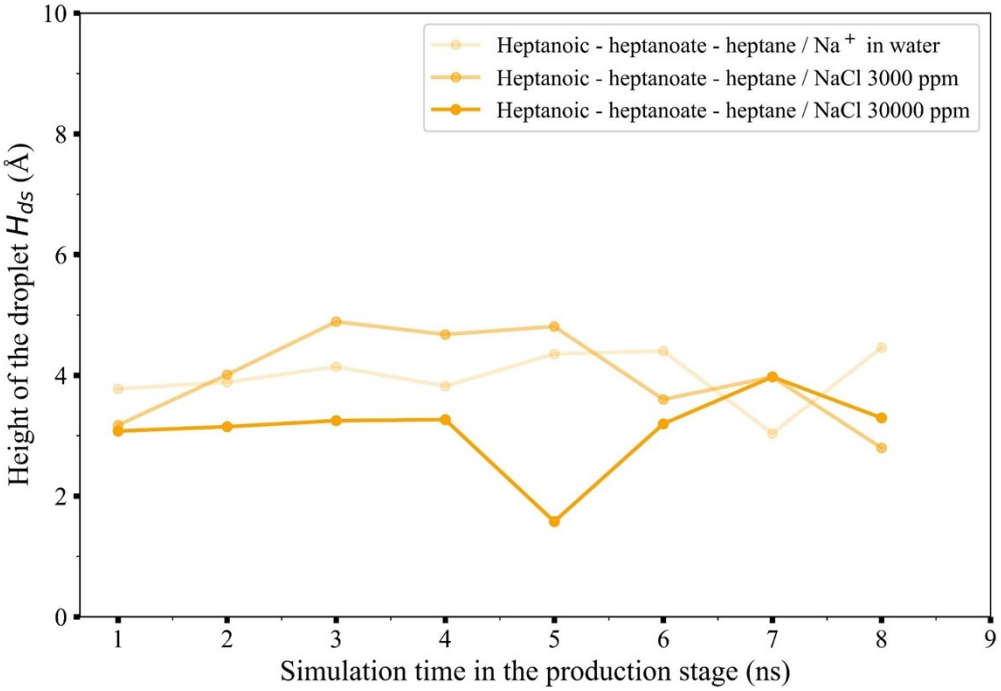


Figure S6. Height of droplet Hds of polar crude oil model (heptanoic acid – heptanoate – heptane) in the SW models at pH = 4.4 versus simulations time in the production stage.

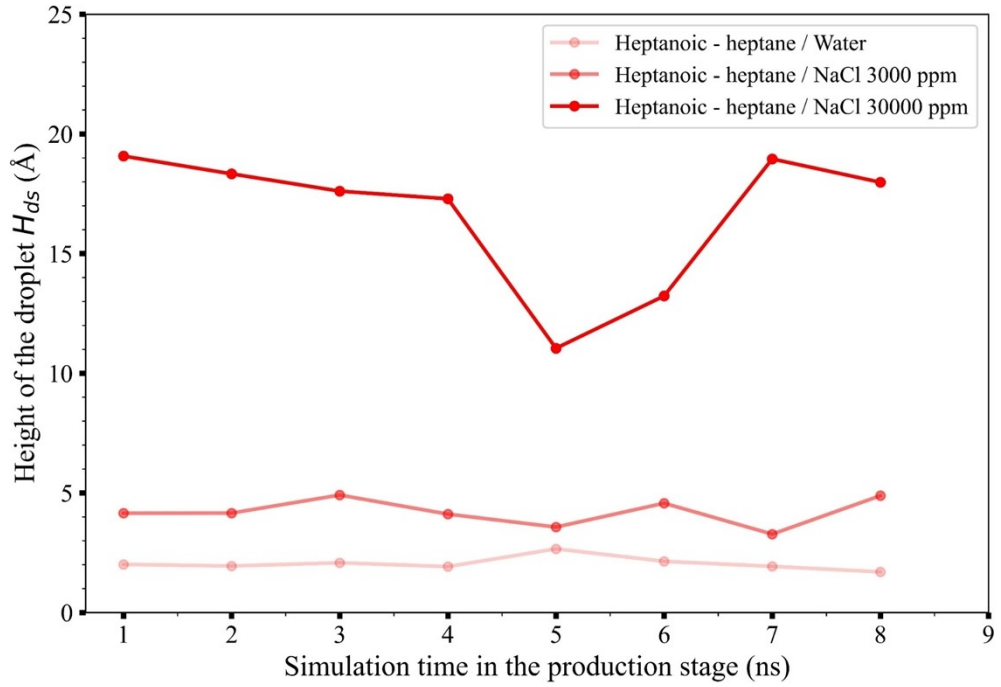


Figure S7. Height of droplet Hds of polar crude oil model (heptanoic acid – heptane) in the SW models at pH << 4.4 versus simulations time in the production stage.

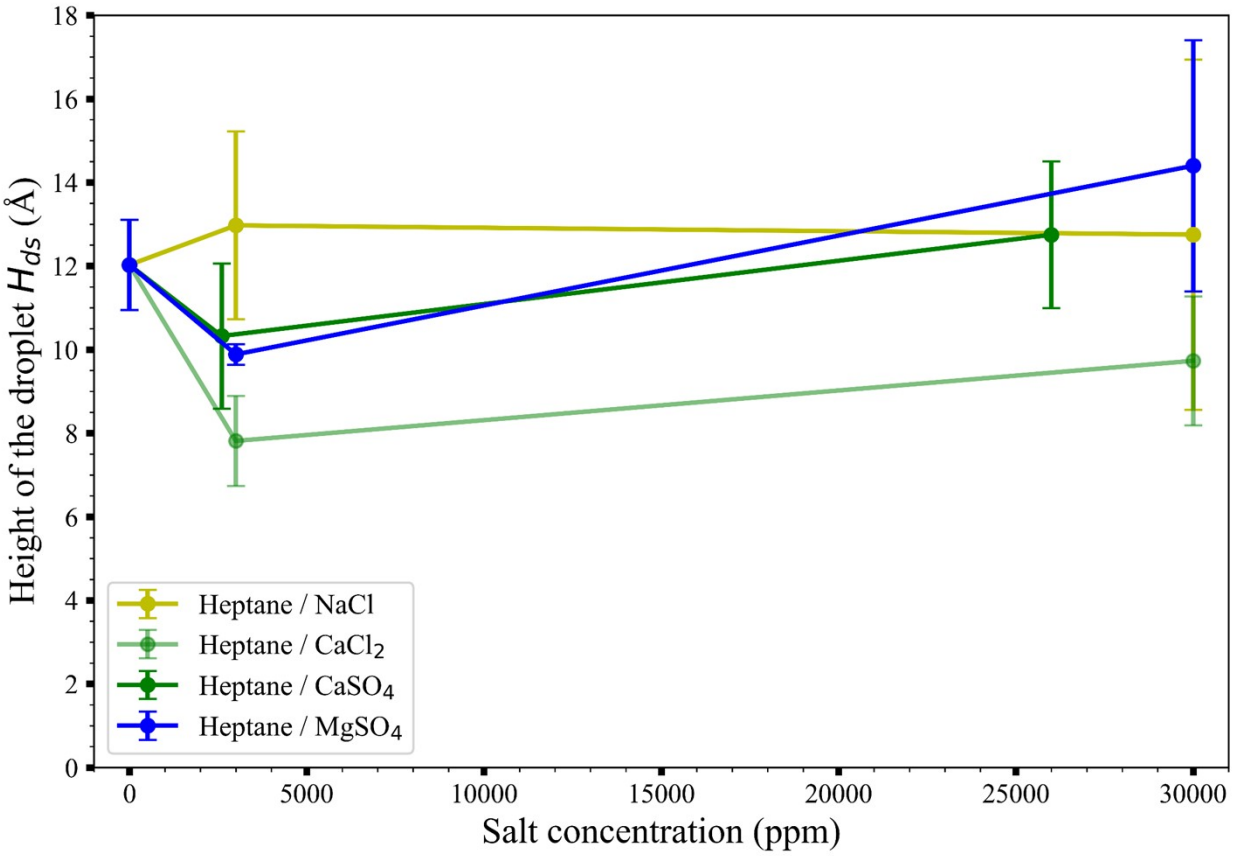


Figure S8. Salinity effect of the SW models on the height of the droplet (H_{ds}) of non-polar crude oil model (heptane) on the calcite surface. Each H_{ds} was calculated for 1 ns and averaged by 5 ns in the production stage.

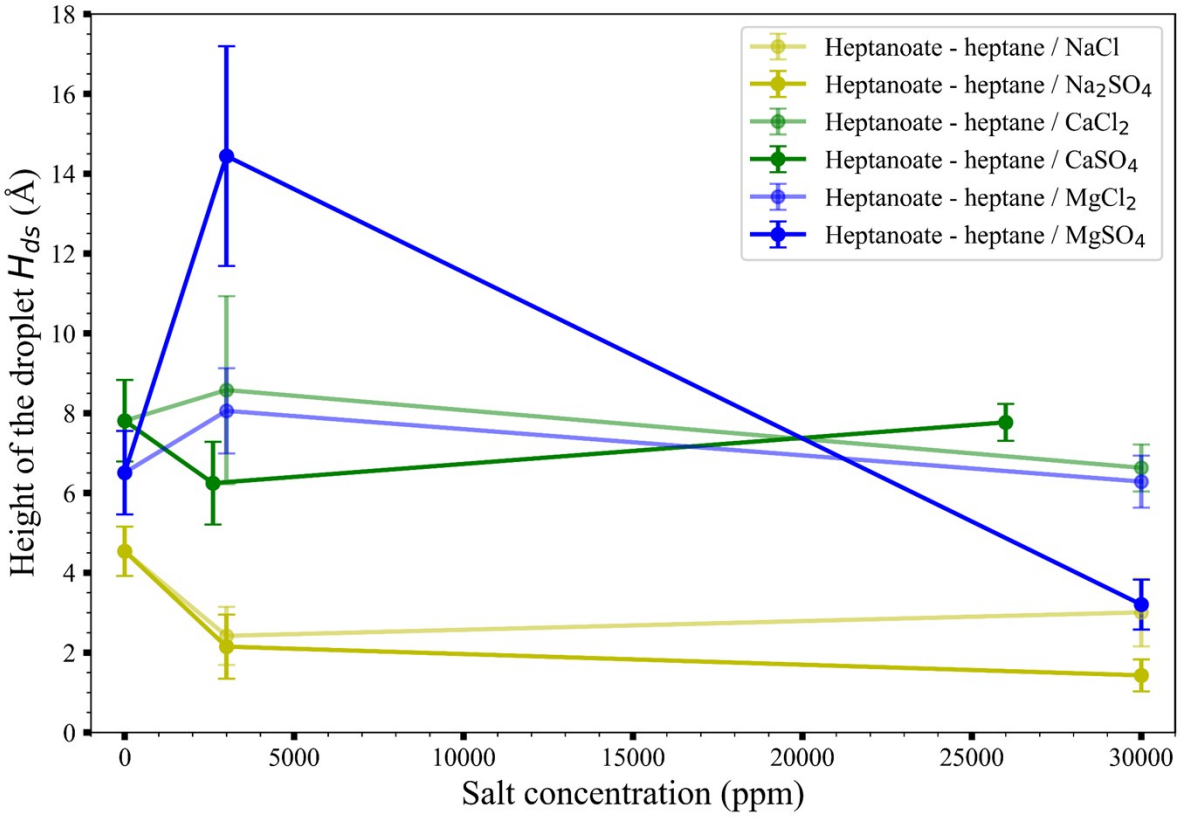


Figure S9. Effect of the SW models salinity at pH >> 4.4 on the H_{ds} of the droplet of polar crude oil model (heptanoate – heptane) on the calcite surface. Each H_{ds} was calculated for 1 ns and averaged to 8 ns in the production stage.

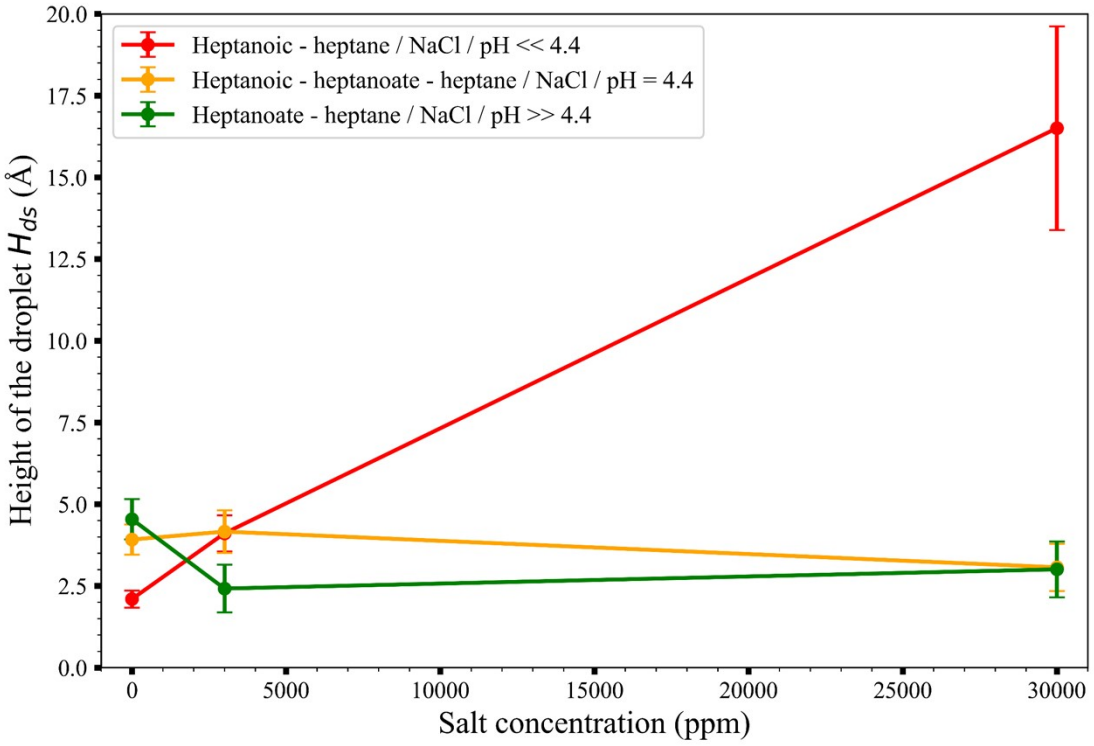


Figure S10. Effect of pH of the NaCl SW model on the height of droplet (H_{ds}) of polar crude oil model on the calcite surface. Each H_{ds} was calculated for 1 ns and averaged to 8 ns in the production stage.

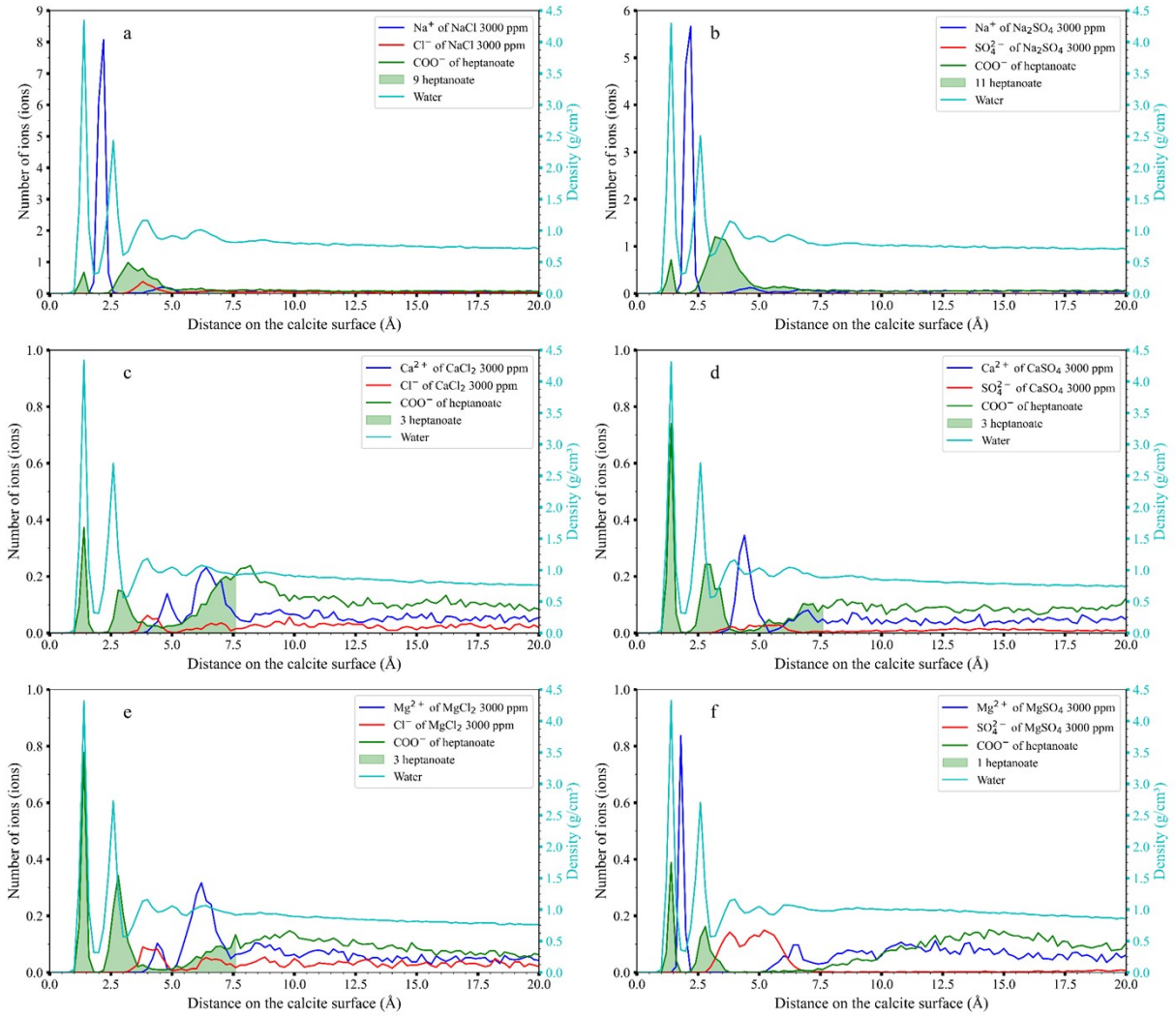


Figure S11. Distribution of cations, distribution of anions, and the one-dimensional mass water density profile of the SW models at pH >> 4.4, distribution of carboxylate groups, and the number of heptanoate between 0 and 7.5 Å (green area) of the polar crude oil model (heptanoate – heptane), on the calcite surface at LSCC. a) NaCl. b) Na_2SO_4. c) $CaCl_2$. d) $CaSO_4$. e) $MgCl_2$. f) $MgSO_4$. These profiles were averaged for 8 ns.

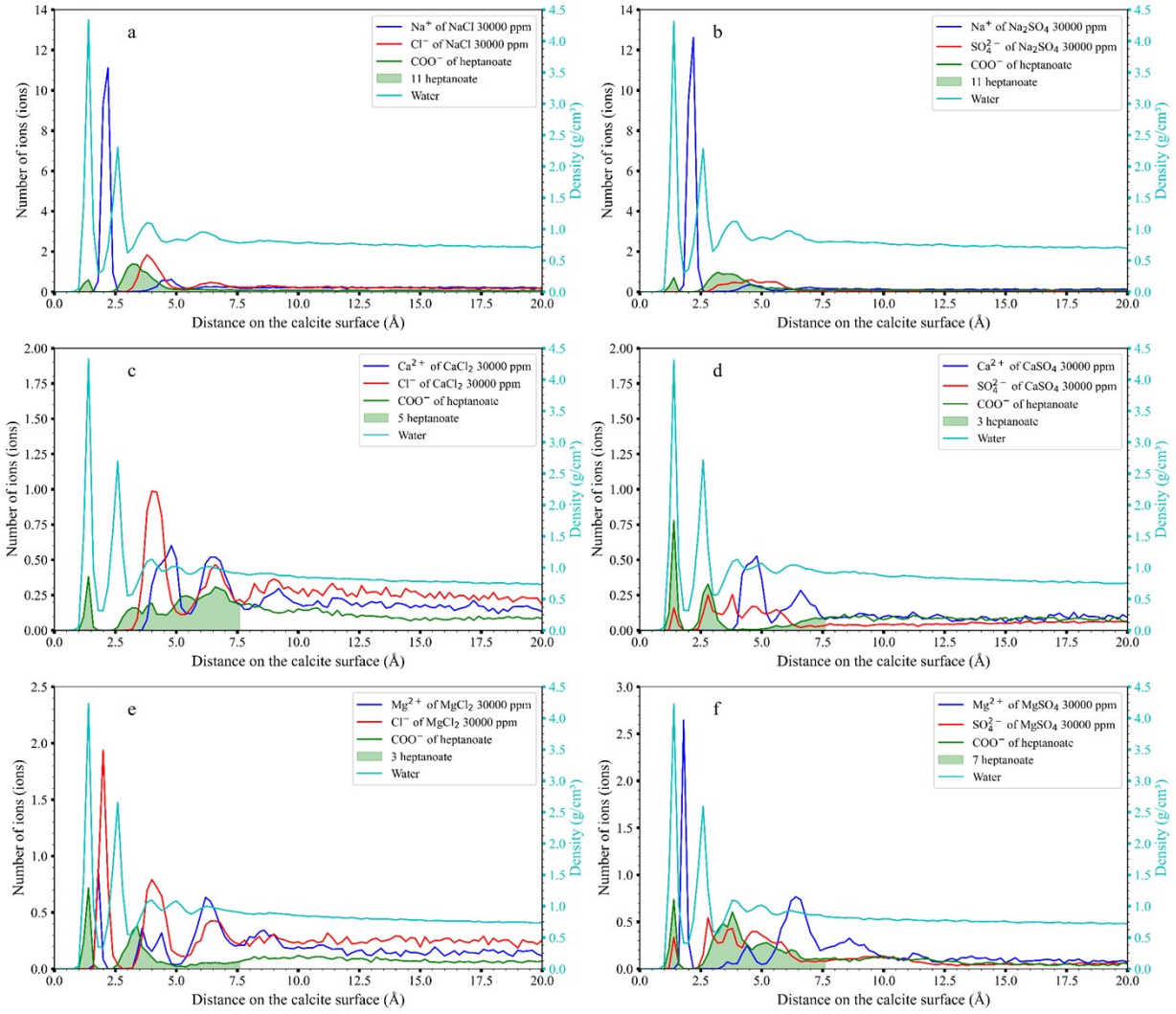


Figure S12. Distribution of cations, distribution of anions, and the one-dimensional mass water density profile of the SW models at pH >> 4.4, distribution of carboxylate groups, and the number of heptanoate between 0 and 7.5 Å (green area) of the polar crude oil model (heptanoate – heptane), on the calcite surface at HSCC. a) NaCl. b) Na_2SO_4. c) $CaCl_2$. d) $CaSO_4$. e) $MgCl_2$. f) $MgSO_4$. These profiles were averaged for 8 ns.