Supporting Information

Kumar and Francisco 10.1073/pnas.1709118114

Computational Details

The BOMD simulations were carried out based on a DFT method implemented in the CP2K (39) code. The droplet system containing 191 water molecules and 1 HMSA (CH_3SO_3H) molecule with and without 1 $(R_1)(R_2)NH$ [for NH_3, $R_1 = R_2 = H$; for CH_3NH_2 or methylamine, $R_1 = H$ and $R_2 = CH_3$; and for $(CH_3)_2NH$ or dimethylamine, $R_1 = R_2 = CH_3$] molecule was examined via BOMD simulations. For studying the droplet systems involving NH_3 or an amine, we used two different starting configurations, namely hydrogen-bonded and nonhydrogen-bonded complex, between HMSA and $(R_1)(R_2)NH$ adsorbed on the water droplet. The dimension of the simulation box is $x = 35$, $y = 35$, and $z = 35$ Å, which is large enough to neglect interactions between adjacent periodic images of water droplet. Before the BOMD simulations, the systems were fully relaxed using a DFT method, in which the exchange and correlation interaction was treated with the Becke–Lee–Yang–Parr functional (41, 42). Grimme's (43, 44) dispersion correction method was applied to account for the weak dispersion interaction. A double-ζ Gaussian basis set combined with an auxiliary basis set and the Goedecker–Teter–Hutter norm-conserved pseudopotentials was adopted to treat the valence electrons and the core electrons, respectively (45, 46). An energy cutoff of 280 Rydberg was set for the plane-wave basis set and 40 Rydberg for the Gaussian basis set. The BOMD simulations were carried out in the constant volume and temperature (NVT) ensemble, with the Nose–Hoover chain method for controlling the temperature (300 K) of the system. The NVT ensemble here refers to an ensemble with three parameters N, V, and T, where N, V, and T correspond to the number of particles in the system, the system's volume and the absolute temperature of the canonical ensemble, respectively. The integration step was set as 1 fs, which had been proven to achieve sufficient energy conservation for the water system.

DFT calculations were also carried out to investigate the properties of the gas-phase hydrogen-bonded complexes of HMSA with one $(R_1)(R_2)NH$ molecule in the absence and presence of one water molecule. All quantum mechanical calculations reported in this work were performed using Gaussian09 (40) software at the standard temperature (298.15 K) and pressure (1 atm). The gas-phase geometries of all of the hydrogen-bonded complexes were fully optimized using the M06-2X (47) DFT method, and the aug-cc-pVTZ (48) basis set (M06-2X/aug-cc-pVTZ) and subsequent normal-mode vibrational frequency analyses were performed to ascertain that the stable minima had all positive vibrational frequencies. The M06-2X/aug-cc-pVTZ–calculated vibrational frequencies were used to estimate the zero-point energy corrections for all of the hydrogen-bonded complexes.

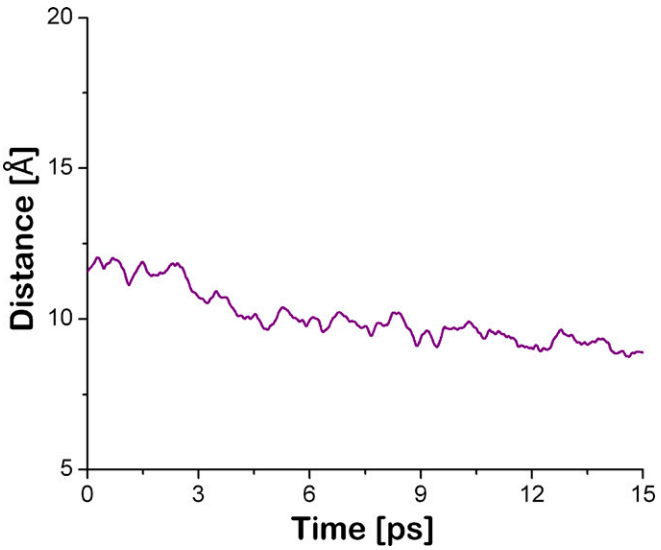


Fig. S1. The distance between the COM of the water droplet and that of HMSA vs. the simulation time. The analysis is based on the BOMD trajectory, with HMSA being initially placed near the water surface.

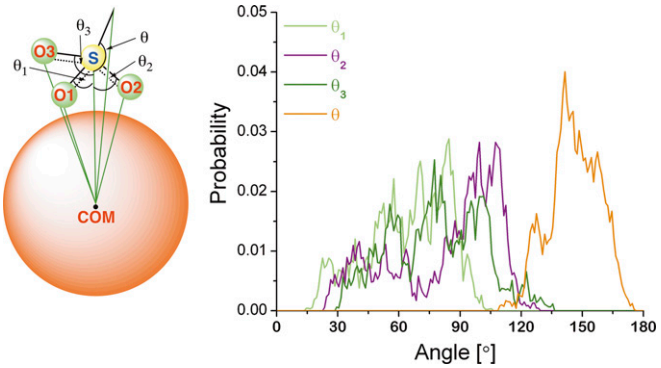


Fig. S2. (*Left*) Definition of angles involving oxygen, sulfur, and carbon atoms of MSA^-, and COM of the water droplet. Here, θ_1, θ_2, and θ_3 are the angles centered at the MSA^- oxygens (i.e., $\theta_1 = \angle$COM.O1.S, $\theta_2 = \angle$COM.O2.S, and $\theta_3 = \angle$COM.O3.S). Here, θ represents the angle centered at the sulfur atom of MSA^- and also involves carbon atom of MSA^- and COM (i.e., $\theta = \angle$COM.S.C.). (*Right*) Angular probability distributions of θ_1, θ_2, θ_3, and θ over the simulated timescale.

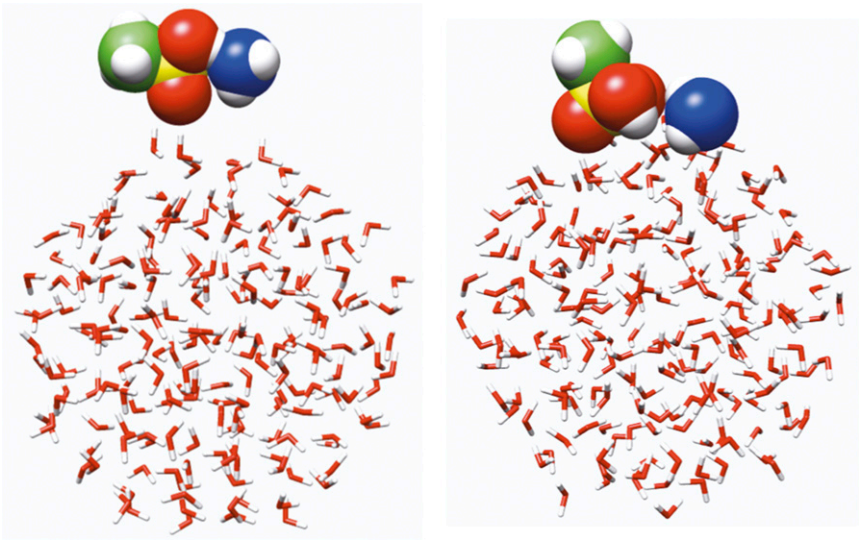


Fig. S3. Initial interfacial positions of the hydrogen-bonded (*Left*) and nonhydrogen-bonded (*Right*) complexes of HMSA with NH_3 on the water droplet. HMSA and NH_3 are shown in ball and stick representation, whereas the water molecules in the droplet are shown in wire representation. Blue, N; green, C; red, O; white, H; yellow, S.

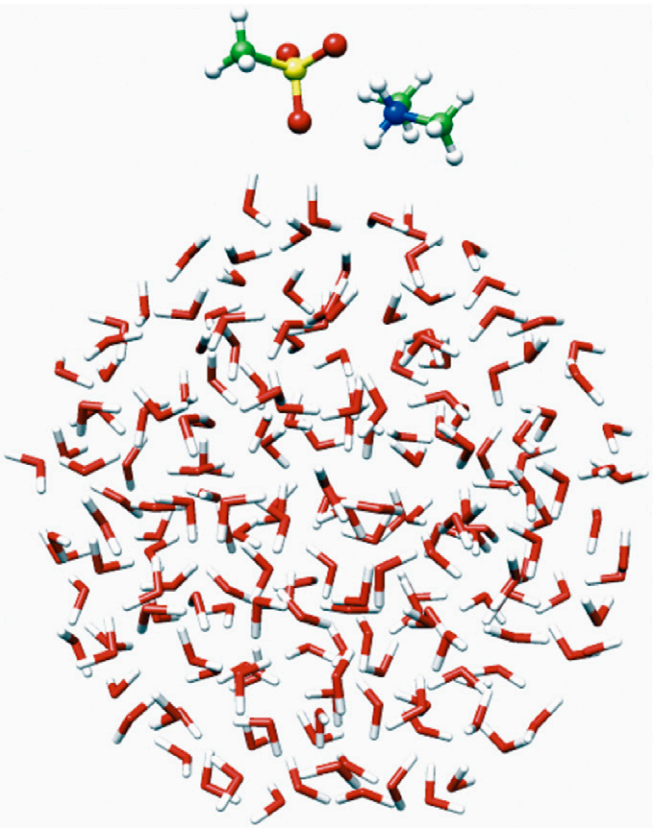


Fig. S4. Optimized geometry of the droplet system consisting of 191 water molecules, 1 HMSA molecule, and 1 dimethylamine molecule. HMSA and dimethylamine are shown in ball and stick representation, whereas the water molecules in the droplet are shown in wire representation. Blue, N; green, C; red, O; white, H; yellow, S.

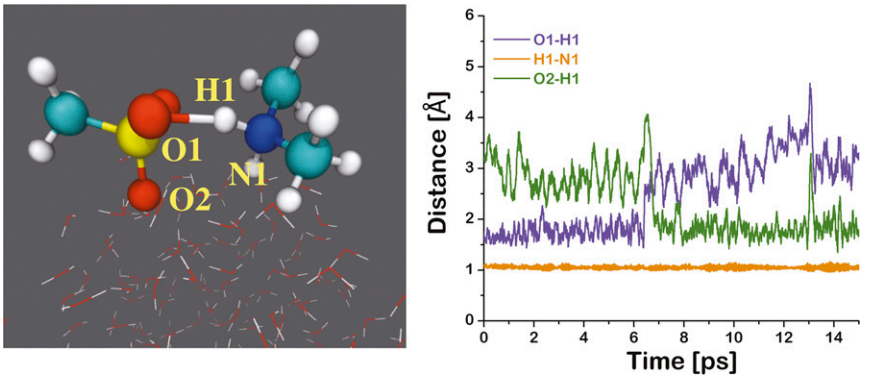


Fig. S5. (*Left*) Snapshot structure taken from the BOMD simulation for the reaction of HMSA with dimethylamine [$(CH_3)_2NH$], which illustrates the formation of the $MSA^{-}\cdot\cdot(CH_3)_2NH_2^{+}$ ion pair particle on the water droplet. (*Right*) Time evolution of key bond distances O1-H1, O2-H1, and H1-N1 involved in the $MSA^{-}\cdot\cdot(CH_3)_2NH_2^{+}$ ion pair-forming reaction.

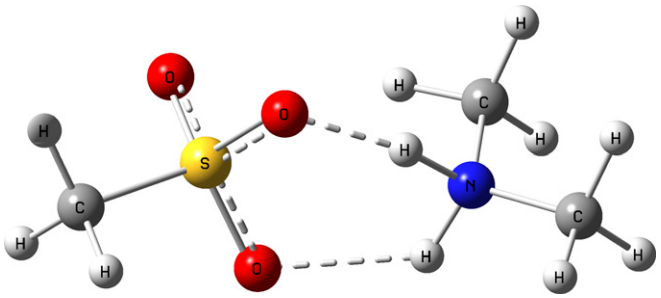


Fig. S6. M06-2X/aug-cc-pVDZ optimized geometry of the gas-phase hydrogen-bonded complex between HMSA and dimethylamine.

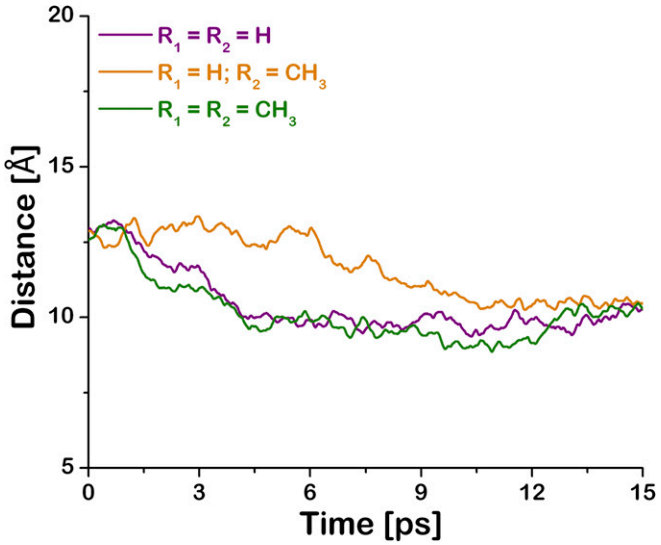


Fig. S7. The distance between the COM of the water droplet and that of $MSA^-\cdot\cdot(R_1)(R_2)\ NH_2^+$ ion pairs vs. the simulation time. The analysis is based on the BOMD trajectory, with the hydrogen-bonded complexes between HMSA and $(R_1)(R_2)NH$ being initially placed near the water surface.

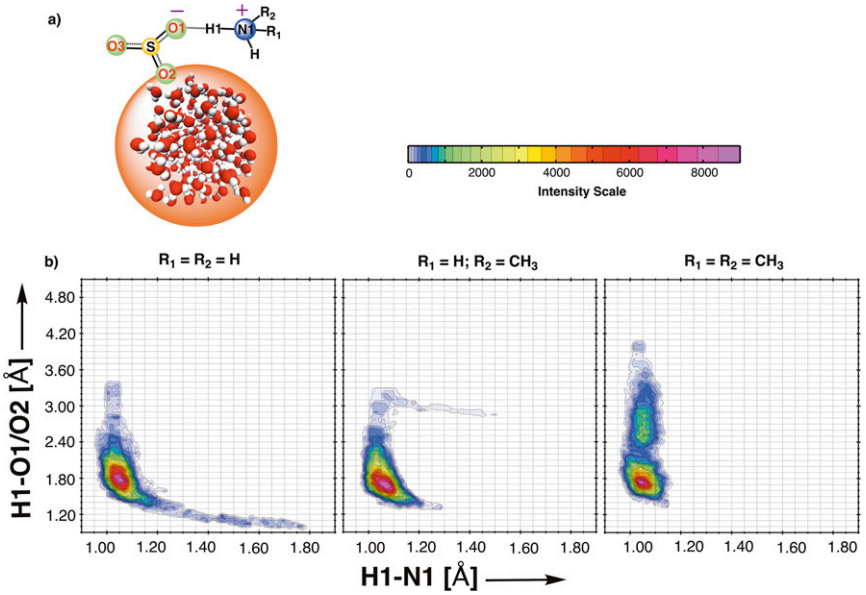


Fig. S8. (*A*) Schematics showing the intraparticle O1··H1-N1 hydrogen bond in the $MSA^-\cdot\cdot(R_1)(R_2)NH_2^+$ ion pair particles and (*B*) CDF involving the O1-H1 and H1-N1 bond distances in the $MSA^-\cdot\cdot(R_1)(R_2)NH_2^+$ particles.

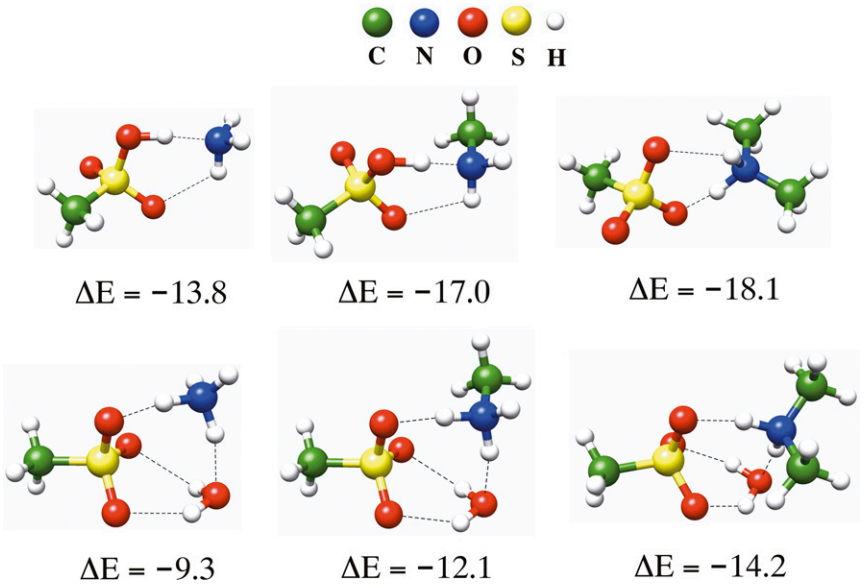


Fig. S9. M06-2X/aug-cc-pVTZ optimized geometries of the gas-phase hydrogen-bonded complexes of HMSA with $(R_1)(R_2)NH$ in the absence (*Upper*) and presence (*Lower*) of one water molecule. The M06-2X/aug-cc-pVTZ–calculated electronic binding energies of the hydrogen-bonded complexes (298.15 K, 1 atm) are also given in kilocalories per mole units. The binding energies of ternary complexes are referenced with respect to HMSA··$(R_1)(R_2)NH + H_2O$.

Table S1. Calculated probabilities of different [m,n] configurations for the $MSA^-\cdot\cdot(R_1)(R_2)NH_2^+$ particles (for NH_3, $R_1 = R_2 = H$; for CH_3NH_2, $R_1 = H$ and $R_2 = CH_3$; and for $(CH_3)_2NH$, $R_1 = R_2 = CH_3$)

	$MSA^-\cdot\cdot(R_1)(R_2)NH_2^+$		
[m,n]	$R_1 = R_2 = H$	$R_1 = H$, $R_2 = CH_3$	$R_1 = R_2 = CH_3$
[0,0]	1	1	30
[1,0]	2	1	69
[0,1]	2	3	0
[1,1]	7	7	0
[1,2]	11	18	0
[1,3]	7	19	0
[1,4]	3	6	0
[0,2]	1	0	0
[2,0]	2	9	0
[2,1]	6	3	0
[2,2]	13	7	0
[2,3]	11	9	0
[2,4]	4	4	0
[0,3]	0	0	0
[3,0]	1	9	0
[3,1]	4	0	0
[3,2]	12	0	0
[3,3]	10	0	0
[3,4]	3	0	0

Here, m and n are the numbers of interfacial water molecules bound to $(R_1)(R_2)NH_2^+$ and MSA^-, respectively.

Table S2. M06-2X/aug-cc-pVTZ–calculated equilibrium constants (K_{eq}) and concentrations (molecules per 1 cm^3) for various HMSA··(R_1)(R_2)NH complexes in the gas phase (1 atm)

	HMSA··NH_3 (R_1 = R_2 = H)		HMSA··CH_3NH_2 (R_1 = H, R_2 = CH_3)		HMSA··$(CH_3)_2NH$ (R_1 = R_2 = CH_3)	
Temperature (K)	K_{eq}	Concentration	K_{eq}	Concentration	K_{eq}	Concentration
200	7.6×10^{-11}	3.3×10^{7}	1.3×10^{-6}	8.1×10^{10}	4.2×10^{-8}	2.6×10^{9}
210	1.4×10^{-11}	6.2×10^{6}	1.8×10^{-8}	1.1×10^{9}	4.8×10^{-9}	3.9×10^{8}
220	3.1×10^{-12}	1.4×10^{6}	2.9×10^{-8}	1.8×10^{9}	6.8×10^{-10}	4.2×10^{7}
230	7.6×10^{-13}	3.3×10^{5}	5.4×10^{-9}	3.3×10^{8}	1.1×10^{-10}	6.8×10^{6}
240	2.1×10^{-13}	9.2×10^{4}	1.2×10^{-9}	7.4×10^{7}	2.2×10^{-11}	1.4×10^{6}
250	6.6×10^{-14}	2.9×10^{4}	2.9×10^{-10}	1.8×10^{7}	4.9×10^{-12}	3.0×10^{5}
260	2.2×10^{-14}	9.7×10^{3}	8.0×10^{-11}	5.0×10^{6}	1.2×10^{-12}	7.4×10^{4}
270	8.2×10^{-15}	3.6×10^{3}	2.5×10^{-11}	1.6×10^{6}	3.5×10^{-13}	2.2×10^{4}
280	3.2×10^{-15}	1.4×10^{3}	8.2×10^{-12}	5.1×10^{5}	1.1×10^{-13}	6.8×10^{3}
290	1.4×10^{-15}	6.2×10^{2}	3.0×10^{-12}	1.9×10^{5}	3.5×10^{-14}	2.2×10^{3}
298.15	7.1×10^{-16}	3.1×10^{2}	1.4×10^{-12}	8.7×10^{4}	1.5×10^{-14}	9.3×10^{2}
300	6.2×10^{-16}	2.7×10^{2}	1.1×10^{-12}	6.8×10^{4}	1.3×10^{-14}	8.1×10^{2}

Table S3. Cartesian coordinates of key species involved in the binary and ternary hydrogen-bonded complexes involving HMSA, NH_3, CH_3NH_2, $(CH_3)_2NH$, and H_2O

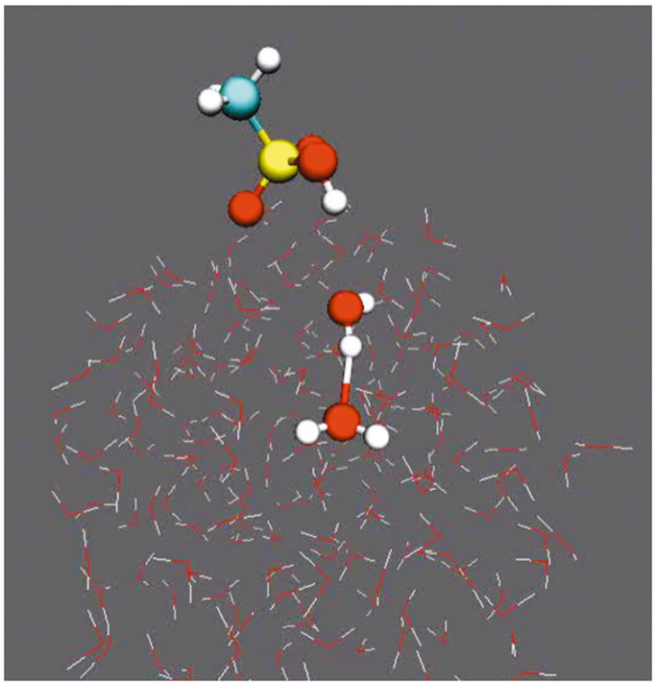
Species	X	Y	Z
HMSA			
S	−0.08558300	−0.13683300	0.06155700
C	1.60961100	0.36553700	0.00757000
H	1.92367900	0.37000500	−1.03197600
H	1.69256000	1.34916500	0.45921700
H	2.16515100	−0.37535600	0.57660900
O	−0.21601200	−1.39333600	−0.61498900
O	−0.61075800	0.04980200	1.39115100
O	−0.76140200	0.98701700	−0.86605000
H	−1.36435300	1.50442400	−0.31508200
H_2O			
O	0.000000	0.119001	0.000000
H	0.768446	−0.476026	0.000000
H	−0.768446	−0.475978	0.000000
NH_3			
N	0.000011	−0.000003	−0.111988
H	0.795810	0.500877	0.261319
H	0.035905	−0.939513	0.261312
H	−0.831789	0.438657	0.261286
CH_3NH_2			
N	0.049408	−0.755833	0.000000
H	−0.436468	−1.113412	0.811683
H	−0.436468	−1.113412	−0.811683
C	0.049408	0.704891	0.000000
H	0.587547	1.061824	0.877072
H	0.587547	1.061824	−0.877072
H	−0.944462	1.164663	0.000000
$(CH_3)_2NH$			
N	−0.000037	0.568129	−0.148481
H	−0.000060	1.336753	0.507833
C	1.204634	−0.223964	0.020244
H	1.262863	−0.961016	−0.782205
H	2.083149	0.415404	−0.048947
H	1.240758	−0.767435	0.975345
C	−1.204539	−0.223942	0.020188
H	−2.083108	0.415571	−0.046401
H	−1.264384	−0.959735	−0.783279
H	−1.239532	−0.769007	0.974432
HMSA··NH_3			
S	0.56484400	0.16662800	0.05564800
C	1.61854000	−1.25553100	0.01335400
H	1.01861200	−2.13557700	0.22341900
H	2.07048600	−1.30694400	−0.97279300
H	2.37526000	−1.10566500	0.77851300
O	−0.42636700	−0.13700100	−1.11770100
H	−1.40192400	−0.16537700	−0.76362800
O	−0.18364500	0.15537900	1.30081300
O	1.35655300	1.32239100	−0.26857500
N	−2.79767200	−0.12454800	−0.02426300
H	−3.37685800	0.67130700	−0.26140200
H	−2.44410500	0.00798900	0.91965100
H	−3.37883100	−0.95291500	−0.04069300
HMSA··CH_3NH_2			
S	−0.85118000	−0.14516900	0.05487800
C	−2.41847500	0.67026600	−0.04857400
H	−2.27284900	1.72190000	0.17710800
H	−2.80283200	0.52682700	−1.05404200
H	−3.06491100	0.19570000	0.68457900
O	−0.04064300	0.60039400	−1.04527500
H	0.96133500	0.76848000	−0.68243200
O	−0.24690200	0.14584600	1.34609000

Table S3. Cont.

Species	X	Y	Z
O	−1.03311500	−1.53112200	−0.30250000
N	2.26856200	0.78186500	−0.00057700
H	1.99433500	1.03569100	0.94354500
C	2.74542400	−0.61041000	−0.03002500
H	1.93476400	−1.25638200	0.30277800
H	2.99752400	−0.87686400	−1.05375500
H	3.61361700	−0.77335600	0.60790900
H	2.98155900	1.42757800	−0.31462900
HMSA··$(CH_3)_2NH$			
S	−1.25109700	−0.17321000	0.05818200
C	−2.39459200	1.09633700	−0.43057100
H	−1.84077700	2.01299300	−0.61056800
H	−2.89601900	0.75769400	−1.33259400
H	−3.10424800	1.22136700	0.38222900
O	−0.29315200	−0.28783800	−1.10082900
H	1.03458800	−0.18995700	−0.53205200
O	−0.52179400	0.34296400	1.23325000
O	−2.01785500	−1.38143800	0.27938700
N	1.92156900	−0.04471900	0.12113800
H	1.48104600	−0.19915200	1.03270000
C	2.99137200	−1.01171100	−0.15981800
H	2.58512900	−2.01692600	−0.09045100
H	3.36248800	−0.84159500	−1.16768900
H	3.80490600	−0.88909100	0.55261100
C	2.32786600	1.36825100	0.03408000
H	2.64056400	1.58111100	−0.98540200
H	1.46488800	1.97494100	0.29475900
H	3.14853800	1.56624600	0.72097100
HMSA··NH_3··H_2O			
S	−0.747326	0.030044	−0.027080
C	−2.487336	−0.131153	0.265344
H	−2.982063	−0.171658	−0.700610
H	−2.650323	−1.044159	0.829917
H	−2.802545	0.741837	0.829549
O	−0.359393	−1.197591	−0.792724
H	1.079001	−1.420019	−0.431463
O	−0.548210	1.253562	−0.805925
O	−0.069210	0.046196	1.280805
N	2.084448	−1.330550	0.001614
H	1.996763	−1.576054	0.984120
H	2.307031	−0.306936	−0.053206
H	2.784682	−1.901115	−0.456875
O	2.157118	1.427136	0.013290
H	1.422578	1.615838	−0.596258
H	1.692523	1.447911	0.861178
HMSA··CH_3NH_2··H_2O			
S	−1.030518	−0.069543	−0.027876
C	−2.678643	−0.610874	0.335479
H	−3.197865	−0.742831	−0.609092
H	−2.611309	−1.546604	0.882156
H	−3.149830	0.161924	0.935845
O	−0.425899	−1.156274	−0.851224
H	1.109995	−0.807680	−0.900221
O	−1.136643	1.191480	−0.769205
O	−0.318743	0.072616	1.255791
N	2.090767	−0.436342	−0.668737
H	1.946030	0.580562	−0.450673
H	2.711719	−0.534157	−1.464787
O	1.372251	2.086615	0.171820
H	0.585640	2.201707	−0.387676
H	0.962111	1.710631	0.966338
C	2.591454	−1.138780	0.535695

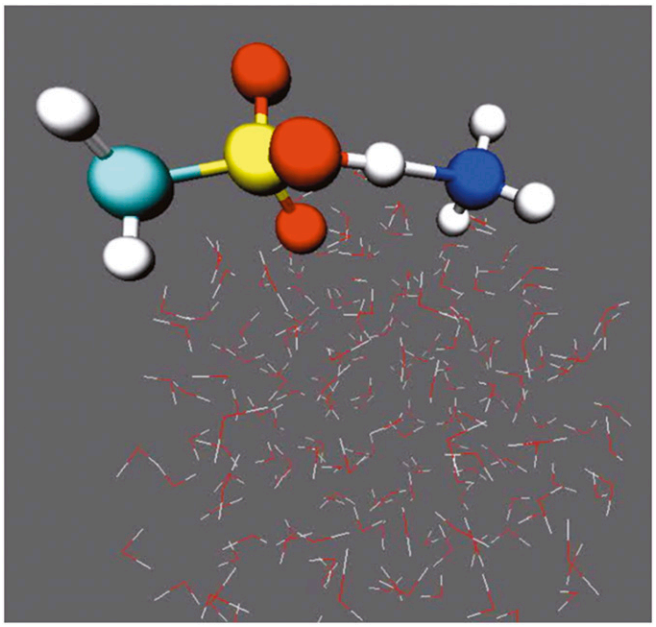
Table S3. Cont.

Species	X	Y	Z
H	1.833958	−1.020512	1.305994
H	2.725117	−2.192317	0.309152
H	3.532763	−0.701213	0.855638
$HMSA{\cdot\cdot}(CH_3)_2NH{\cdot\cdot}H_2O$			
S	1.318400	−0.127257	−0.067287
C	2.982631	−0.712967	0.104331
H	2.979848	−1.518547	0.832418
H	3.312537	−1.063443	−0.869066
H	3.588598	0.121681	0.444574
O	0.526756	−1.297710	−0.538696
H	−0.988552	−0.794798	−0.357658
O	0.866034	0.311837	1.265970
O	1.337649	0.960110	−1.053258
N	−1.884304	−0.289002	−0.082496
H	−1.605515	0.719476	−0.062099
C	−2.949676	−0.512884	−1.072662
H	−2.599011	−0.185294	−2.047244
H	−3.188078	−1.573188	−1.107604
H	−3.834536	0.052860	−0.789725
C	−2.230748	−0.702424	1.292112
H	−2.469877	−1.763301	1.293049
H	−1.362373	−0.514974	1.919104
H	−3.088199	−0.128560	1.636919
O	−0.849843	2.283790	0.133363
H	−0.168717	2.190027	−0.554704
H	−0.338417	2.022624	0.914379



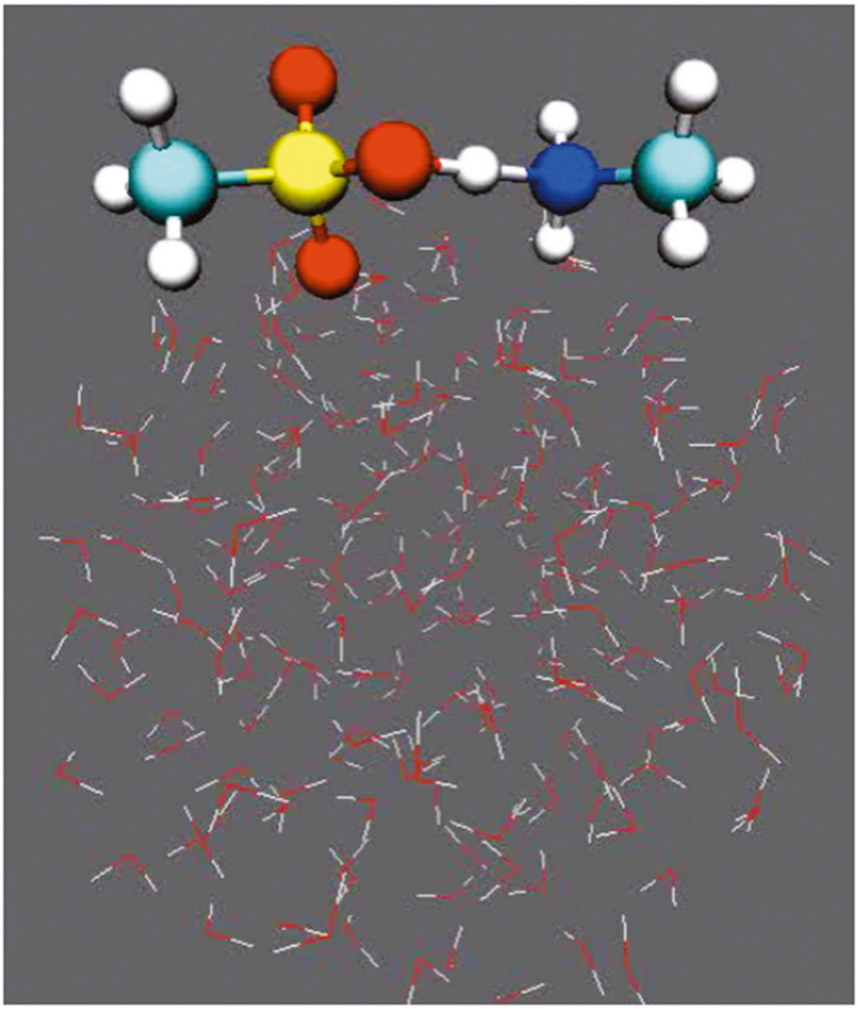
Movie S1. Trajectories of the BOMD simulations for HMSA at the air–water interface.

Movie S1



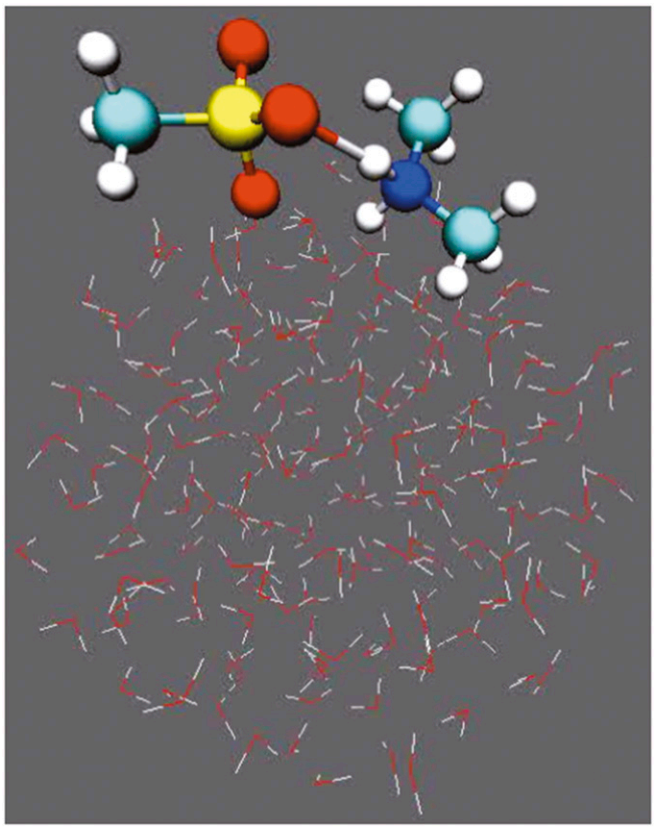
Movie S2. Trajectories of the BOMD simulations showing the interaction between HMSA and NH_3 at the air–water interface.

Movie S2



Movie S3. Trajectories of the BOMD simulations showing the interaction between HMSA and methylamine at the air–water interface.

Movie S3



Movie S4. Trajectories of the BOMD simulations showing the interaction between HMSA and dimethylamine at the air–water interface.

Movie S4