Supporting Information

Simulated solvation of organic ions II: Study of linear alkylated carboxylate ions in water nanodrops and in liquid water. Propensity for air/water interface and convergence to bulk solvation properties

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I. QUANTUM COMPUTATIONS AT THE CBS LIMIT

All quantum calculations have been performed by using the GAUSSIAN09 package of programs [1]. To compute accurate interaction energies of $\text{RCOO}^-/(\text{water})_m$ systems, we optimized first the system geometries at the MP2/aug-cc-pVTZ level of theory. From the optimized geometries, we computed then the total energies of the systems by performing single point energy calculations at the MP2/aug-cc-pVXZ level, with X = D, T, Q. The corresponding Hartree-Fock and correlation energy components, E_{HF} and E_{corr} , were used to extrapolate the system total energies to the complete basis set (CBS) limit, using a three-point exponential formula for E_{HF} [2, 3] and a two-point extrapolation for E_{corr} [4].

II. MOLECULAR DYNAMICS, FREE ENERGY COMPUTATIONS, ION/WATER POTENTIAL OF MEAN FORCE AND ION LOCATION PROBABILITY

MD simulations in condensed phase were performed by considering periodic boundary conditions and the Smooth Particle Mesh Ewald (SPME) summation technique [5]. The cutoff distance of the direct energy term was set to 12 Å, the expansion of the B-spline functions was set to 8, and the interpolation grid size was set 1 Å. No surface term was considered. The Newtonian equations of motion were solved using the multi-time-step r-RESPAp algorithm [6], with two time steps: 1 fs for short-range intermolecular interactions (including U^{rep} , U^{dips} and U^{hb}) and 5 fs for the remaining long-range electrostatic interactions.

For large clusters $(N_w > 300)$, we used the same MD propagator, whereas for small clusters, we used a standard velocity-Verlet propagator, with a time step of 2 fs.

For NVT simulations, we used the generalized Gaussian moment thermostat [7], and in the NPT ensemble, the Nosé-Hoover barostat [8]. The water O-H bonds and \angle HOH angles were both constrained to their equilibrium values by using the iterative RATTLE procedure, regardless of the thermodynamic ensemble considered (the convergence criterion was set to 10^{-6} Å).

To compute the potential of mean force (PMF) corresponding to the interaction of an ion with the droplet center of mass (COM), we applied the umbrella sampling technique. To this end, in the droplet simulations, the ion position d is restrained by a harmonic potential $U^{res} = k_c (d - d_c)^2$, with the harmonic constant k_c set to 5 kcal mol⁻¹. For all systems, we performed 40 simulations, corresponding to reference ion/COM distances d_c ranging from 0 to 19.5 Å, and regularly spaced by 0.5 Å. For ions interacting at the air/liquid water interface, the PMF are computed from simulations where the ion is restrained by the same potential U^{res} . However, we consider in this latter case the geometrical parameter z, that is the projection on the axis orthogonal to the air/water interface of the distance between the ion and the simulation cell center (SCC). The total energy conservation along these simulations is ensured according to the protocol proposed in Ref. [9]. The sampling protocol is the same as for droplets, except for d_c , whose value ranges from 15 to 34.5 Å. The PMF are estimated from the ion/COM and ion/SCC distance distribution functions computed along the simulations and post-processed according to the Umbrella Integration method [10].

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FIGURES



FIG. 1. $CH_3COO^-/(H_2O)_n$ cluster definition. In bold dashed lines, the carboxylate/water strong hydrogen bonds and the distances mentioned in Table II between the carboxylate and the hydrogen atoms belonging to the water molecules of the second hydration shell. In thin dashed lines, the hydrogen bonds between water molecules.



FIG. 2. Comparison of the model and the ab initio energy profiles corresponding to the dihedral angle $\angle O - C - C - C$ in propanoate. Ab initio computations were performed at the MP2/aug-cc-pVTZ level of theory.



FIG. 3. Comparison of the model and the ab initio energy profiles corresponding to the dihedral angle Ψ_1 in butanoate. Ab initio computations were performed at the MP2/aug-cc-pVTZ level of theory.



FIG. 4. Comparison of the model and the ab initio energy profiles corresponding to the dihedral angle $\angle C - C - C - C$ in butane. Ab initio computations were performed at the MP2/aug-cc-pVTZ level of theory.



FIG. 5. Carboxylate PMF (a) and water density (b) at the air/liquid water interface. The PMF do not include the δ PMF correction. For (a), the vertical dashed line indicates the interface position.



FIG. 6. Carboxylate location density probability P(r) in water droplet. (a): HCOO⁻ (—) and CH₃COO⁻ (- -); (b): C₂H₅COO⁻ (—) and C₃H₇COO⁻ (- -); (c): C₄H₉COO⁻ (—) and C₅H₁₁COO⁻ (- -). Black: $N_w = 50$; blue: $N_w = 100$; green: $N_w = 300$; orange: $N_w = 600$; red: $N_w = 1000$.



FIG. 7. Effect of the TS_{geom} term on the location density probability for $N_w = 1000$ droplet systems. In full dark lines, the density probabilities computed by accouting for TS_{geom} (*i.e.* the ones already plotted in Figure 6). In dashed lines, the corresponding density probabilities computed by omitting TS_{geom} .



FIG. 8. $\Delta \bar{R}_C$ values from air/liquid water simulations. Black: ethanoate; blue: propanoate; green: butanoate; orange: pentanoate; red: hexanoate. The position of the vertical dashed line corresponds to the air/liquid water interface.



FIG. 9. Example of dihedral angle Ψ_n distributions (n = 4 - 6) for hexanoate at the air/liquid water interface from 10-ns scale simulations sampled each 1 ps.



FIG. 10. In full lines, ratio of the anti vs. gauche conformations for the dihedral angles $\Psi_{n=1,2,3}$ for hexanoate as a function of d_c , for $N_w = 1000$ droplet simulations. Red line: Ψ_1 ; green line: Ψ_2 ; blue: Ψ_3 . The vertical dashed line indicates the air/droplet interface position. Here, ten more umbrella sampling simulations than in the paper were performed, corresponding to $d_c = 20 - 30$ Å. In dashed lines, the corresponding profiles from air/liquid water simulations, shifted so that the interface position matches the droplet one.

TABLES

Energy term	Unit	Parameter	Value	Parameter	Value		
$U^{qq'}$	e	$q_{\rm C_{COO^-}}$	0.80	$q_{\rm O_{COO^-}}$	-0.80		
	e	$q_{ m CH_2}$	-0.14	$q_{ m CH_3}$	-0.21		
	e	$q_{\rm C^1H_2}$	-0.34	$q_{\rm C^1H_3}$	-0.41		
_	e	$q_{ m H}$	0.07				
U^{pol}	${ m \AA}^3$	$\alpha_{\rm C_{COO^-}}$	0.80	$\alpha_{0_{COO^{-}}}$	1.00		
	$ m \AA^3$	$lpha_{ m C_{methyl}}$	2.10				
	Å ⁻³	$c_{\rm all-atoms}$	0.30				
U^{rep}	kcal mol $^{-1}$	$a_{\mathrm{C}_{\mathrm{COO}^{-}},\mathrm{O}_{\mathrm{w}}}$	250 000	$a_{\mathrm{C}_{\mathrm{methyl}},\mathrm{O}_{\mathrm{w}}}$	2 000 000		
	kcal mol $^{-1}$	$a_{\mathrm{C}_{\mathrm{COO}^{-}},\mathrm{H}_{\mathrm{w}}}$	90 000	$a_{\mathrm{C}_{\mathrm{methyl}},\mathrm{H}_{\mathrm{w}}}$	75000		
	kcal mol $^{-1}$	$a_{O_{COO^{-}},O_{w}}$	10 700	$a_{\rm H_{methyl},O_w}$	60 000		
	kcal mol $^{-1}$	$a_{\rm O_{COO^-},H_w}$	75 000	$a_{\rm H_{methyl}, H_w}$	60 000		
	$Å^{-1}$	$b_{\rm C_{COO^-},O_w}$	4.300	$b_{\rm C_{methyl},O}$	4.80		
	$Å^{-1}$	$b_{\rm C_{COO^-},H_w}$	4.500	$b_{\rm C_{methyl}, H_w}$	6.00		
	$Å^{-1}$	$b_{\rm O_{COO^-},O_w}$	3.00	$b_{\rm H_{methyl},O_w}$	6.00		
	$\rm \AA^{-1}$	$b_{\rm O_{COO^-}, H_w}$	7.00	$b_{\rm H_{methyl}, H_w}$	6.00		
U^{disp}	Å kcal mol ⁻⁶	$r^*_{C_{\text{COO}^-},O_w}$	3.3447	$r^*_{O_{\text{COO}^-},O_w}$	0.0		
	Å kcal mol ⁻⁶	$r^*_{C_{ ext{methyl}},O_w}$	2.9780				
U^{shb}	Å	r^e_{shb}	1.90				
	$Å^{-1}$	γ_r	2.00	γ_r'	0.30		
	rad	ψ_e	0.0				
	rad^{-1}	γ_{ψ}	0.70				
	kcal mol ^{-1}	d_e	2.60				
	-	ξ	-0.10				

TABLE I. The ion/water model parameter set. "all-atoms" refers to parameters that are used regardless of the atom type. $C^{1}H_{3}$ and $C^{1}H_{2}$ refer to the alkyl carbon atom linked to the COO⁻ moiety, for ethanoate and larger carboxylates, respectively.

TABLE II. Quantum and model results for the clusters $CH_3COO^-/(H_2O)_n$ shown in Figure 1. Quantum BE: cluster binding energy at the CBS limit (i.e., binding energy at 0 K, not ZPEcorrected). Model BE: cluster binding energy given by the model. Quantum R_{O_{COO-},H_w} : distance between the oxygen atoms of the COO⁻ moiety and of the hydrogen atoms of the water molecules, from MP2/aug-cc-pVTZ computations. Model R_{O_{COO-},O_w} : model distances. All BE in kcal mol⁻¹ and all distances in Å. The superscript corresponds to the HB labeling of Figure 1. The stepwise quantum energies $\Delta E_{n-1,n}$ (connecting the lowest energy isomers) are 20.1, 15.5, 16.6, and 14.7 kcal mol⁻¹ while for comparison, the experimental stepwise enthalpies $-\Delta H_{n-1,n}$ are 16.2, 13.3, 12.0, and 11.0 kcal mol⁻¹ [11–14].

Cluster	Quantum BE	Quantum $R_{O_{\text{COO}-},H_w}$	Model BE	Model $R_{O_{\text{COO}-},H_w}$
1	-20.1	1.96	-19.9	1.95
2-1	-35.6	1.67^{1}	-35.5	1.69^{1}
		1.80^{2}		1.72^{2}
2-2	-33.2	1.86^{1}	-32.3	1.87^{1}
		4.23^{2}		4.31^{2}
		5.56^{3}		4.89^{2}
3-1	-52.2	1.77^{1}	-51.7	1.70^{1}
		1.80^{2}		1.78^{2}
		1.93^{3}		1.84^{3}
3-2	-46.1	1.71^{1}	-44.5	1.78^{1}
		1.89^{2}		1.82^{2}
		3.80^{3}		4.09^{2}
		4.28^{2}		4.15^{2}
4-1	-66.9	1.84^{1}	-67.7	1.80^{1}
		1.92^{2}		1.84^{2}
		1.85^{2}		1.80^{3}
		1.93^{2}		1.85^{4}
4-2	-65.0	1.74^{1}	65.5	1.74^{1}
		1.87^{2}		1.80^{2}
		1.89^{3}		1.82^{3}
		1.95^{4}		1.76^{4}
4-3	-63.8	1.68^{1}	-62.1	1.66^{1}
		1.90^{2}		1.82^{2}
		1.80^{3}		1.79^{3}
		4.01^{4}		3.87^{4}

TABLE III. Quantum NPA charges for the most stable $CH_3COO^-/(H_2O)_{N_w}$ clusters ($N_w = 0 - 4$) at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory. For OC and HC atom types, the values provided are averaged. All charges in e.

N_w	OC	СО	CH	HC
0	-0.89	0.93	-0.63	0.16
1	-0.89	0.93	-0.63	0.16
2	-0.88	0.95	-0.62	0.18
3	-0.88	0.95	-0.62	0.18
4	-0.90	0.96	-0.62	0.18

TABLE IV. Number n of structures from the Cambridge Data Base where the dihedral angles Ψ_n range from 30 to 90° and from 145 to 180°, respectively.

n	Ψ_1	Ψ_2	Ψ_3
pentanoate	11/18	8/21	-
hexanoate	17/41	7/51	5/53

TABLE V. Ion solvation enthalpies (in kcal mol⁻¹) of ethanoate and hexanoate inside and at the air/water interface of 600 H₂O molecule droplets, based on data extracted from Figure 8 of the main manuscript (the subscript *iw* refers to ion/water interactions and *ww* to water/water ones). ^a Absolute solvation factor enthalpies extracted from Figure 8 near the COM and at the air/water interface, respectively. ^b Differences between hexanoate and ethanoate in the solvation factors near the COM and at the air/water interface, respectively. ^c Sum of the combined (*iw* + *ww*) hexanoate-ethanoate solvation enthalpy differences near the COM and at the air/water interface. ^d Sum of the combined *iw* hexanoate-ethanoate solvation factor enthalpy differences near the COM and at the air/water interface, respectively. ^e Attributing the hexanoate-ethanoate differences to the contributions of 4 added CH₂ groups in hexanoate. The contribution per CH₂ group to each solvation term may be obtained by dividing by 4 the Δ values. The enthalpy contribution per CH₂ group to the difference between column 9 and column 8 for each solvation factor.

	In solution (near COM)		At the interface			Contribution per CH_2 group ^e			
	$ethanoate^{a}$	$hexanoate^a$	Δ^b	$ethanoate^{a}$	$hexanoate^a$	Δ^b	COM	interface	$COM \rightarrow interface$
U_{iw}	-129	-134	-5.0	-124	-122	+2	-1.25	+0.5	+1.75
U_{ww}	-5413	-5410	+3.0	-5415	-5415	0.0	+0.75	0.0	-0.75
$U_{iw} + U_{ww}$			-2^{c}			$+2^{c}$			+1.0
U_{iw} details									
U^{disp}	-12	-24	-12	-6	-8.5	-2.5	-3.0	-0.6	+2.4
U^{shb}	-13	-13	0.0	-12.0	-12.0	0.0	0.0	0.0	0.0
U^{qq}	-114.5	-114.0	+0.5	-106.5	-106.0	+0.5	0.12	+0.12	0.0
U^{pol}	-15.5	-13.0	+2.5	-22	- 18	+4.0	+0.6	+1.0	+0.4
U^{rep}	+26.5	+30.5	+4.0	+21.5	+22.0	+0.5	+1.0	+0.1	-0.9
Total			-5.0^{d}			$+2.5^{d}$			+ 1.9