The Stability of Positively Charged Solutes in Water: A Transition From Hydrophobic to Hydrophilic

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Supplementary Materials

Tables

Table S1: Description of system parameters used in MD simulations and average volumes from the last 5ns of 10ns NPT (1atm) MD for neutral and charged cavities.

r_{HC} (Å)	# water molecules	Initial cell length (Å)	Equilibrated <Volume> (Å^3)			
			q_c = 0e	q_c = 0.1e	q_c = 0.5e	q_c = 1.0e
0.0001	216	18.77	6876.4	6536.4	6534.3	6565.5
1	340	22.00	11067.2	10348	10344.9	10386.7
2	442	24.00	14807.5	13585.3	13557.9	13614.3
3	526	26.00	18231.7	16382.9	16317.0	16384.0
4	683	28.00	24112.3	21517.2	21405.2	21483.2
5	805	30.00	29262.8	25776.2	25589.4	25670.1
6	952	32.00	35441.7	30964.2	30675.7	30767.1
7	1163	34.00	43968.5	38315.9	37919.6	38007.0
8	1398	36.00	53625.7	46634	46090.1	46184.5
9	1583	38.00	62058.4	53698.3	52997.8	53088.5
10	1818	40.00	72455.6	62593.8	61710.0	61779.8
12	2329	42.00	95816.7	82598.8	81274.4	81334.2
15	3305	44.00	141283.1	121799.4	119589.9	119612

Table S2: Comparison of the calculated free energy of solvation for Helium and 3 alkali metals using the 2PT method and our local Yukawa potential for electrostatics, compared to previous computational results and experiments. The solvation free energy is obtained as: $\Delta G^0 = A^{solute}_{water} - A^{bulk}_{water} - A^{solute}_{vacuum} + \Delta A^{solute}_{water}\left(0 -> 1e^-\right) - PV$ where the 1st term of the right hand side is the energy of the neutral species, the 2nd term is the bulk water energies that are obtained from 5 independent simulations of the free water box, the 3rd term is the vacuum energy of the neutral species as obtained from the CODATA thermodynamic tables[1], and the 4th term is the energy required to charge from 0 to +1e- ionic state. All energies are in kJ/mol.

solute	**[a]LJ12-6**		**vacuum -> solution**			**0 → +1e$^-$**			**[b]ΔG_{2PT}**	**[c]ΔG_{TI}**	**[d]ΔG_{exp}**
	ε (kj/mol)	σ (Å)	ΔA	ΔE	TΔS	ΔA	ΔE	TΔS			
He	0.180	2.90	22.59	-9.92	-32.51	--	--	--	25.08		29.41[e]
Li	0.047	2.91	13.70	-0.95	-14.65	-317.03	-364.41	-47.38	-442.22	-525[f]	-475
Na	0.109	3.18	17.51	-5.51	-23.02	-296.88	-322.64	-25.76	-399.60	-398	-365
K	0.356	3.30	44.34	-7.04	-51.38	-230.26	-313.62	-83.36	-306.18	-271	-295

[a] $E_{LJ12-6}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, from Reference[2] for Helium and Reference[3] for ions

[b]This work. We include a finite size correction of -122.75 kJ/mol as suggested in Reference[4] and a correction of PV = RT = 2.49 kJ/mol according to the Gibbs – Helmholtz relation: G = A + PV

[c]Thermodynamic Integration results from Reference [4]

[d]Experimental results from Marcus in Reference [5]

[e]Experimental results from Abraham in Reference [6]

[f]From Reference [7]

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