Solvation free energy of single ions: Correction

Table 1 gives from literatures some experimental and MD simulation results of solvation free energy as well as the positions of the first maximum of the RDF for alkali and halide ions. We can see that the experimental data themselves vary a lot. Furthermore the LJ parameters for ions in the literature are extremely dispersed. Therefore, we focused on a single series of force field parameters for halide anions and alkali cations taken from ref [1] based on SPC/E water, as shown in table 1 and 2.

Ion	$-\Delta G_{solv}^{exp\,(a)}$	$-\Delta F_{solv}^{exp\,(b)}$	$-\Delta G_{solv}^{exp\,(c)}$	$R_1^{(d)}$	σ [Å]$^{(e)}$	ϵ [kJ·mol^{-1}]$^{(e)}$	$-\Delta G_{solv}^{MD\,(e)}$	$R_1^{MD(e)}$
F$^-$	465	374.5	428.8	2.08	3.434	0.465	430	2.74
Cl$^-$	340	318.4	304.2	2.36	4.394	0.416	306	3.23
Br$^-$	315	289.5	227.4	2.80	4.834	0.211	279	3.35
I$^-$	275	252.3	240.0	2.89	5.334	0.158	241	3.55
Li$^+$	475	511.0	529.4	3.14	2.874	0.000615	520	1.91
Na$^+$	365	411.5	423.8	2.63	3.814	0.000615	414	2.28
K$^+$	295	337.2	352.0	3.19	4.534	0.000615	347	2.54
Rb$^+$	275	316.0	329.3	3.37	no data	no data	no data	no data
Cs$^+$	250	283.8	no data	3.65	5.174	0.000615	300	2.79

Table 1: Free energy [kJ·mol^{-1}] and first maximum of ion-water oxygen RDF [Å] for alkali and halide ions from experimental and MD simulation result. (a). Ref [3]. (b). Ref [4]. (c) Ref [5]. (e) Ref [1] from MD simulation. (d) Ref [2].

Ion	σ [Å]$^{(e)}$	ϵ [kJ·mol^{-1}]$^{(e)}$	ΔG_{solv}^{MD}	$\Delta \Omega_{solv}^{dipole}$	$\Delta \Omega_{solv}^{nmax3}$	R_1^{MD}	R_1^{dipole}	R_1^{nmax3}
F$^-$	3.434	0.465	-430	-805	-351	2.74	2.71	2.71
Cl$^-$	4.394	0.416	-306	-521	-233	3.23	3.21	3.21
Br$^-$	4.834	0.211	-279	-464	-205	3.35	3.37	3.37
I$^-$	5.334	0.158	-241	-388	-166	3.55	3.54	3.54
Li$^+$	2.874	0.000615	-520	-870	-480	1.91	2.13	2.13
Na$^+$	3.814	0.000615	-414	-742	-412	2.28	2.29	2.38
K$^+$	4.534	0.000615	-347	-623	-358	2.54	2.54	2.54
Cs$^+$	5.174	0.000615	-300	-528	-317	2.79	2.79	2.79
Li$^+$	1.374	1.538	-521	-889	-492	1.96	2.13	2.13
Na$^+$	2.134	1.538	-415	-749	-419	2.34	2.46	2.38
K$^+$	2.774	1.538	-345	-610	-360	2.68	2.71	2.71
Cs$^+$	3.334	1.538	-300	-512	-318	2.98	3.04	3.04
Li$^+$	1.474	0.65	-523	-891	-490	1.96	2.13	2.13
Na$^+$	2.234	0.65	-416	-753	-415	2.33	2.38	2.37
K$^+$	2.894	0.65	-344	-612	-358	2.65	2.63	2.71
Cs$^+$	3.434	0.65	-299	-517	-318	2.93	2.96	2.96

Table 2: Free energies [kJ·mol^{-1}] and first RDF maximum [Å] of single ions from MDFT results compared to MD results

The results shows in table 2 are calculated with $L = 32$ Å, nfft = 96; and $m_{max} = 3$ to ensure that the $\mathcal{F}_{id}$ and $\mathcal{F}_{ext}$ terms calculated by using the DCF at $n_{max} = 3$ or the dipole DCF are exactly the same. The free energies given by MDFT with $n_{max} = 3$ is not perfect, but lie in the same order of magnitude as MD. For negative ions, there is always a shift at ~ 80 kJ·mol^{-1} (knowing that the correction of type-C is at 82 kJ·mol^{-1} but we cannot tell what the shift is). For positive ions, the magnitude of free energy is slightly underestimated with small σ, and slightly overestimated for large σ. On the other hand, the free energies given by dipole DCF is too large in magnitude. In contrast, the position of the first solvation maximum for the three methods do not vary between them (apart from Li$^+$ which is very small). But if we look at the RDF of charged CH$_4$ series, we can see that $n_{max} = 3$ still works better. We can conclude that the results in energy with a DCF at $n_{max} = 3$ works better than the dipolar approximation, which is a positive sign for our developments.

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