Supporting information for:

$B(OH)_4^-$ Hydration and Association in Sodium Metaborate Solutions by X-Ray Diffraction and Empirical Potential Structure Refinement

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Content:

Table S1 Bond lengths and angles used to describe the molecules $B(OH)_4^-$ and H_2O

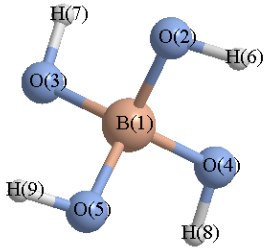
	Bonds/Å			Angle/°				Dihedral angle/°				
	atom 1	atom 2	distance	atom 1	atom 2	atom 3	Angle	atom 1	atom 2	atom 3	atom 4	Angle
 $B(OH)_4^-$	1	2	1.48965	2	1	3	106.93602	3	1	2	6	-162.13789
	1	3	1.48965	2	1	4	106.95973	4	1	2	6	-38.86043
	1	4	1.48889	2	1	5	114.61903	5	1	2	6	79.52378
	1	5	1.48943	3	1	4	114.65141	2	1	3	7	38.9278
	2	6	0.96238	3	1	5	106.9454	4	1	3	7	-79.44763
	3	7	0.96177	4	1	5	106.96913	5	1	3	7	162.15872
	4	8	0.96238	1	2	6	106.74967	2	1	4	8	162.13585
The structure was based on the crystal structure and optimized with Gaussian at B3LYP/Aug –cc-pvdz	5	9	0.96268	1	3	7	106.77118	3	1	4	8	-79.50208
				1	4	8	106.76966	5	1	4	8	38.87816
				1	5	9	106.80371	2	1	5	9	79.46024
								3	1	5	9	-38.87276
								4	1	5	9	-162.16083
								3	1	2	6	-162.13789
 H_2O	1	2	0.9650	1	2	3	109.450					
	2	3	0.9650									

Table S2 EPSR simulation boxes setup details.

simulation name	# water molecules	# Na^+ cations	# anions	Density /atoms $Å^{-3}$	Box side length /Å	Iterations times
Water	1000	-	-	0.099987	31.074	10000
B1N1	1000	18	18	0.10315	31.353	11000
B1N2	1000	55	55	0.10735	32.100	12000
B1N3	1000	125	125	0.11128	33.677	13200

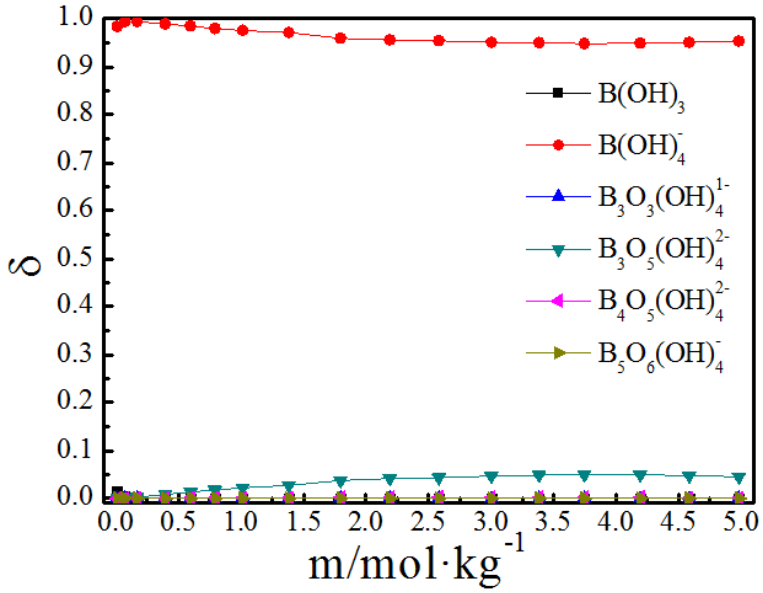


Fig. S1. The distribution of boron species with salt concentration in aqueous $NaB(OH)_4$ solutions at 298.15 K

■,H_3BO_3 ; ●, $B(OH)_4^-$; ▲, $[B_3O_3(OH)_4]^-$; ▼, $B_3O_3(OH)_5^{2-}$;★, $B_4O_5(OH)_4^{2-}$; ▶, $B_5O_6(OH)_4^-$

See: Zhou Y. Fang C. Fang Y., Chin. J. Chem. Eng. 2013, 21 (9): 1048-1056.

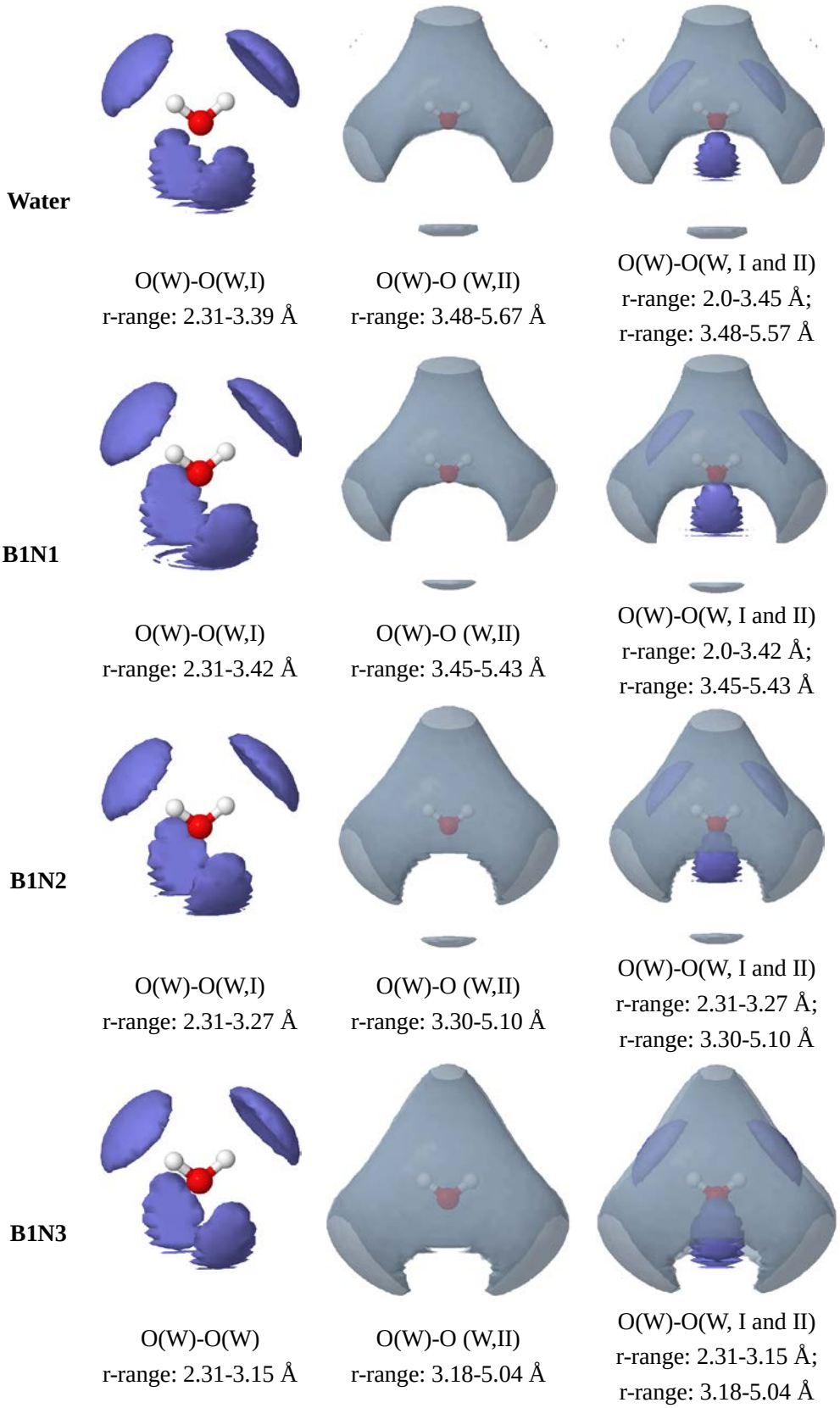


Fig. S2 Spatial density functions of water molecules around a central water molecule in pure water and three aqueous $NaB(OH)_4$ solutions. The dark blue lobes represent the first sphere and the grayish blue and semitransparent lobes ones represent of the second sphere. The red and white ball in the center represent O and H atom, respectively.

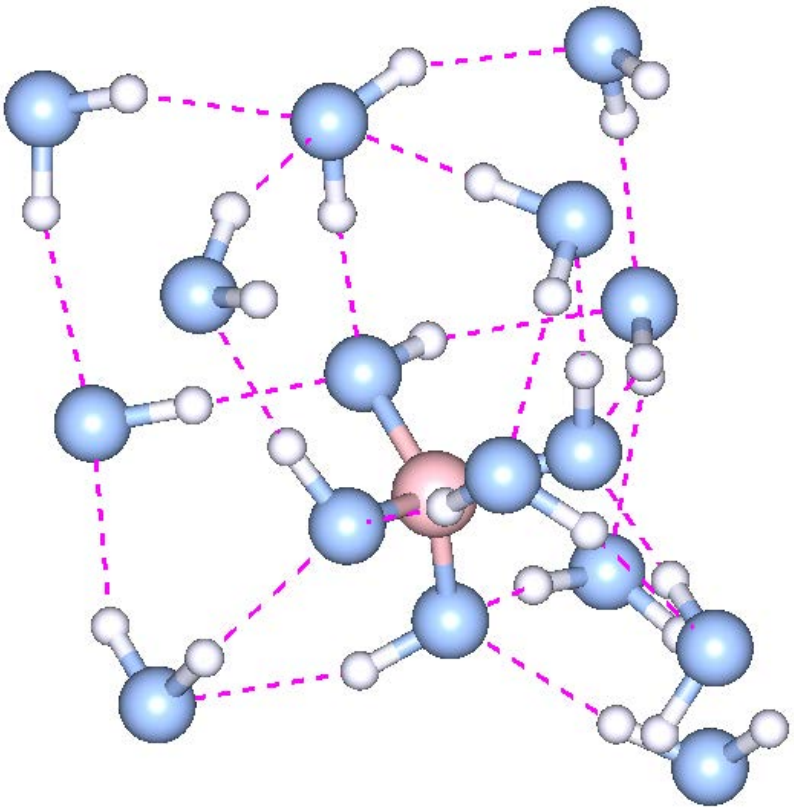
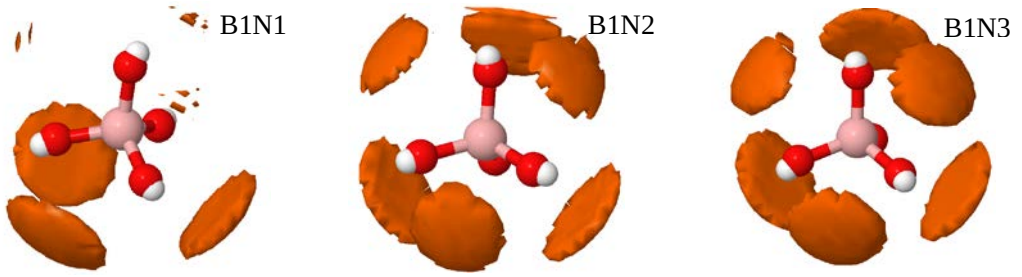
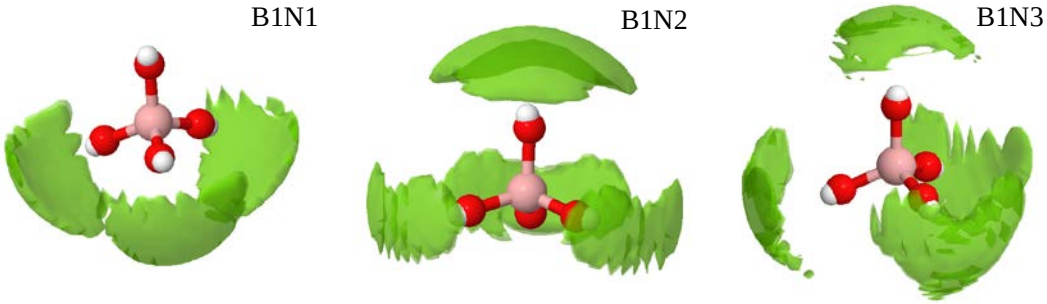


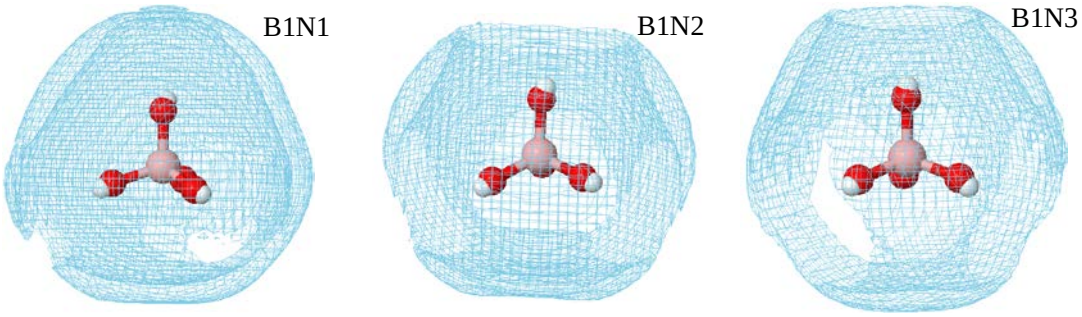
Fig. S3. One of the optimized lowest-energy structures of aqua-$B(OH)_4^-$ $[B(OH)_4\ (H_2O)_{12}]^-$ at B3LYP/aug-cc-pVDZ level.



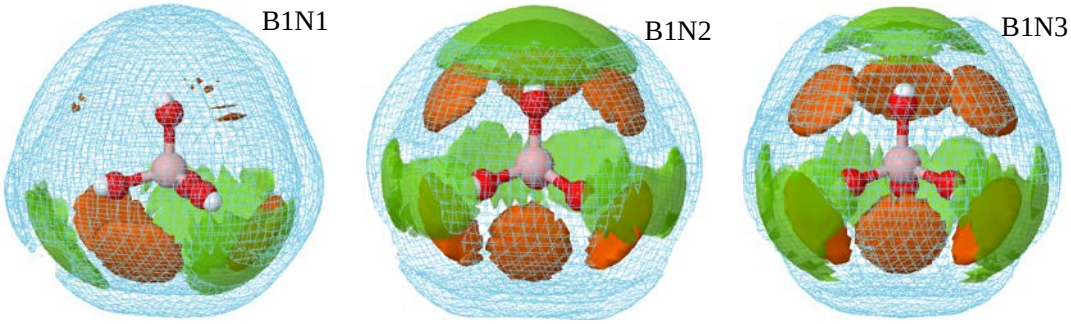
SDFs of Na^+-$B(OH)_4^-$ (tetrahedral edge shared form) r-range: 2.5-3.1Å



SDFs of Na^+-$B(OH)_4^-$ (tetrahedral-corner-shared form) r-range: 3.2-4.2 Å



SDFs of water-$B(OH)_4^-$ ($B(OH)_4^-$ hydration) r-range: 3.30-5.10 Å



Combined

Fig. S4 Spatial density functions for hydrated water molecules and sodium ions to the central $B(OH)_4^-$. The SDFs surfaces showing the top 25% probability density for correlations of hydrated water molecules to the central $B(OH)_4^-$ within the cutoff distance of 5.0 Å (blue and transparency grid);The top 35% probability density for correlations of Na^+ to the central $B(OH)_4^-$ within the cutoff distance of the local minimal of $g_{Na\text{-}B(r)}$, the tetrahedral-edge-shared bidentate ion pairs (red lobes) and tetrahedral-corner-shared monodentate ion pairs (green and semitransparent lobes). The pink, red

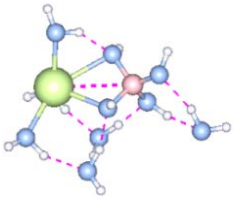
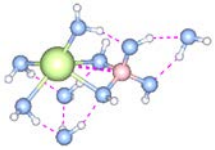
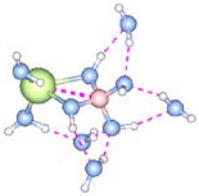
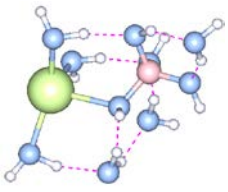
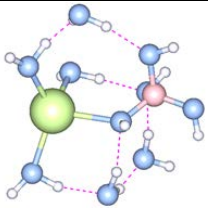
and white balls in the centre represent B, O and H atom of $B(OH)_4^-$, respectively.

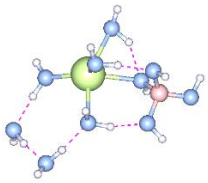
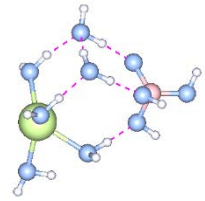
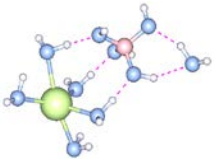
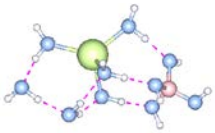
Table S3 Detailed energy parameters of $NaB(OH)_4(H_2O)_6$ in the gas and aqueous phase at B3LYP/ aug-cc-pVDZ level.

	Clusters Hartree	Na^+ Hartree	$B(OH)_4^-$ Hartree	Water Hartree	BSSE Hartree	Delta kcal/mol	Gscrf kcal/mol	Gss kcal/mol	Gsolv kcal/mol
	CBIP-A								
E0	-949.327	-162.092	-328.364	-458.534	0.005	-208.352	-23.750	-0.712	-232.814
E	-949.304	-162.091	-328.358	-458.522	0.005	-205.409	-23.750	-0.712	-229.871
H	-949.303	-162.090	-328.357	-458.521	0.005	-206.628	-23.750	-0.712	-231.090
G	-949.380	-162.107	-328.394	-458.574	0.005	-188.566	-23.750	-0.712	-213.028
	CBIP-B								
E0	-949.330	-162.092	-328.363	-458.537	0.005	-208.556	-22.140	-0.712	-231.408
E	-949.306	-162.091	-328.358	-458.524	0.005	-205.705	-22.140	-0.712	-228.558
H	-949.305	-162.090	-328.357	-458.523	0.005	-206.926	-22.140	-0.712	-229.779
G	-949.382	-162.107	-328.392	-458.578	0.005	-188.301	-22.140	-0.712	-211.154
	CBIP-C								
E0	-949.318	-162.092	-328.363	-458.529	0.006	-205.201	-25.350	-0.712	-231.263
E	-949.293	-162.091	-328.357	-458.519	0.006	-200.990	-25.350	-0.712	-227.053
H	-949.292	-162.090	-328.356	-458.518	0.006	-202.210	-25.350	-0.712	-228.272
G	-949.373	-162.107	-328.392	-458.570	0.006	-186.681	-25.350	-0.712	-212.743
	CSIP-A								
E0	-949.328	-162.092	-328.364	-458.527	0.005	-213.237	-23.770	-0.712	-237.720
E	-949.304	-162.091	-328.357	-458.515	0.005	-210.338	-23.770	-0.712	-234.821
H	-949.303	-162.090	-328.356	-458.515	0.005	-211.558	-23.770	-0.712	-236.040
G	-949.381	-162.107	-328.393	-458.569	0.005	-193.043	-23.770	-0.712	-217.525
	CSIP-B								
E0	-949.330	-162.092	-328.363	-458.534	0.005	-210.733	-24.130	-0.712	-235.575
E	-949.306	-162.091	-328.357	-458.522	0.005	-208.272	-24.130	-0.712	-233.114
H	-949.305	-162.090	-328.356	-458.521	0.005	-209.491	-24.130	-0.712	-234.333
G	-949.384	-162.107	-328.393	-458.575	0.005	-190.316	-24.130	-0.712	-215.158
	CSIP-C								
E0	-949.327	-162.092	-328.363	-458.544	0.004	-203.099	-24.540	-0.712	-228.351
E	-949.303	-162.091	-328.357	-458.531	0.004	-200.328	-24.540	-0.712	-225.580
H	-949.302	-162.090	-328.356	-458.530	0.004	-201.548	-24.540	-0.712	-226.800
G	-949.382	-162.107	-328.392	-458.585	0.004	-184.097	-24.540	-0.712	-209.349
	SIP-A								
E0	-949.323	-162.092	-328.364	-458.520	0.005	-215.029	-24.790	-0.712	-240.532
E	-949.299	-162.091	-328.358	-458.508	0.005	-211.714	-24.790	-0.712	-237.217
H	-949.298	-162.090	-328.357	-458.507	0.005	-212.934	-24.790	-0.712	-238.437
G	-949.379	-162.107	-328.393	-458.562	0.005	-195.160	-24.790	-0.712	-220.662
	SIP-B								
E0	-949.322	-162.092	-328.364	-458.520	0.005	-214.034	-24.890	-0.712	-239.636

E	-949.297	-162.091	-328.358	-458.508	0.005	-210.626	-24.890	-0.712	-236.228
H	-949.296	-162.090	-328.357	-458.507	0.005	-211.845	-24.890	-0.712	-237.447
G	-949.376	-162.107	-328.393	-458.562	0.005	-193.737	-24.890	-0.712	-219.340
	SIP-C								
E0	-949.329	-162.092	-328.364	-458.539	0.004	-206.652	-25.530	-0.712	-232.895
E	-949.305	-162.091	-328.358	-458.526	0.004	-204.074	-25.530	-0.712	-230.317
H	-949.304	-162.090	-328.357	-458.526	0.004	-205.294	-25.530	-0.712	-231.537
G	-949.382	-162.107	-328.392	-458.581	0.004	-186.490	-25.530	-0.712	-212.732

Table S4 Bond parameters of $NaB(OH)_4(H_2O)_6$ at B3LYP/ Aug-cc-pVDZ level.

Clusters	Atom pair	Bond length/Å					Averaged/Å
	Na-O(W)	2.297	2.321	2.337			2.318
	Na-O(B)	2.401	2.593				2.497
	Na-B	3.037					3.037
	B-O(W)	3.572	3.240	3.765			3.526
CBIP-A							
	Na-O(W)	2.375	2.429	2.273			2.359
	Na-O(B)	2.503	2.431				2.467
	Na-B	2.928					2.928
CBIP-B	B-O(W)	3.335					3.335
	Na-O(W)	2.304	2.243				2.273
	Na-O(B)	2.247	2.427				2.337
	Na-B	2.847					2.847
	B-O(W)	3.568	3.425	3.317	3.294		3.401
CBIPC							
	Na-O(W)	2.305	2.273	2.269			2.282
	Na-O(B)	2.405					2.405
	Na-B	3.313					3.313
	B-O(W)	3.424	3.844	3.370	3.623	3.905	3.633
CSIP-A							
	Na-O(W)	2.257	2.263	2.341			2.287
	Na-O(B)	2.367					2.367
	Na-B	3.448					3.448
	B-O(W)	3.451	3.691	3.807	3.811		3.690
CSIP-B							

 CSIP-C	Na-O(W)	2.473	2.385	2.413	2.262		2.383
	Na-O(B)	2.403					2.403
	Na-B	3.349					3.349
	B-O(W)	3.492	3.440	3.878			3.603
 SIP-A	Na-O(W)	2.366	2.322	2.251	2.273	2.366	2.303
	Na-O(B)	/					/
	Na-B	4.689					4.689
	B-O(W)	3.5	3.73	3.826			3.685
 SIP-B	Na-O(W)	2.336	2.453	2.346	2.363	2.425	2.385
	Na-O(B)	/					/
	Na-B	4.14					4.140
	B-O(W)	3.56	3.693	3.321	3.709		3.571
 SIP-C	Na-O(W)	2.344	2.344	2.273	2.254		2.304
	Na-O(B)	/					/
	Na-B	4.093					4.093
	B-O(W)	3.614	3.663	3.705			3.661

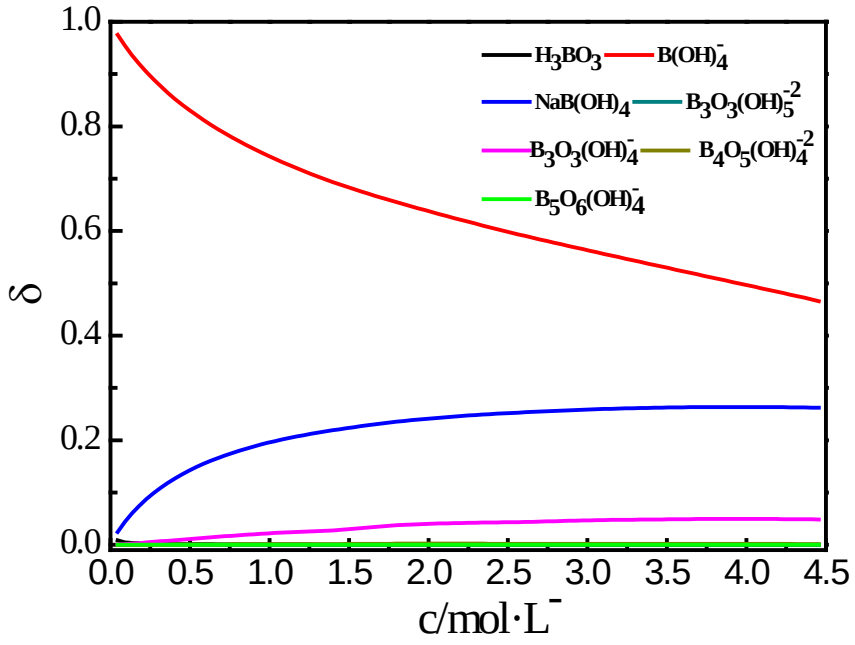


Fig. S5 Speciation of polyborates and ion association (in the apparent form of $NaB(OH)_4$) *vs* concentration in aqueous $NaB(OH)_4$ solutions at 298.15K and 1atm.

（using the ion association constant suggested by Rowe *et al*. *J. Solution Chem.*, ***19***, *149(1990)*.）

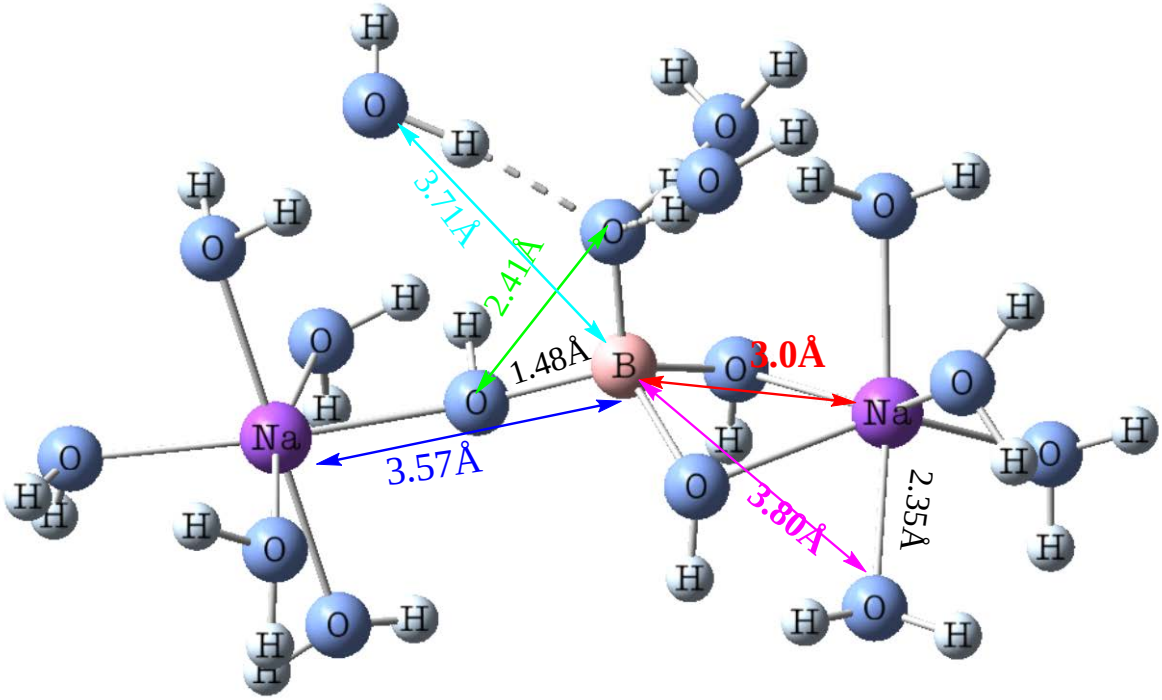


Fig. S6 A schematic view of distances related to $B(OH)_4^-$ hydration and $B(OH)_4^-$-Na^+ association in aqueous sodium metaborate solutions