Supporting information

Ion hydration and association in aqueous potassium tetrahydroxyborate solutions

Fayan Zhu[a], Toshio Yamaguchi[b]*, Koji Yoshida[b], Wenqian Zhang[a], Hongyan Liu[a], Yongquan Zhou[a], Chunhui Fang[a]

([a] Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 81008; Key Laboratory of Salt Lake Resources Chemistry of Qinghai province, Xining 81008)

([b] Department of Chemistry, Faculty of Science, Fukuoka University, 8–19–1 Nanakuma, Jonan, Fukuoka 814–0180, Japan.)

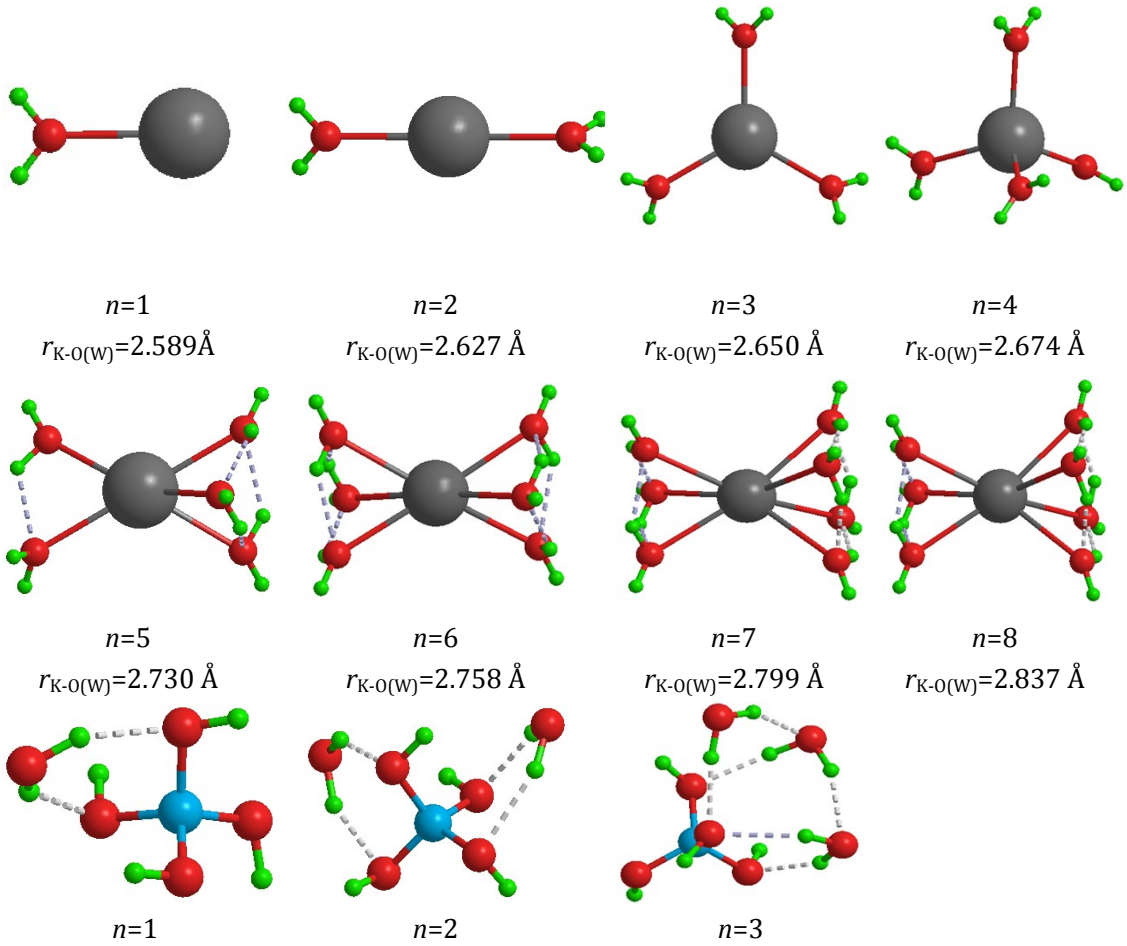


Fig. S1 Low-lying structures of $[K(H_2O)_{n=1-8}]^+$ and $[B(OH)_4\text{-}(H_2O)_{n=1-3}]^-$ clusters, optimized at the m062x/6-311++G(2df, 2pd) level of theory. The gray, red, light blue and white balls represent K, O, B, and H atoms, respectively.

Table S1 Energy date of $[K(H_2O)_{n=1-8}]^+$ and $[B(OH)_4^-(H_2O)_{n=1-3}]^-$ clusters

n	$E_{scf} + E_{ZPE}$	E_{BSSE}	E_{total}
	$[K(H_2O)_{n=1-8}]^+$		
1	-676.1745	0.0002653	-676.1742
2	-752.6025	0.0003213	-752.6022
3	-829.0277	0.0002830	-829.02746
4	-905.4499	0.000310	-905.4496
5	-981.8727	0.001017	-981.8717
6	-1058.2950	0.001054	-1058.2939
7	-1134.7170	0.001077	-1134.7159
8	-1211.1379	0.001216	-1211.1367
	$[B(OH)_4^-(H_2O)_{n=1-3}]^-$		
1	-404.7517	0.00125301	-404.7504
2	-481.1801	0.001235	-481.1788
3	-557.6055	0.001231	-557.6042

n: the number of water molecule;

Average energy (ΔE_{0n}) and successive energy ($\Delta E_{n,n-1}$) were computed according to

$$\Delta E_{0n} = \left\{ M(K^+) + nM(H_2O) - M[K(H_2O)_n]^+ \right\}/n \quad (1)$$

$$\Delta E_{n,n-1} = M(H_2O) + M[K(H_2O)_{n-1}]^+ - M[K(H_2O)_n]^+ \quad (2)$$

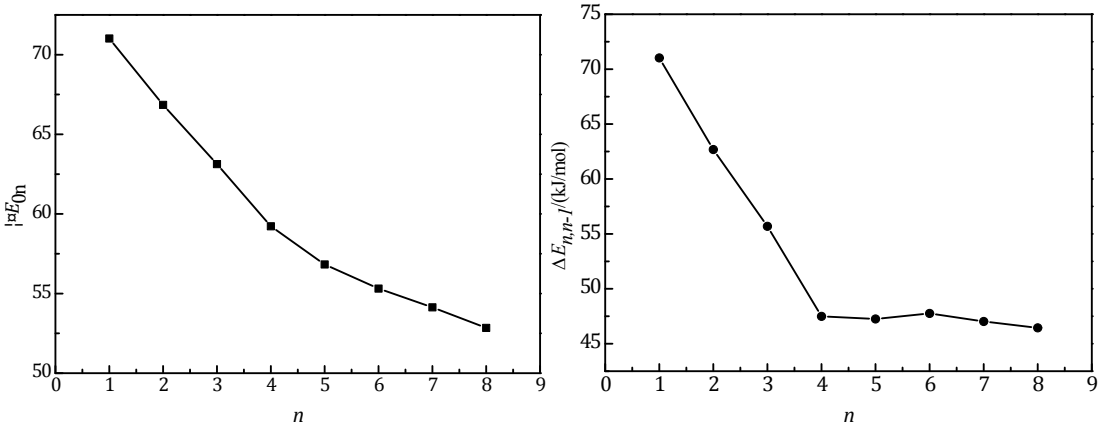
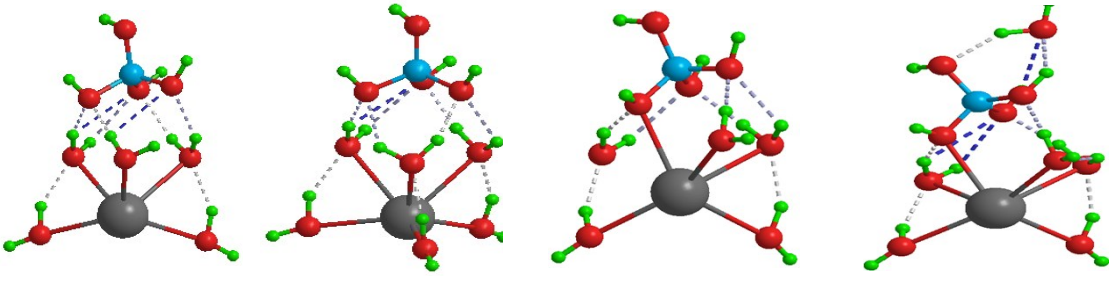
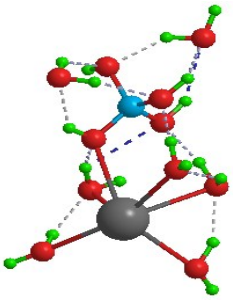


Fig. S2 Relationship between ΔE_{0n} (left) and $\Delta E_{n,n-1}$ (right) with different n values

SIP and MCIP

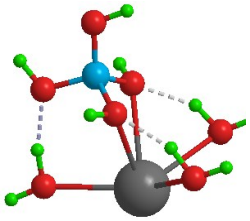


SIP-A SIP-B MCIP5 MCIP6

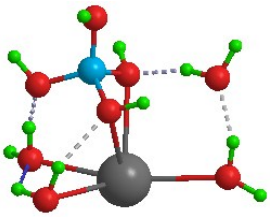


MCIP7

BCIP/3



BCIP



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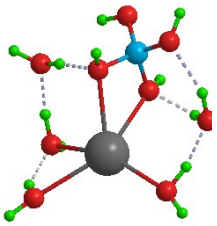

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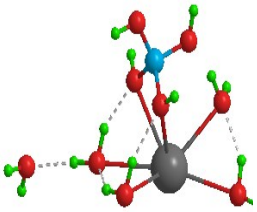

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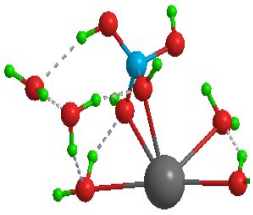

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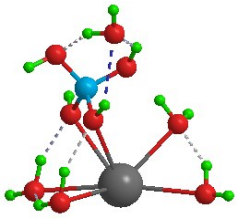

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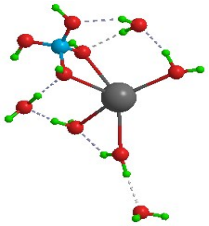

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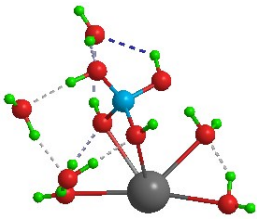

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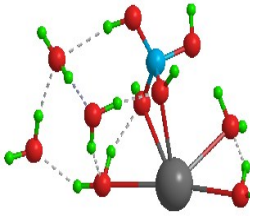

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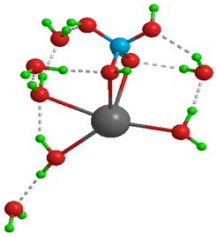

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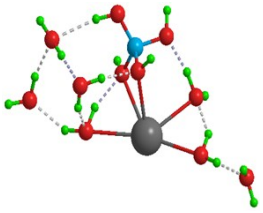

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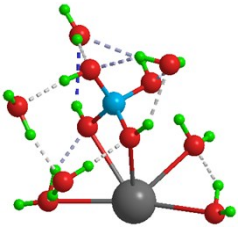
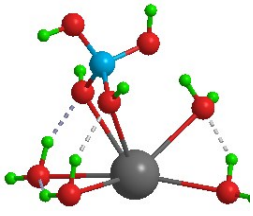
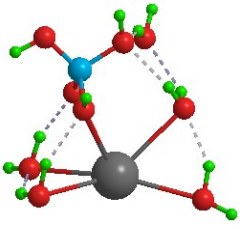


BCIP 4c

BCIP/4



BCIP 0



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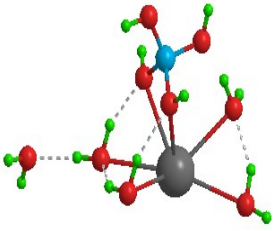

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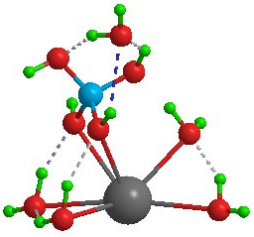

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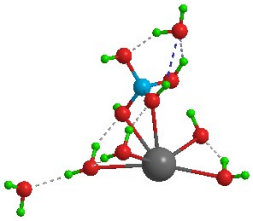

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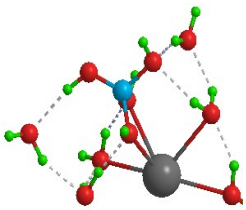

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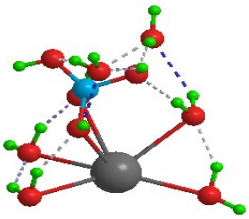

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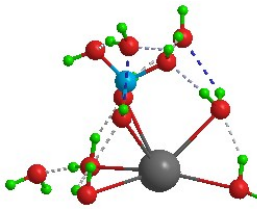

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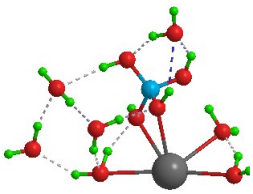

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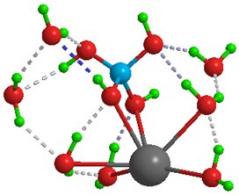
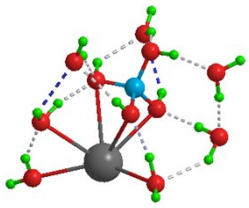


BCIP 3c

TCIP



TCIP

Fig. S3 Low-lying structures of ion pairs, optimized at the m062x/6-311++G(2df, 2pd) level of theory. The gray, light blue, red, and green balls represent K, B, O, and H atoms, respectively.

Table S2 Energy dates of ion pairs

	SCF	ZPC	BSSE	SPE+BSSE
		SIP		
SIP-A	-1310.5732	0.1895	0.003876	-1310.3798
SIP-B	-1387.0175	0.2134	0.004154	-1386.8000
		MCIP		
MCIP5	-1310.3886	0.2392	0.0005851	-1310.1488
MCIP6	-1386.8065	0.2151	0.001081	-1386.5903
MCIP7	-1463.4666	0.2414	0.001330135829	-1463.22387
		BCIP/3		
BCIP0	-1157.6848	0.1374	0.002740	-1157.5447
BCIP1a	-1234.1320	0.1637	0.000823	-1233.9674
BCIP 2a	-1310.5712	0.1890	0.001652	-1310.3806
BCIP 2b	-1310.5663	0.1884	0.000616	-1310.3772
BCIP 2c	-1310.5716	0.1901	0.001299	-1310.3802
BCIP 2d	-1310.5767	0.1903	0.001102	-1310.3853
BCIP 3a	-1387.0062	0.2133	0.000603	-1386.7923
BCIP 3b	-1387.0177	0.2162	0.001155	-1386.8003
BCIP 3c	-1387.0177	0.2162	0.001112	-1386.8003
BCIP 4a	-1463.4591	0.2400	0.001390	-1463.2177

BCIP 4b	-1463.4525	0.2405	0.000583	-1463.2114
BCIP 4c	-1463.4636	0.2427	0.001367	-1463.2196
		BCIP/4		
BCIP 0	-1234.1317	0.1642	0.003033	-1233.9645
BCIP 1a	-1310.5773	0.1908	0.001265	-1310.3853
BCIP 1b	-1310.5663	0.1884	0.000616	-1310.3772
BCIP 1c	-1310.5767	0.1903	0.001102	-1310.3853
BCIP 2a	-1387.0114	0.2144	0.001095	-1386.7959
BCIP 2b	-1387.0167	0.2169	0.001100	-1386.7987
BCIP 2c	-1387.0233	0.2164	0.001139	-1386.8057
BCIP 3a	-1463.4577	0.2409	0.000613	-1463.2162
BCIP 3b	-1463.4635	0.2421	0.001740	-1463.2196
BCIP 3c	-1463.4642	0.2426	0.001310	-1463.2203
		TCIP		
TCIP	-1463.4640	0.2420	0.001158	-1463.2209

Table S3 Structural parameters of ion pairs

Clusters	Atom pair	Bond length/Å						Averaged/Å
SIP-A	K-O(W)	2.655	2.652	2.783	2.742	2.649		2.696
	K-O(B)							
	K-B	4.473						4.473
	B-O(W)	3.434	3.168	3.374				3.325
SIP-B	K-O(W)	2.667	2.670	2.807	2.817	2.775	2.668	2.734
	K-O(B)							
	K-B	4.632						4.632
	B-O(W)	3.281	3.263	3.344				3.296
MCIP7	K-O(W)	2.911	2.812	2.716	2.660	2.659		2.752
	K-O(B)	2.728						2.728
	K-B	3.708						3.708
	B-O(W)	2.973	3.042	3.421	3.403	3.431		3.254
BCIP-A	K-O(W)	2.857	2.784	2.773	2.649			2.766
	K-O(B)	2.746	2.667					2.707
	K-B	3.333						3.333
	B-O(W)	3.226	3.639	3.664	3.775	3.298	3.380	3.497
BCIP-B	K-O(W)	2.704	2.698	2.673				2.692
	K-O(B)	2.617	2.737					2.677
	K-B	3.205						3.205
	B-O(W)	3.732	3.554	3.590	2.964	3.310	3.015	3.361
TCIP	K-O(W)	2.645	2.746	2.889				2.760
	K-O(B)	2.926	2.698	2.704				2.776
	K-B	2.964						2.964
	B-O(W)	3.145	3.575	2.935	3.446	3.485	3.669	3.376

* BCIP-A= BCIP 3c with 4-coordinated; BCIP-B= BCIP 4c with 3-coordinated