

Aluminum Speciation in Biological Environments. The Deprotonation of Free and Aluminum Bound Citrate in Aqueous Solution

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Table 1: Comparison between the pK_a values of the four titratable groups computed with B3LYP, PBE0 and M062X functionals for the citric acid in solution and interacting with Al(III) at two level of theories: SMD and UAHF (see Methodology section).

Specie	Exper. ^(a)	B3LYP		PBE0		M062X	
		SMD	UAHF	SMD	UAHF	SMD	UAHF
Free citric acid							
$[H_3L]$	2.87	0.3	1.4	0.1	1.4	0.2	1.4
$[H_2L]^{-1}$	4.27	4.5	4.9	4.4	5.0	4.2	4.8
$[HL]^{-2}$	5.57	5.1	5.2	5.1	5.4	5.0	5.4
$[L]^{-3}$	11.6 ^(b) /14.4 ^(c)	25.5	10.2	25.8	12.0	24.9	16.6
Al-bound citric acid (1st shell)							
$[Al.LH_3]^{+3}$	-	-16.0	-14.5	-17.1	-15.5	-16.3	-15.2
$[Al.LH_2]^{+2}$	-	-8.4	-8.0	-8.2	-8.1	-9.8	-10.1
$[Al.LH]^{+1}$	2.33	-6.2	0.6	-7.3	-0.6	-6.4	-0.3
$[Al.L]$	3.58	6.2	5.4	6.0	5.6	4.1	3.8

(a) ref. [1] (b) ref. [2] (c) ref. [3]

References

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