

Extending the semi-empirical PM6 method for carbon oxyacid pK_a prediction to sulfonic acids: Application towards congener-specific estimates for the environmentally and toxicologically relevant C_1 through C_8 perfluoroalkyl derivatives

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Abstract: A positive bias in the semi-empirical PM6 method for estimating pK_a values of sulfonic acids was corrected by a correlation developed between non-adjusted PM6 pK_a values and the corresponding experimentally obtained/estimated acidity constants for a range of representative alkyl, aryl, and halogen substituted sulfonic acids. Application of this correction to PM6 values allows for extension of this computational method to a new acid functional group.

Keywords: pK_a , sulfonic acids, estimation, semi-empirical, PM6 method, perfluoroalkyl derivatives.

Running head: pK_a Prediction for Sulfonic Acids

Sulfonic acids (Fig. (1)) are widely used compounds with applications as dyes, catalysts, surface active agents, pharmaceuticals, and as anion exchange resins [1]. There is substantial interest in methods for estimating their acidity constants to provide insights regarding environment fate, pharmacological activity, and suitability for targeted industrial applications. Often large numbers of sulfonic acid derivatives need to be screened, necessitating rapid and reasonably accurate (i.e., within ± 1 unit) methods for pK_a prediction for which ab initio approaches may be too time consuming. The most recent PM6 semi-empirical method [2] in MOPAC 2007 [3] contains a pK_a prediction function that was source validated for a range of carboxylic acids and alcohols and an oxime (benzophenone oxime) and a hydroxamic acid (benzohydroxamic acid) with an average unsigned error of 0.31 pK_a units. However, to the best of our knowledge, this algorithm has not yet been tested and validated/adjusted for other heteroatom acids such as sulfonic acids. Such work will allow a broadening of the PM6 method's currently high utility in both pure and applied chemistry.

As part of our studies on the congener-specific environmental partitioning of perfluorinated sulfonic acids (PFSA) [4], we conducted initial geometry optimizations and generated acidity constant estimates using the pK_a function in the PM6 basis set with MOPAC 2007 for all 161 C_1 through C_8 perfluoroalkyl congeners (Table 1). Gas phase molecular structures were initially optimized with the MM2 molecular mechanics energy-minimization method [5] using a minimum RMS gradient of 0.100. The gas phase structures were then further optimized using the PM3 [6] semiempirical method in MOPAC 2000 [7] with a minimum RMS gradient of 0.100 and a closed shell (restricted) wave function. The gas phase PM3 optimized geometries from MOPAC 2000 were used as the input geometries for gas phase PM6 [2] geometry optimization in MOPAC 2007 [3]. Geometry optimizations and pK_a predictions in MOPAC 2007 were conducted with the following keywords in the input file header: PM6; PKA; BONDS; CHARGE=0; LET; DDMIN=0.0; GNORM=0.0; XYZ; GRAPHF.

The non-adjusted pK_a values generated by the PM6 method for the C_1 through C_8 PFSA ranged from -1.7 to +3.5, and generally declined with an increase in branching of the perfluoroalkyl chain. Concerns regarding the potential accuracy of the original PM6 generated data for these compounds was raised when we compared our pK_a value predicted for the well-known perfluorooctane sulfonic acid (PFOS; C_8 PFSA 89) at +3.2 with a prior estimate of -3.3 using the ACD/I-Lab Web Service [8], as well as general knowledge about the known strong acidity of the sulfonic acid moiety.

In an attempt to develop a general correction factor for the overestimated PM6 pK_a values of sulfonic acids, we conducted a literature search to obtain reliable experimentally obtained and/or estimated values extrapolated to aqueous solution across as wide a range of pK_a measurements as possible. Because of the leveling effect of water for strong acids and bases [9], and the resulting difficulty in both determining acidity/basicity constants in non-aqueous solvents and relating them to an aqueous scale [10-12], reports of sulfonic acid ionization [9,13-56] have considerable variations in values for the same compounds among different literature sources across a range of methods. For example, benzene sulfonic acid has reported pK_a values of -6.5 [57] and +0.70 [58] in two well-known sources. The most reliable dataset appears to be that of Guthrie [36], who provided pK_a values for a range of alkyl, aryl, and halogen substituted sulfonic acids, and his value of -2.8 for benzene sulfonic acid has been validated by Benoit et al. [44] who obtained a

Insert
Figure 1

Insert
Table 1

similar value of -2.5. When plotted against each other, the experimental dataset of Guthrie [36] and Benoit et al. [44] correlates well with the non-adjusted PM6 data (Fig. (1)).

Insert
Figure 2

These findings suggest that the PM6 method for estimating pK_a values of carbon oxyacids can be extended to sulfonic acid pK_a prediction by transforming non-adjusted PM6 pK_a estimates ($pK_a(\text{PM6})_{\text{nonadj}}$) through the following regression equation that appears to apply over a range of about six pK_a units: $pK_a(\text{PM6})_{\text{adj}} = 0.71 \pm 0.06 \times pK_a(\text{PM6})_{\text{nonadj}} - 7.8 \pm 0.3$ (error bars are standard errors). We then used this correction method to adjust the estimated pK_a values of the C₁ through C₈ PFSA (Table 1) to obtain final results which range from -5.3 to -9.0, generally about seven to nine pK_a units below the non-adjusted values. Our specific findings on PFSA pK_a values provide greater reliability than has previously been established in the literature that all members of this compound class will be essentially completely dissociated in aquatic systems. For example, in a typical freshwater system with pH of 6.5, our pK_a values suggest that $<10^{-9}$ % of these compounds will be in the molecular form.

In a more general sense, the work also demonstrates that the three-dimensional geometric structure based PM6 method for estimating pK_a values can be broadened through the use of correction factors linked to established experimental data. This approach allows for potentially more robust methods of estimating pK_a values across a wide range of organic and inorganic acids than can currently be obtained from two-dimensional constitutional, fragment, and topological systems.

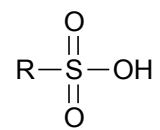
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R=alkyl, aryl

Fig. (1).

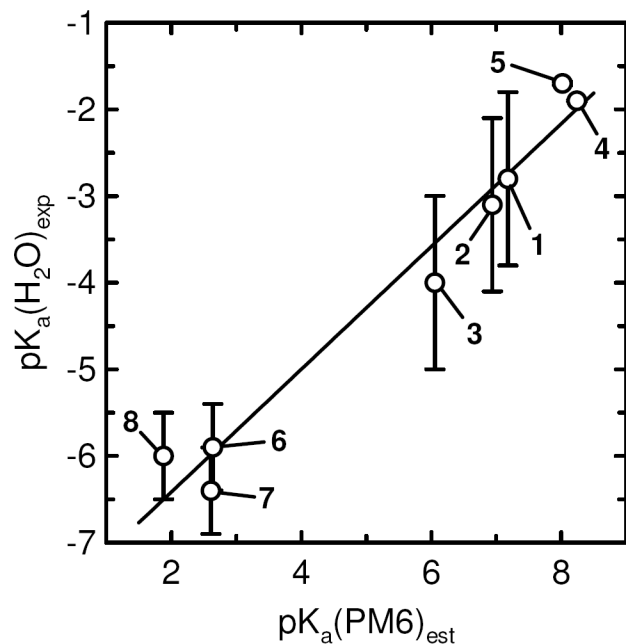


Fig. (2). Comparison between experimentally obtained/estimated pK_a values in water ($pK_a(\text{H}_2\text{O})_{\text{exp}}$; \pm errors in source literature) and using the PM6 method ($pK_a(\text{PM6})_{\text{est}}$) for the following representative aryl, alkyl, and halogen substituted sulfonic acids: **1**, phenyl; **2**, 4-bromophenyl; **3**, 4-nitrophenyl; **4**, methyl; **5**, ethyl; **6**, perfluoromethyl; **7**, fluoro; and **8**, chloro. A regression line with slope= 0.71 ± 0.06 (\pm std. error) and y-intercept= -7.8 ± 0.3 is shown ($r=0.982$, $F_{\text{cal}}=165 > F_{\text{crit}}=6$, std. error=0.38, C.V.=0.10, PRESS=1.74).

Table 1. Non-adjusted and adjusted PM6 predicted pK_a values for the C₁ through C₈ perfluorinated sulfonic acid (PFSA) congeners at 298 K. Error bars on adjusted pK_a values are standard errors about the mean estimate.

HG ^a	Substitution	# ^b	Non-adjusted pK _a	Adjusted pK _a	HG	Substitution	#	Non-adjusted pK _a	Adjusted pK _a
C ₁	methyl	1	2.8	-5.8±0.4	C ₈	1-isopropyl-1'-methylbutyl	9	-0.3	-8.0±0.3
C ₂	ethyl	1	2.8	-5.8±0.4		1-isopropyl-2-methylbutyl	1	0.6	-7.4±0.3
C ₃	n-propyl	1	3.2	-5.5±0.5		1-isopropyl-3-methylbutyl	11	1.3	-6.9±0.4
	isopropyl	2	1.6	-6.7±0.4		2-isopropyl-3-methylbutyl	1	2.6	-6.0±0.4
C ₄	1,1'-dimethylethyl	1	-0.7	-8.3±0.3		1-ethyl-1',2-dimethylbutyl	2	-0.8	-8.4±0.3
	1-methylpropyl	2	2.3	-6.2±0.4		1-ethyl-1,3-dimethylbutyl	3	-0.6	-8.2±0.3
	2-methylpropyl	3	2.5	-6.0±0.4		1-ethyl-2,2'-dimethylbutyl	4	0.9	-7.2±0.3
	n-butyl	4	3.3	-5.5±0.5		1-ethyl-2,3-dimethylbutyl	5	1.5	-6.7±0.4
C ₅	1-ethylpropyl	1	2.3	-6.2±0.4		1-ethyl-3,3'-dimethylbutyl	6	0.9	-7.2±0.3
	1,1'-dimethylpropyl	2	-0.6	-8.2±0.3		2-ethyl-1,1'-dimethylbutyl	7	-0.6	-8.2±0.3
	1,2-dimethylpropyl	3	1.7	-6.6±0.4		2-ethyl-1,2-dimethylbutyl	8	1.2	-6.9±0.4
	2,2'-dimethylpropyl	4	2.1	-6.3±0.4		2-ethyl-1,3-dimethylbutyl	9	1.0	-7.1±0.3
	1-methylbutyl	5	1.8	-6.5±0.4		2-ethyl-2',3-dimethylbutyl	20	1.8	-6.5±0.4
	2-methylbutyl	6	2.5	-6.0±0.4		2-ethyl-3,3'-dimethylbutyl	22	2.6	-6.0±0.4
	3-methylbutyl	7	2.7	-5.9±0.4		1,1',2,2'-tetramethylbutyl	2	-0.9	-8.4±0.3
	n-pentyl	8	3.2	-5.5±0.5		1,1',2,3-tetramethylbutyl	3	-0.3	-8.0±0.3
C ₆	1-ethyl-1'-methylpropyl	1	-0.3	-8.0±0.3		1,1',3,3'-tetramethylbutyl	24	-1.2	-8.7±0.2

	1-ethyl-2-methylpropyl	2	1.6	-6.7±0.4		1,2,2',3-tetramethylbutyl	2		
	1,1',2-trimethylpropyl	3	-0.4	-8.1±0.3		1,2,3,3'-tetramethylbutyl	6	1.2	-6.9±0.4
	1,2,2'-trimethylpropyl	4	1.2	-6.9±0.4		2,2',3,3'-tetramethylbutyl	27	1.0	-7.1±0.3
	1-ethylbutyl	5	2.1	-6.3±0.4		1-methyl-1'-propylbutyl	28	1.8	-6.5±0.4
	2-ethylbutyl	6	1.6	-6.7±0.4		2-methyl-1-propylbutyl	29	-1.1	-8.6±0.2
	1,1'-dimethylbutyl	7	-0.6	-8.2±0.3		3-methyl-1-propylbutyl	3	1.9	-6.5±0.4
	1,2-dimethylbutyl	8	1.7	-6.6±0.4		1-ethyl-1'-methylpentyl	3	1.0	-7.1±0.3
	1,3-dimethylbutyl	9	1.6	-6.7±0.4		1-ethyl-2-methylpentyl	1	-0.1	-7.9±0.3
	2,2'-dimethylbutyl	10	2.0	-6.4±0.4		1-ethyl-3-methylpentyl	3	2.0	-6.4±0.4
	2,3-dimethylbutyl	11	2.4	-6.1±0.4		1-ethyl-4-methylpentyl	3	1.8	-6.5±0.4
	3,3'-dimethylbutyl	12	2.9	-5.7±0.4		2-ethyl-1-methylpentyl	4	2.1	-6.3±0.4
	1-methylpentyl	13	2.2	-6.2±0.4		2-ethyl-2'-methylpentyl	3	1.3	-6.9±0.4
	2-methylpentyl	14	3.5	-5.3±0.5		2-ethyl-3-methylpentyl	3	0.9	-7.2±0.3
	3-methylpentyl	15	3.2	-5.5±0.5		2-ethyl-4-methylpentyl	7	2.1	-6.3±0.4
	4-methylpentyl	16	3.1	-5.6±0.5		3-ethyl-1-methylpentyl	3	2.0	-6.4±0.4
	n-hexyl	17	3.2	-5.5±0.5		3-ethyl-2-methylpentyl	4	2.0	-6.4±0.4
C ₇	1,1'-diethylpropyl	18	-0.1	-7.9±0.3		3-ethyl-3'-methylpentyl	4	2.4	-6.1±0.4
	1-ethyl-1',2-dimethylpropyl	19	-0.5	-8.2±0.3		3-ethyl-4-methylpentyl	42	2.9	-5.7±0.4
	1-ethyl-2,2'-dimethylpropyl	20	0.9	-7.2±0.3		1-isopropylpentyl	4	1.9	-6.5±0.4

						4		
1-isopropyl-2-methylpropyl	4	1.3	-6.9±0.4		2-isopropylpentyl	45	2.0	-6.4±0.4
1,1',2,2'-tetramethylpropyl	5	-0.5	-8.2±0.3		1,1',2-trimethylpentyl	4		
						6	-0.4	-8.1±0.3
1-ethyl-1'-methylbutyl	6	0.6	-7.4±0.3		1,1',3-trimethylpentyl	4		
						7	-0.7	-8.3±0.3
1-ethyl-2-methylbutyl	7	1.9	-6.5±0.4		1,1',4-trimethylpentyl	4		
						8	-0.9	-8.4±0.3
1-ethyl-3-methylbutyl	8	1.7	-6.6±0.4		1,2,2'-trimethylpentyl	4		
						9	1.2	-6.9±0.4
2-ethyl-1-methylbutyl	9	0.9	-7.2±0.3		1,2,3-trimethylpentyl	50	1.0	-7.1±0.3
2-ethyl-2'-methylbutyl	10	1.4	-6.8±0.4		1,2,4-trimethylpentyl	5		
						1	1.5	-6.7±0.4
2-ethyl-3-methylbutyl	11	1.4	-6.8±0.4		1,3,3'-trimethylpentyl	52	1.6	-6.7±0.4
1,1',2-trimethylbutyl	12	-0.4	-8.1±0.3		1,3,4-trimethylpentyl	5		
						3	2.0	-6.4±0.4
1,1',3-trimethylbutyl	13	-0.9	-8.4±0.3		1,4,4'-trimethylpentyl	54	1.7	-6.6±0.4
1,2,2'-trimethylbutyl	14	1.2	-6.9±0.4		2,2',3-trimethylpentyl	55	1.6	-6.7±0.4
1,2,3-trimethylbutyl	15	1.5	-6.7±0.4		2,2',4-trimethylpentyl	5		
						6	1.8	-6.5±0.4
1,3,3'-trimethylbutyl	16	1.6	-6.7±0.4		2,3,3'-trimethylpentyl	57	1.7	-6.6±0.4
2,2',3-trimethylbutyl	17	2.3	-6.2±0.4		2,3,4-trimethylpentyl	58	2.6	-6.0±0.4
2,3,3'-trimethylbutyl	18	2.8	-5.8±0.4		2,4,4'-trimethylpentyl	59	1.5	-6.7±0.4
1-isopropylbutyl	19	-0.2	-7.9±0.3		3,3',4-trimethylpentyl	6		
						0	2.6	-6.0±0.4
1-propylbutyl	20	1.2	-6.9±0.4		3,4,4'-trimethylpentyl	6		
						1	2.8	-5.8±0.4
1-ethylpentyl	21	2.1	-6.3±0.4		1-propylpentyl	6	1.7	-6.6±0.4

		1					2		
	2-ethylpentyl	22	1.3	-6.9±0.4		2-propylpentyl	6		
		2					3	2.3	-6.2±0.4
	3-ethylpentyl	3	3.0	-5.7±0.4		1-ethylhexyl	6		
		3					4	2.1	-6.3±0.4
	1,1'-dimethylpentyl	24	-0.6	-8.2±0.3		2-ethylhexyl	6		
		24					5	3.0	-5.7±0.4
	1,2-dimethylpentyl	25	1.7	-6.6±0.4		3-ethylhexyl	6		
		25					6	3.3	-5.5±0.5
	1,3-dimethylpentyl	2				4-ethylhexyl	6		
		6	1.8	-6.5±0.4			7	3.0	-5.7±0.4
	1,4-dimethylpentyl	27	2.2	-6.2±0.4		1,1'-dimethylhexyl	6		
		27					8	-0.1	-7.9±0.3
	2,2'-dimethylpentyl	28	2.0	-6.4±0.4		1,2-dimethylhexyl	6		
		28					9	1.7	-6.6±0.4
	2,3-dimethylpentyl	29	2.0	-6.4±0.4		1,3-dimethylhexyl	7		
		29					0	2.0	-6.4±0.4
	2,4-dimethylpentyl	3	2.2	-6.2±0.4		1,4-dimethylhexyl	7		
		0					1	2.2	-6.2±0.4
	3,3'-dimethylpentyl	3	3.0	-5.7±0.4		1,5-dimethylhexyl	72	1.7	-6.6±0.4
		1					72		
	3,4-dimethylpentyl	3	2.7	-5.9±0.4		2,2'-dimethylhexyl	7		
		2					3	2.1	-6.3±0.4
	4,4'-dimethylpentyl	3	2.5	-6.0±0.4		2,3-dimethylhexyl	7		
		3					4	3.3	-5.5±0.5
	1-methylhexyl	3	2.2	-6.2±0.4		2,4-dimethylhexyl	75	3.4	-5.4±0.5
		4					75		
	2-methylhexyl	3	2.2	-6.2±0.4		2,5-dimethylhexyl	7		
		5					6	3.5	-5.3±0.5
	3-methylhexyl	3	2.7	-5.9±0.4		3,3'-dimethylhexyl	7		
		6					7	2.9	-5.7±0.4
	4-methylhexyl	3	3.3	-5.5±0.5		3,4-dimethylhexyl	7		
		7					8	3.1	-5.6±0.5

	5-methylhexyl	3 8	3.4	-5.4±0.5		3,5-dimethylhexyl	7 9	2.7	-5.9±0.4
	n-heptyl	3 9	3.3	-5.5±0.5		4,4'-dimethylhexyl	8 0	3.2	-5.5±0.5
C ₈	1-ethyl-1',2,2'-trimethylpropyl	1	-0.6	-8.2±0.3		4,5-dimethylhexyl	8 1	3.3	-5.5±0.5
	1-ethyl-1'-isopropylpropyl	2	-1.7	-9.0±0.2		5,5'-dimethylhexyl	82	3.3	-5.5±0.5
	1-isopropyl-1',2-dimethylpropyl	3	-0.4	-8.1±0.3		1-methylheptyl	8 3	1.8	-6.5±0.4
	1-isopropyl-2,2'-dimethylpropyl	4	0.2	-7.7±0.3		2-methylheptyl	8 4	3.5	-5.3±0.5
	1-tert-butylbutyl	5	0.8	-7.2±0.3		3-methylheptyl	85	2.8	-5.8±0.4
	1,1'-diethylbutyl	6	0.4	-7.5±0.3		4-methylheptyl	8 6	3.1	-5.6±0.5
	1,2-diethylbutyl	7	1.8	-6.5±0.4		5-methylheptyl	8 7	3.3	-5.5±0.5
	2,2'-diethylbutyl	8	2.2	-6.2±0.4		6-methylheptyl	8 8	3.2	-5.5±0.5
						n-octyl	8 9	3.2	-5.5±0.5

^aHG=homologue group for the perfluoroalkyl chain.

^bCongener numbers are those published elsewhere [4].