

# Critical evaluation of implicit solvent models for predicting aqueous oxidation potentials of neutral organic compounds

## Supporting Information

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	Aqueous	Acetonitrile
Phenol	2.02	2.09
4-Chlorophenol	2.03	2.11
4-Cyanophenol	2.39	2.49
4-Methoxyphenol	1.49	1.51
4-Methylphenol	1.88	1.94
3,4-Dimethoxyphenol	1.21	1.18
2,4,6-Trimethylphenol	1.62	1.66
Anisole	1.92	1.94
1,2-Dimethoxybenzene	1.58	1.54
1,3-Dimethoxybenzene	1.87	1.85
1,4-Dimethoxybenzene	1.42	1.39
1,2,4-Trimethoxybenzene	1.29	1.23
Aniline	1.26	1.29
4-Toluidine	1.09	1.11
N-Methylaniline	1.04	1.05
N,N'-Dimethylaniline	0.88	0.87
p-Phenylenediamine	0.58	0.59
Indole	1.48	1.51
1-Methylindole	1.35	1.38
2-Methylindole	1.29	1.32
Piperidine	1.33	1.32
DABCO	0.58	0.52
N-Butylamine	1.82	1.82
Triethylamine	0.97	0.90
DMS	1.89	1.93
DMD	1.63	1.66
Thioanisole	1.68	1.71

Table S1. Computed oxidation potentials (in V) in aqueous or acetonitrile solvents computed from CBS-QB3 (or ROCBS-QB3) gas phase ionization energies and SMD/M06-2X/6-31G(d) free energies of solvation.

	Aqueous							Acetonitrile				
	M06-2X/ 6-31G(d)	B3LYP 6-31G(d)	M06-2X/ aug-cc-pVTZ	M06-2X/ 6-31G(d)	M06-2X/ 6-31G(d)	M06-2X/ 6-31G(d)	BZ/ cc-pVTZ	M06-2X/ 6-31G(d)	M06-2X/ 6-31G(d)	M06-2X/ 6-31G(d)	M06-2X/ 6-31G(d)	BZ/ TZP
	SM8	SM8	SMD	SMD	C-PCM	IEF-PCM	COSMO-RS	SM8	SMD	C-PCM	IEF-PCM	COSMO-RS
Phenol	0.43	0.42	0.43	0.46	0.75	0.75	0.49					
4-Chlorophenol	0.50	0.49	0.50	0.50	0.76	0.76	0.53					
4-Cyanophenol	0.59	0.60	0.59	0.62	0.96	0.96	0.81					
4-Methoxyphenol	0.21	0.20	0.17	0.19	0.42	0.42	0.25					
4-Methylphenol	0.37	0.37	0.34	0.36	0.64	0.63	0.42					
3,4-Dimethoxyphenol	0.12	0.11	0.01	0.04	0.25	0.25	0.12					
2,4,6-Trimethylphenol	0.45	0.45	0.39	0.40	0.65	0.65	0.50	0.23	0.22	0.46	0.46	0.39
Anisole	0.24	0.23	0.22	0.23	0.48	0.48	0.40	-0.20	-0.12	0.15	0.14	0.11
1,2-Dimethoxybenzene	0.20	0.20	0.17	0.20	0.39	0.39	0.41	-0.25	-0.20	0.06	0.06	0.08
1,3-Dimethoxybenzene	0.38	0.17	0.08	0.10	0.32	0.32	0.28	-0.16	-0.12	0.15	0.15	0.14
1,4-Dimethoxybenzene	0.09	0.09	0.03	0.05	0.27	0.26	0.21	-0.25	-0.21	0.05	0.05	0.03
1,2,4-Trimethoxybenzene	0.22	0.23	0.14	0.16	0.34	0.34	0.34	-0.16	-0.14	0.13	0.13	0.11
Aniline	0.13	0.13	0.18	0.21	0.48	0.48	0.12	-0.12	0.08	0.37	0.36	0.09
4-Toluidine	0.11	0.11	0.13	0.15	0.42	0.42	0.10	-0.08	0.07	0.35	0.34	0.11
N-Methylaniline	0.07	0.07	0.06	0.08	0.34	0.34	0.12	-0.11	-0.01	0.27	0.27	0.12
N,N'-Dimethylaniline								-0.15	-0.10	0.17	0.17	0.13
p-Phenylenediamine	-0.12	-0.12	-0.08	-0.03	0.21	0.20	-0.17	-0.37	-0.16	0.09	0.09	-0.28
Indole	0.14	0.14	0.17	0.20	0.43	0.43	0.23	-0.13	0.02	0.25	0.25	0.15
1-Methylindole	0.06	0.07	0.04	0.07	0.30	0.30	0.22	-0.20	-0.11	0.12	0.12	0.10
2-Methylindole	0.18	0.18	0.10	0.19	0.42	0.42	0.23	-0.08	0.01	0.24	0.23	0.15
Piperidine								-0.33	-0.22	0.12	0.12	-0.05
DABCO								-0.13	-0.09	0.24	0.24	0.16
N-Butylamine								-0.13	0.19	0.55	0.55	0.26
Triethylamine								-0.28	-0.29	0.07	0.07	0.05
DMS	0.09	0.09	0.24	0.23	0.42	0.42	0.37					
DMDS	0.13	0.13	0.24	0.24	0.35	0.34	0.31					
Thioanisole	0.19	0.18	0.22	0.23	0.42	0.42	0.34	0.03	0.13	0.32	0.32	0.30

Table S2. Deviation of  $\Delta\Delta G_{solv}$  from experiment in aqueous phase or acetonitrile for various computational methods, in eV.

	Expt.	Calc.	Error
Phenol	-0.274	-0.267	0.007
4-Chlorophenol	-0.269	-0.277	-0.008
4-Cyanophenol	-0.312	-0.361	-0.049
4-Methoxyphenol	-0.344	-0.314	0.030
4-Methylphenol	-0.265	-0.248	0.018
3,4-Dimethoxyphenol	---	-0.339	---
2,4,6-Trimethylphenol	-0.233	-0.197	0.036
Anisole	-0.100	-0.099	0.001
1,2-Dimethoxybenzene	-0.177	-0.185	-0.008
1,3-Dimethoxybenzene	-0.144	-0.136	0.007
1,4-Dimethoxybenzene	-0.195	-0.144	0.051
1,2,4-Trimethoxybenzene	---	-0.224	---
Aniline	-0.244	-0.242	0.002
4-Toluidine	-0.211	-0.220	-0.009
N-Methylaniline	-0.195	-0.204	-0.008
N,N'-Dimethylaniline	-0.147	-0.147	0.000
p-Phenylenediamine	-0.358	-0.426	-0.068
Indole	-0.274	-0.247	0.027
1-Methylindole	-0.180	-0.166	0.014
2-Methylindole	-0.244	-0.244	0.001
Piperidine	-0.225	-0.159	0.065
DABCO	-0.293	-0.465	-0.172
N-Butylamine	-0.202	-0.157	0.045
Triethylamine	-0.139	-0.061	0.078
DMS	-0.066	-0.027	0.038
DMDS	-0.077	-0.071	0.006
Thioanisole	-0.129	-0.111	0.018
		<i>MUE:</i>	0.031
		<i>MSE:</i>	0.005

Table S3. Experimental aqueous free energies of solvation for neutral compounds, calculated from aqueous solubilities and vapor pressures at 298 K,<sup>1</sup> together with calculated values from SMD/M06-2X/6-31G(d), and the resulting errors, in eV.

	SMD	SM8	C-PCM	IEF-PCM	COSMO-RS
Phenol	0.47	0.47	0.83	0.83	0.52
4-Chlorophenol	0.50	0.53	0.82	0.82	0.51
4-Cyanophenol	0.57	0.57	0.94	0.94	0.67
4-Methoxyphenol	0.22	0.28	0.53	0.53	0.27
4-Methylphenol	0.37	0.42	0.71	0.71	0.44
3,4-Dimethoxyphenol	---	---	---	---	---
2,4,6-Trimethylphenol	0.43	0.51	0.72	0.72	0.55
Anisole	0.23	0.24	0.45	0.45	0.40
1,2-Dimethoxybenzene	0.19	0.23	0.36	0.36	0.37
1,3-Dimethoxybenzene	0.10	0.33	0.29	0.29	0.27
1,4-Dimethoxybenzene	0.10	0.14	0.28	0.28	0.24
1,2,4-Trimethoxybenzene	---	---	---	---	---
Aniline	0.21	0.17	0.52	0.52	0.15
4-Toluidine	0.14	0.12	0.43	0.43	0.10
N-Methylaniline	0.07	0.09	0.37	0.37	0.16
N,N'-Dimethylaniline	---	---	---	---	---
p-Phenylenediamine	-0.10	-0.11	0.24	0.24	-0.22
Indole	0.23	0.20	0.48	0.48	0.24
1-Methylindole	0.08	0.10	0.30	0.30	0.25
2-Methylindole	0.19	0.21	0.44	0.44	0.22
Piperidine	---	---	---	---	---
DABCO	---	---	---	---	---
N-Butylamine	---	---	---	---	---
Triethylamine	---	---	---	---	---
DMS	0.27	0.15	0.38	0.38	0.40
DMDS	0.24	0.14	0.30	0.30	0.33
Thioanisole	0.25	0.23	0.40	0.40	0.36

Table S4. Computed error (computed value minus experimental value) in aqueous solvation free energy of the oxidized open shell species in aqueous solution ( $\Delta G^*_{solv,A^{+}}$ ), expressed in units of eV, using different implicit solvent models.

References:

- (1) *Physical/Chemical Property Database (PHYSPROP)*. SRC Environmental Science Center: Syracuse, NY, 2013. <http://www.syrres.com> (Accessed March 20, 2013).