

Modeling Temperature Dependency of Amine Basicity Using PCM and SM8T Implicit Solvation Models

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Supporting Information Placeholder

Supporting information

1. Table1: pKa values from PCM solvation model

Temp (K)	Piperazine	Morpholine	Piperidine	AEP	DMEDA	2-methylPZ	1-methylPZ	1-ethylPZ	MDEA	MEA
298	11.72	8.78	7.11	12.71	9.879	11.36	9.38	11.8	9.57	7.51
303	11.56	8.67	7.01	12.52	9.741	11.19	9.24	11.62	9.43	7.41
313	11.24	8.43	6.84	12.17	9.47	10.87	8.99	11.29	9.18	7.22
323	10.94	8.22	6.67	11.84	9.215	10.58	8.76	10.98	8.93	7.04
333	10.65	8.02	6.52	11.52	8.975	10.29	8.54	10.69	8.72	6.88
343	10.38	7.83	6.38	11.22	8.75	10.03	8.33	10.42	8.52	6.72
353	10.13	7.66	6.24	10.95	8.544	9.786	8.13	10.16	8.3	6.58
363	9.893	7.48	6.11	10.69	8.343	9.549	7.95	9.915	8.12	6.43
373	9.668	7.32	5.99	10.43	8.154	9.331	7.77	9.685	7.94	6.30
383	9.455	7.17	5.87	10.2	7.974	9.119	7.61	9.467	7.78	6.19
393	9.253	7.03	5.76	9.978	7.809	8.918	7.45	9.254	7.62	6.07

2. Table 2: pKa values from SM8T solvation model

Temp (K)	Piperazine	Morpholine	Piperidine	AEP	DMEDA	2-methylPZ	1-methylPZ	1-ethylPZ	MDEA	MEA
298	11.06	9.35	9.22	12.12	11.87	10.93	8.73	11.7	7.85	13.20
303	10.9	9.21	9.09	11.94	11.69	10.77	8.62	11.53	7.75	13.00
313	10.6	8.96	8.86	11.6	11.37	10.47	8.4	11.21	7.55	12.60
323	10.32	8.73	8.64	11.29	11.07	10.19	8.19	10.91	7.37	12.23
333	10.06	8.5	8.43	10.99	10.78	9.928	8	10.63	7.2	11.88
343	9.806	8.29	9.05	10.7	10.51	9.676	7.81	10.36	7.04	11.55
353	9.569	8.09	8.05	10.43	10.26	9.438	7.63	10.11	6.88	11.24
363	9.344	7.9	7.87	10.18	10.02	9.214	7.47	9.864	6.73	10.94
373	9.13	7.72	7.7	9.936	9.786	8.999	7.3	9.635	6.59	10.66

Table 3: Potential conformers of Protonated AEP

Aminoethylpiperazine and protonated aminoethylpiperazine has a large number of potential conformers, and therefore, for the protonated form of the molecule, there is less confidence in the determination of the most stable conformer. Conformer search for protonated AEP and AEP was done using M06/6-311++G (d,p) and B3LYP/6-311++G(d,p) level using energy profile density functional calculations. Both for AEP and protonated AEP, ten conformers (M1-M10) are given by energy profile calculations. Table 2 lists Eaq, dipole moment, energy of HOMO and LUMO of all these conformers for M06 and B3LYP basis set.

Conformers (Protonated AEP)	M06-6-311++G (d, p)				B3LYP-6-311++G (d,p)			
	Dipole (Debye)	Eaq (KJ/mol)	E HOMO (KJ/mol)	E LUMO (KJ/mol)	Dipole (Debye)	Eaq (KJ/mol)	E HOMO (KJ/mol)	E LUMO (KJ/mol)
M1	10.06	-1055921.06	-934.40	-519.92	10.20	- 1056727.42	-894.47	-477.15
M2	9.64	-1055922.16	-943.06	-519.89	10.02	- 1056725.70	-895.80	-476.92
M3	9.68	-1055916.08	-935.26	-519.73	9.91	- 1056721.76	-894.31	-476.96
M4	9.81	-1055909.80	-927.73	-519.72	9.98	- 1056716.75	-888.68	-477.22
M5	9.91	-1055910.88	-926.18	-520.03	10.10	- 1056717.34	-886.20	-477.61
M6	9.98	-1055917.18	-929.33	-520.46	10.19	- 1056722.33	-888.68	-478.02
M7	9.96	-1055920.60	-935.66	-521.23	10.19	- 1056725.14	-894.76	-478.80
M8	7.52	-1055912.47	-971.81	-506.76	10.05	- 1056718.06	-898.34	-479.85
M9	7.73	-1055901.42	-970.36	-506.86	10.41	- 1056704.34	-903.27	-479.85
M10	7.97	-1055893.94	-961.62	-506.60	10.64	- 1056697.56	-897.68	-479.12

Table 4: Comparison of experimental, PCM and SM8T pKa data at a temperature range of 273 K- 323 K for Morpholine.

Table 4 gives the pKa measurements of morpholine with PCM and SM8T solvation models and their comparison with experimental results at a temperature range of 273 to 323 K. It also lists the errors of PCM pKa values and SM8T pKa values with respect to experimental values at that particular temperature. PCM model shows an average error of 2.2 pKa units and SM8T model shows an average error of 3.8 pKa units for morpholine. On comparison of PCM and SM8T pKa results within themselves, we find out that the results deviates on an average of 1.6 pKa units, and this deviation increases as we go higher in the temperature.

Temp (K)	pKa			Error in pKa:		
	Exp	PCM	SM8T	PCM vs SM8T	PCM vs exp	SM8T vs Exp
273	9.11	7.32	5.88	1.44	1.79	3.23
278	8.98	7.08	5.59	1.50	1.90	3.39
283	8.85	6.86	5.31	1.54	1.99	3.54
288	8.73	6.65	5.06	1.59	2.08	3.67
293	8.61	6.44	4.82	1.62	2.17	3.79
298	8.49	6.25	4.60	1.65	2.24	3.89
303	8.38	6.07	4.39	1.68	2.31	3.99
308	8.27	5.89	4.19	1.70	2.38	4.08
313	8.16	5.72	4.01	1.71	2.44	4.15
318	8.06	5.56	3.83	1.72	2.50	4.22
323	7.96	5.40	3.67	1.73	2.55	4.29

Table 5: Gas phase protonation energies at 298 K using DFT method

Amine studied	Amine		Protonated Amine		Gas. Phase protonation energy	
	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)
PZ	-267.892595	-267.688922	-268.252675	-268.044348	-0.360	-0.355
Morpholine	-287.775183	-287.573096	-288.126234	-287.919329	-0.351	-0.346
Piperidine	-251.848128	-251.644998	-252.201519	-251.992941	-0.353	-0.348
AEP	-401.829298	-401.529315	-402.187598	-401.882469	-0.358	-0.353
DMEDA	-269.082231	-268.868137	-269.439285	-269.219368	-0.357	-0.351
2-methylPZ	-307.195352	-306.959668	-307.55573	-307.315141	-0.360	-0.355
1-methylPZ	-307.186064	-306.950797	-307.53951	-307.299981	-0.353	-0.349
1-ethylPZ	-346.484755	-346.216558	-346.84618	-346.572602	-0.361	-0.356
MDEA	-403.500872	-403.228255	-403.85941	-403.581498	-0.359	-0.353
MEA	-210.395638	-210.246354	-210.73456	-210.582474	-0.340	-0.336

*All values are in Hartrees

Table 6: solvation energies (All values are in Kcal/mol) at 298 K using PCM and SM8T model by using DFT theory.

Amine studied	PCM (B3LYP/6-311++G(d,p))		SM8T (B3LYP/6-311++G(d,p))	
	Amine	Protonated Amine	Amine	Protonated Amine
PZ	-13.06	-71.42	-10.061	-67.515
Morpholine	-12.67	-72.7	-9.414	-70.207
Piperidine	-6.17	-62.46	-4.201	-63.352
AEP	-13.82	-74.63	-9.649	-69.662
DMEDA	-10.64	-68.39	-7.57	-68.02
2-methylPZ	-11.29	-68.96	-8.055	-65.146
1-methylPZ	-10.25	-69.59	-8.296	-66.756
1-ethylPZ	-9.79	-67.4	-7.626	-65.113
MDEA	-13.92	-70.32	-11.44	-65.509
MEA	-11.65	-76.7	-9.144	-81.937

Table 7: Comparison of B3LYP and M06 basis set free energy of protonation in solution calculations for MEA using PCM model.

Temperature	ΔG^*_{aq} (PCM) (Kcal/mol)		pKa (PCM)	
	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)
298	12.909	12.908	9.50	9.50
303	12.945	12.943	9.37	9.37
313	13.014	13.008	9.12	9.11
323	13.083	13.075	8.88	8.88
333	13.153	13.141	8.66	8.65
343	13.222	13.207	8.45	8.44
353	13.301	13.283	8.26	8.25
363	13.360	13.340	8.07	8.06
373	13.430	13.406	7.90	7.88
383	13.514	13.487	7.74	7.72
393	13.579	13.549	7.58	7.56

* As, we see the results are quite identical to each other and temperature dependencies of pKa values are not much dependent on choice of basis set in the calculations. Hence, B3LYP functional was used in all further calculations.

Table 8: Comparison of B3LYP and M06 basis set free energy of protonation in solution calculations for MEA using SM8T model.

Temperature	ΔG^*_{aq} (SM8T) (Kcal/mol)		pKa (SM8T)	
	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)	B3LYP/6-311++G(d,p)	M06/6-311++G(d,p)
298	12.9084	12.9079375	9.50	9.50
303	12.9252575	12.9229125	9.35	9.35
313	12.956245	12.950135	9.08	9.07
323	12.983605	12.9756125	8.82	8.81
333	13.0118475	13.00009	8.57	8.56
343	13.036835	13.02194	8.34	8.33

353	13.0608225	13.04279	8.11	8.10
363	13.0824375	13.061895	7.90	7.89
373	13.1041525	13.0804725	7.70	7.69

Amine	Exp pKa	Empirical Model pKa	Model 2 pKa (Present Model)		Abs errors		
					Empirical Model	Model 2	
			PCM	SM8T		PCM	SM8T
PZ	9.14	9.17	9.17	9.17	0.027	0.030	0.030
Morpholine	7.95	7.95	7.95	7.94	0.000	0.000	0.010
Piperidine	10.38	10.38	10.37	10.40	0.001	0.010	0.020
AEP	8.77	8.86	8.86	8.85	0.092	0.090	0.080
2-methylPZ	8.97	8.95	8.93	8.94	0.025	0.040	0.030
1-methylPZ	8.65	8.55	8.54	8.57	0.102	0.110	0.080
1-ethylPZ	8.72	8.60	8.59	8.60	0.116	0.130	0.120
MDEA	8.08	8.08	8.07	8.08	0.007	0.000	0.010
MEA	8.813	8.88	8.88	8.82	0.067	0.070	0.000
Average Error					Abs	0.048	0.053
						0.042	

Table 9: Comparison of accuracy of pKa calculation with empirical model and Model 2 (present model) at 323K.

***In the empirical model, ΔS^0 values are fitted to experimental pKa values.**

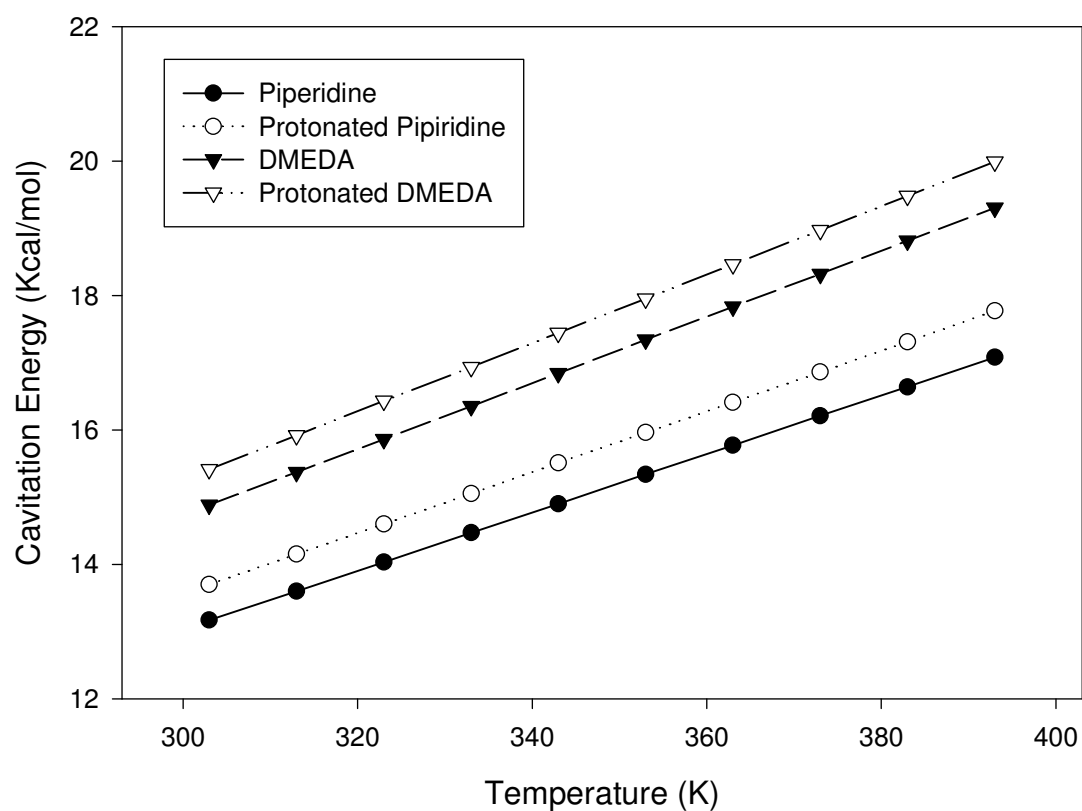


Figure 1: Cavitation energy changes as a function of temperature in PCM solvation free energy results for piperidine and DMEDA in temperature range of 298-393K.