Solvent-mediated modification of thermodynamics and kinetics of monoethanolamine regeneration reaction in amine-stripping carbon capture: computational chemistry study

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Supplementary Material

Table S1: Comparison between activation energies (kcal/mol) obtained by combining the DFT frequency calculations at 298.15 K and 1 bar, and DLPNO-CCSD(T) coupled-cluster electronic energies to those obtained purely from DFT calculations. All calculation used water as a solvent and employed the Def2-TZVP basis set.

	Zwitterion				Carbamic acid				Carbamate			
Functional	Forward		Backward		Forward		Backward		Forward		Backward	
	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC
B3LYP	9.28	9.97	2.88	5.09	0.26	0.13	6.96	6.71	34.04	33.97	37.31	36.69
TPSS	6.26	8.19	1.80	4.20	-0.17	0.10	4.94	6.39	31.76	33.84	32.53	36.04
TPSSh	9.30	10.80	3.04	4.56	-0.22	-0.04	6.20	6.67	32.60	33.94	36.03	37.78
TPSS0	**10.08**	**11.13**	**4.93**	**4.74**	**-0.27**	**-0.22**	**7.77**	**6.96**	**33.85**	**33.94**	**37.63**	**36.85**
M06	8.59	8.10	2.06	5.61	2.07	0.81	6.03	5.35	33.04	34.09	36.94	35.98
M062X	5.92	7.14	6.32	4.86	-0.52	0.08	5.38	4.87	33.90	33.95	38.12	36.19
M06L	8.60	7.79	0.50	5.37	0.30	-0.97	5.98	5.86	34.24	33.81	36.18	36.10
revM06L	10.55	8.86	3.00	5.36	-0.14	-0.72	7.11	6.96	34.95	33.86	40.85	37.59
SCANfunc	3.24	6.36	4.51	3.65	-1.64	-1.27	4.48	5.30	32.06	33.66	35.66	35.88
wB97	7.57	8.17	6.67	5.00	1.32	0.79	7.61	5.47	34.92	33.89	39.66	37.75
wB97X	7.65	8.57	6.21	4.93	0.37	0.07	7.44	5.77	34.68	33.93	38.95	37.01
wB97X-D3	8.65	9.71	5.93	4.93	-0.06	0.06	6.48	5.50	34.09	33.96	38.39	37.18
wB97X-D4	7.36	8.83	6.30	4.87	-0.39	-0.08	6.02	5.57	34.21	33.96	38.58	37.48
wB97X-3BJ	7.44	8.86	6.31	4.81	-0.47	-0.20	6.03	5.61	34.35	33.92	38.26	37.45
CAM-3LYP	8.15	9.48	5.58	4.84	-0.37	-0.19	6.39	5.70	34.02	34.06	37.71	36.19

Table S2: Comparison between Gibbs free energies (kcal/mol) obtained by combining the DFT frequency calculations at 298.15 K and 1 bar, and DLPNO-CCSD(T) coupled-cluster electronic energies to these obtained purely from DFT calculations. All calculation used water as a solvent and employed the Def2-TZVP basis set.

	Zwitterion				Carbamic acid				Carbamate			
Functional	Forward		Backward		Forward		Backward		Forward		Backward	
	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC	DFT	DFT + CC
B3LYP	6.40	4.88	-6.40	-4.88	-6.70	-6.58	6.70	6.58	-3.26	-2.73	3.26	2.73
TPSS	4.45	3.99	-4.45	-3.99	-5.11	-6.29	5.11	6.29	-0.77	-2.20	0.77	2.20
TPSSh	6.26	6.24	-6.26	-6.24	-6.42	-6.71	6.42	6.71	-3.43	-3.84	3.43	3.84
TPSS0	**5.16**	**6.39**	**-5.16**	**-6.39**	**-8.04**	**-7.18**	**8.04**	**7.18**	**-3.78**	**-2.91**	**3.78**	**2.91**
M06	6.53	2.49	-6.53	-2.49	-3.96	-4.54	3.96	4.54	-3.90	-1.88	3.90	1.88
M062X	-0.39	2.27	0.39	-2.27	-5.90	-4.79	5.90	4.79	-4.22	-2.24	4.22	2.24
M06L	8.10	2.42	-8.10	-2.42	-5.68	-6.83	5.68	6.83	-1.94	-2.29	1.94	2.29
revM06L	7.55	3.50	-7.55	-3.50	-7.25	-7.68	7.25	7.68	-5.90	-3.73	5.90	3.73
SCANfunc	-1.27	2.71	1.27	-2.71	-6.12	-6.58	6.12	6.58	-3.60	-2.22	3.60	2.22
wB97	0.90	3.17	-0.90	-3.17	-6.29	-4.67	6.29	4.67	-4.74	-3.86	4.74	3.86
wB97X	1.45	3.63	-1.45	-3.63	-7.07	-5.70	7.07	5.70	-4.27	-3.08	4.27	3.08
wB97X-D3	2.73	4.78	-2.73	-4.78	-6.54	-5.44	6.54	5.44	-4.30	-3.22	4.30	3.22
wB97X-D4	1.06	3.96	-1.06	-3.96	-6.41	-5.64	6.41	5.64	-4.36	-3.52	4.36	3.52
wB97X-D3BJ	1.12	4.05	-1.12	-4.05	-6.50	-5.81	6.50	5.81	-3.91	-3.53	3.91	3.53
CAM-B3LYP	2.57	4.64	-2.57	-4.64	-6.76	-5.89	6.76	5.89	-3.69	-2.13	3.69	2.13

Table S3: Effect of including dispersion and geometrical counterpoise corrections on the zwitterion formation activation energy (kcal/mol) in the case of water. Activation energies were obtained by combining the DFT frequency calculations at 298.15 K and 1 bar, and DLPNO-CCSD(T) coupled-cluster electronic energies. All calculation used water as a solvent and employed the Def2-TZVP basis set. ΔE_{exp} is the deviation from experimental activation energy (kcal/mol).

Functional	Without dispersion and counterpoise corrections	ΔE_{exp}	With both counterpoise and dispersion corrections	ΔE_{exp}	With dispersion correction only	ΔE_{exp}	With counterpoise correction only	ΔE_{exp}
B3LYP	9.54	1.61	9.47	1.68	9.12	1.68	9.97	1.18
TPSS	7.81	3.34	8.39	2.76	8.13	2.03	8.19	2.96
TPSSh	10.39	0.76	8.91	2.24	8.61	3.02	10.80	0.35
TPSS0	10.69	0.46	8.37	2.78	8.06	2.54	**11.13**	**0.02**