Determination of Partial Molar Volumes from Free Energy Perturbation Theory

Supporting Information

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Table S1. Experimental and Computed Densities (g/cm^3) of Water at 25 °C and at Elevated Pressures (atm)

Experiment[a,b]				TIP4P	
Pressure	**Density**	**Pressure**	**Density**	**Pressure**	**Density**
1.00	1.00	1973.85	1.07	1	1.00
98.69	1.00	2171.23	1.08	250	1.02
197.38	1.01	2368.62	1.08	500	1.03
296.08	1.01	2566.00	1.09	750	1.04
394.77	1.01	2763.39	1.10	1000	1.05
493.46	1.02	2960.77	1.10	1500	1.07
592.15	1.02	3158.15	1.11	2000	1.09
690.85	1.03	3355.54	1.11	2500	1.10
789.54	1.03	3552.92	1.12	3000	1.12
888.23	1.03	3750.31	1.12	3500	1.13
986.92	1.04	3947.69	1.13	4000	1.14
1085.62	1.04	4441.15	1.14	5000	1.17
1184.31	1.05	4934.62	1.15	6000	1.19
1283.00	1.05	5428.08	1.16	7000	1.21
1381.69	1.05	5921.54	1.17	8000	1.23
1480.38	1.06	6415.00	1.18		
1579.08	1.06	6908.46	1.19		
1677.77	1.06	7401.92	1.20		
1776.46	1.07	7895.39	1.21		
1875.15	1.07	8388.85	1.22		

[a] Ref.50. [b] Ref. 59.

Figure S1. Density of TIP4P water at elevated pressures; experiment (blue), computed (red).

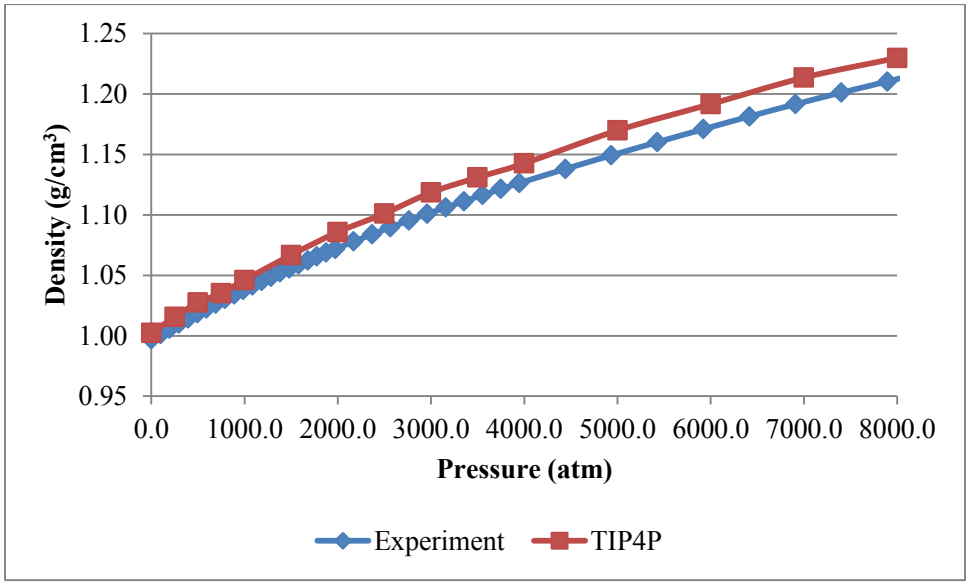

Table S2. Experimental and Computed Densities (g/cm^3) of Carbon Tetrachloride at 25 °C and at Elevated Pressures (atm)

Experiment[a,b]		OPLS-AA CCl_4	
Pressure	**Density**	**Pressure**	**Density**
0.99	1.58	1.0	1.52
100.67	1.60	250.0	1.57
201.33	1.62	500.0	1.60
400.69	1.64	750.0	1.64
601.04	1.67	1000.0	1.66
801.38	1.69		
1000.74	1.71		

[a] Ref. 56. [b] Ref. 55.

Figure S2. Density of carbon tetrachloride at elevated pressures; experiment (blue), computed (red)

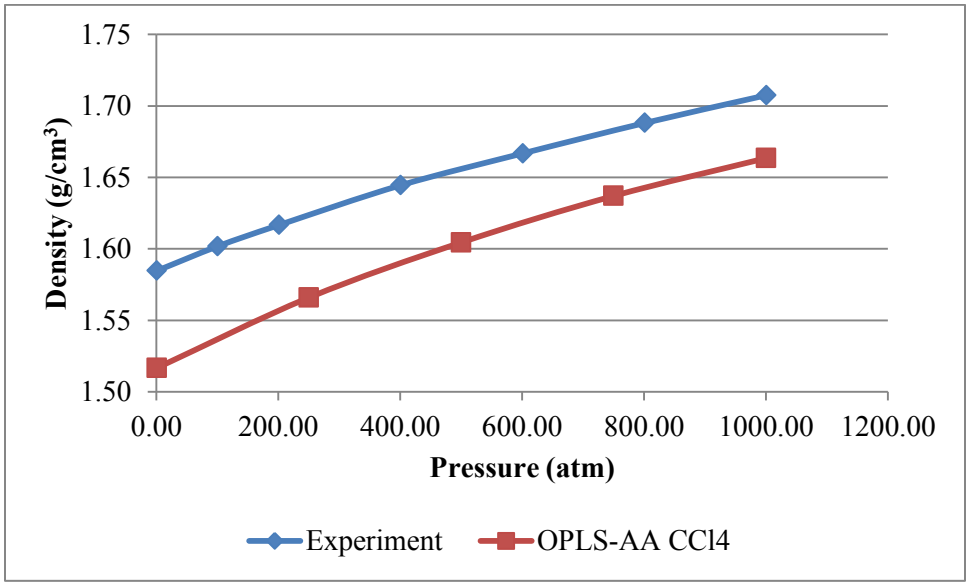

Table S3. Experimental and Computed Densities (g/cm^3) of Benzene at 25 °C and at Elevated Pressures (atm)

Experiment[a,b]		OPLS-AA Benzene	
Pressure	**Density**	**Pressure**	**Density**
1	0.87	1	0.86
100	0.88	50	0.86
200	0.89	200	0.88
300	0.90	350	0.89
400	0.90	500	0.90
500	0.91	650	0.91
600	0.92	800	0.92
700	0.92	1000	0.93
800	0.93		
900	0.93		
1000	0.94		

[a] Ref. 60. [b] Ref. 55.

Figure S3. Density of benzene at elevated pressures; experiment (blue), computed (red)

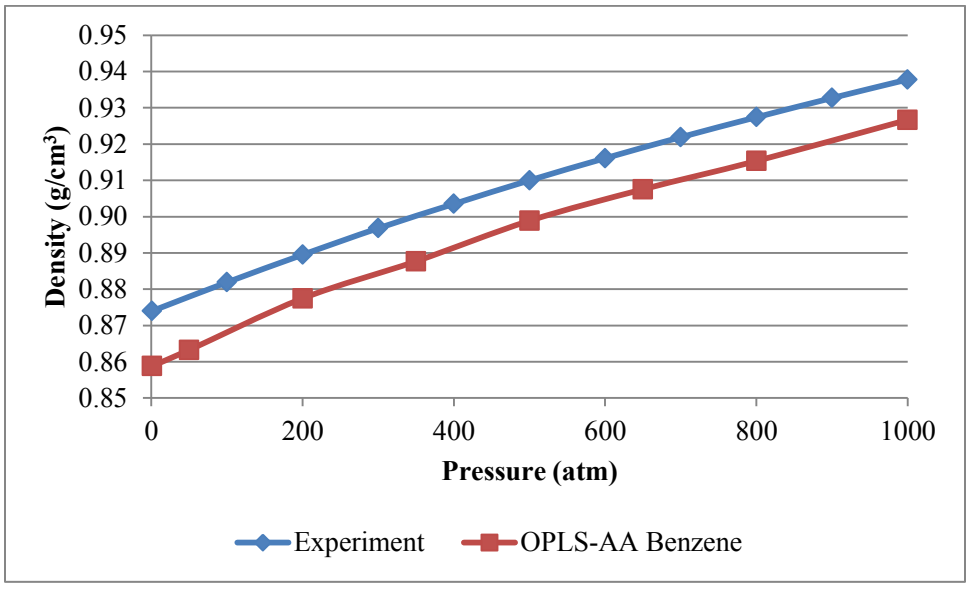

Table S4. Extrapolated, Experimental Free Energies of Solvation (kcal/mol) in Three Solvents at Increasing Pressure (atm) at 25 °C[a]

Water			Carbon Tetrachloride			Neat Benzene	
Pressure	**ΔG_{solv} (H_2O)**	**ΔG_{solv} (C_6H_6)**	**Pressure**	**ΔG_{solv} (CCl_4)**	**ΔG_{solv} (C_6H_6)**	**Pressure**	**ΔG_{solv} (C_6H_6)**
1[b]	-6.33[c]	-0.86[c]	1	-4.40[d]	-4.50[e]	1	-4.56[d]
1000	-5.89	1.15	250	-3.81	-3.95	50	-4.45
2000	-5.46	3.17	500	-3.23	-3.41	200	-4.13
3000	-5.02	5.18	750	-2.64	-2.86	350	-3.80
4000	-4.58	7.20	1000	-2.05	-2.31	500	-3.48
5000	-4.14	9.21				650	-3.15
6000	-3.70	11.23					
7000	-3.27	13.24					
8000	-2.83	15.26					
$V°$	18.1[f]	83.1[g]		97.1[f]	90.5[h]		89.5[f]

[a] Partial molar volumes and ΔG_{solv} at 1 atm were used to estimate ΔG_{solv} at pressures up to 8000 atm. [b] ΔG_{solv}s at 1 atm are from experiment. [c] Ref. 70. [d] Ref. 78. [e] Ref. 71. [f] Partial molar volumes were obtained from experimental densities at 25 °C. [g] Ref. 34. [h] Ref. 63.

Figure S4. Computed free energy changes by annihilating benzene's electrostatic (ΔG(–Q); blue) and Lennard-Jones (ΔG(–LJ); red) non-bonded parameters in TIP4P water at elevated pressures. Linear fits are shown as dashed lines; equations and correlation coefficients are color coded for each ΔG.

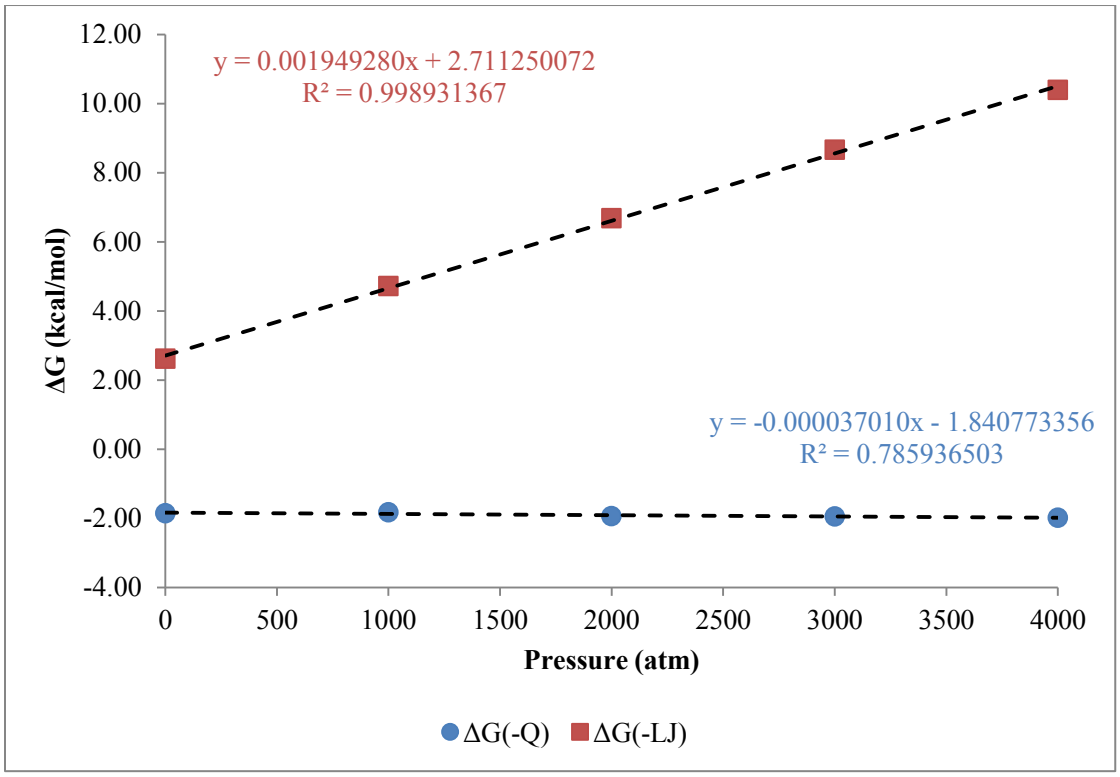

Table S5. Computed Free Energy Changes (kcal/mol) by Annihilating Benzene's Electrostatic (ΔG(–Q)) and Lennard-Jones (ΔG(–LJ)) Nonbonded Parameters in TIP4P Water at Elevated Pressures (atm) at 25 °C

Pressure	ΔG(-Q)	ΔG(-LJ)
1	-1.86	2.62
1000	-1.80	4.72
2000	-1.94	6.68
3000	-1.95	8.66
4000	-1.99	10.39

Table S6. Computed Relative Free Energies of Hydration ($\Delta\Delta G_{hyd}$; kcal/mol) at Elevated Pressures (atm)[a]

Ph–X → Ph–Y		1	500	1000	1500	2000	2500	3000	3500	4000
CH_3	H	0.31	0.12	-0.21	-0.17	-0.37	-0.74	-0.74	-0.96	-1.23
F	H	-0.27	-0.40	-0.38	-0.47	-0.52	-0.54	-0.50	-0.54	-0.62
Cl	H	-0.44	-0.50	-0.71	-0.88	-0.97	-1.05	-1.32	-1.43	-1.53
OH	H	5.14	5.21	5.16	5.14	5.23	5.02	5.15	5.11	4.89
NH_2	H	4.40	4.68	4.70	4.48	4.73	4.56	4.54	4.71	4.72
OCH_3	H	0.65	0.30	0.00	-0.17	-0.50	-0.54	-1.09	-1.26	-1.54
CHO	H	3.12	3.06	2.85	2.48	2.43	2.19	2.63	1.96	1.77
$COCH_3$	H	3.08	2.87	2.82	1.97	1.85	1.68	1.77	0.84	0.47
NO_2	H	2.18	2.53	2.07	1.96	1.80	1.73	1.42	1.52	1.16
OCH_3	OH	-4.50	-4.83	-5.32	-5.35	-5.60	-5.89	-6.14	-6.49	-6.58
NHMe	NH_2	-0.90	-1.15	-1.34	-1.69	-1.92	-2.26	-2.18	-2.39	-2.87
NMe_2	NHMe	-0.91	-1.35	-1.62	-1.66	-1.86	-2.02	-2.18	-2.28	-2.60
$COCH_3$	$CONH_2$	-6.68	-7.00	-7.33	-7.50	-7.78	-7.79	-7.91	-8.32	-8.40
CONHMe	$CONH_2$	-2.99	-2.99	-3.66	-3.70	-4.40	-4.33	-4.54	-4.83	-4.82
$CONMe_2$	CONHMe	-2.80	-2.84	-2.86	-3.21	-3.66	-3.81	-4.21	-4.34	-4.67

[a] all standard uncertainties are less than 0.15 kcal/mol.