Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information:

Predicting Hydration Gibbs Energies of Alkyl-aromatics Using Molecular Simulation: A Comparison of Current Force Fields and the Development of a New Parameter Set for Accurate Solvation Data

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Table S1: LJ and electrostatic contributions to the predicted hydration Gibbs energies of benzene and linear alkylbenzenes using the TraPPE-UA force field. All data in kJ/mol. The subscripts give the statistical accuracy of the last decimal point shown. Abbreviations as detailed in the main manuscript.

Solute	ΔG^{LJ}	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{hyd}G^{\exp}$
BZ	4.5_5	0	4.5_5	-3.62
MB	5.5_6	0	5.5_6	-3.71
EB	6.6_6	0	6.6_6	-3.33
PB	7.1_{10}	0	7.1_{10}	-2.23
BB	7.9_9	0	7.9_9	-1.66
PeB	9.1_6	0	9.1_6	-0.96
			AAD	**9.4_6**
BZ*	5.5_5	-5.04_9	0.5_5	-3.62
			AAD	**4.2**

* Considering an explicit hydrogen description of the aromatic ring.

Table S2: LJ and electrostatic contributions to the predicted hydration Gibbs energies of benzene and linear alkylbenzenes using the OPLS-AA force field. All data in kJ/mol. The subscripts give the statistical accuracy of the last decimal point shown.

Solute	ΔG^{LJ}	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{hyd}G^{\exp}$
BZ	6.8_2	-8.2_1	-1.4_2	-3.62
MB	12.1_5	-12.24_8	-0.1_5	-3.71
EB	16.4_4	-11.70_8	4.7_4	-3.33
PB	19.4_4	-11.17_8	8.2_4	-2.23
BB	22.0_5	-11.18_8	10.8_5	-1.66
PeB	26.3_2	-11.09_8	15.2_2	-0.96
			AAD	**8.8 ± 4.9**

Table S3: LJ and electrostatic contributions to the predicted hydration Gibbs energies of benzene and linear alkylbenzenes using the Gromos-EH force field. All data in kJ/mol. The subscripts give the statistical accuracy of the last decimal point shown.

Solute	ΔG^{LJ}	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{hyd}G^{\exp}$
BZ	7.6_5	-12.66_8	-5.2_5	-3.62
MB	7.9_4	-9.23_7	-1.4_4	-3.71
EB	8.7_6	-9.53_7	-0.8_6	-3.33
PB	9.0_6	-9.44_7	-0.5_6	-2.23
BB	9.9_7	-9.54_7	0.3_7	-1.66
PeB	10.7_8	-9.49_7	1.2_8	-0.96
			AAD	**2.1 ± 0.3**

Table S4: LJ and electrostatic contributions to the predicted hydration Gibbs energies of benzene and linear alkylbenzenes using the Gromos-UA force field. All data in kJ/mol. The subscripts give the statistical accuracy of the last decimal point shown.

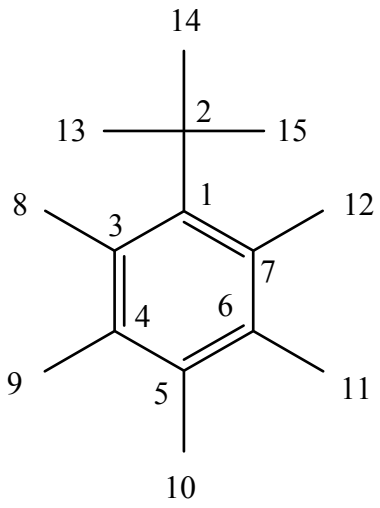
Solute	ΔG^{LJ}	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{hyd}G^{\exp}$
BZ	1.7_6	0	1.7_6	-3.62
MB	2.5_3	0	2.5_3	-3.71
EB	3.3_3	0	3.3_3	-3.33
PB	4.0_3	0	4.0_3	-2.23
BB	4.1_8	0	4.1_8	-1.66
PeB	4.5_9	0	4.5_9	-0.96
			AAD	**5.9** ± 0.4

Tables S5-S12: CHelpG and NPA charges for the different molecules studied

- **Table S5:** Benzene (BZ)

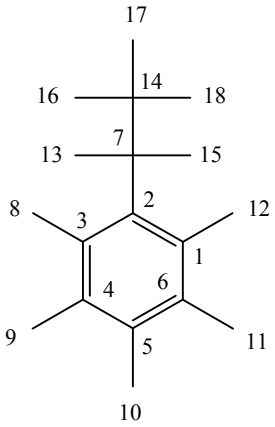
Atom	**CHelpG**	**NPA**
C_1	(4x) -0.062	-0.245
C_2	(2x) -0.103	
H_1	(4x) 0.072	0.245
H_2	(2x) 0.085	

- **Table S6:** Toluene (MB)



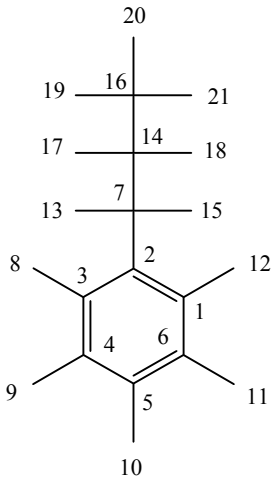
Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	0.212	-0.042	6	-0.026	-0.238	11	0.072	0.245
2	-0.223	-0.709	7	-0.203	-0.241	12	0.098	0.240
3	-0.212	-0.240	8	0.109	0.240	13	0.066	0.245
4	-0.020	-0.238	9	0.069	0.245	14	0.059	0.252
5	-0.155	-0.254	10	0.094	0.245	15	0.059	0.252

- **Table S7:** Ethylbenzene (EB)



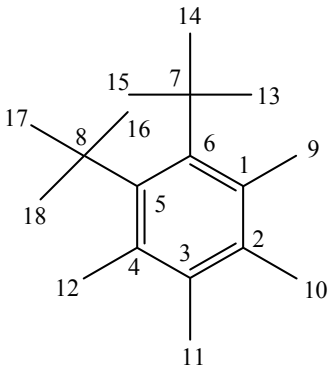
Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	-0.167	-0.239	7	0.033	-0.488	13	-0.016	0.247
2	0.093	-0.036	8	0.105	0.240	14	0.164	-0.690
3	-0.167	-0.239	9	0.075	0.245	15	-0.016	0.246
4	-0.063	-0.239	10	0.080	0.245	16	-0.035	0.239
5	-0.096	-0.253	11	0.075	0.245	17	-0.054	0.239
6	-0.063	-0.239	12	0.105	0.245	18	-0.054	0.239

- **Table S8:** Propylbenzene (PB)



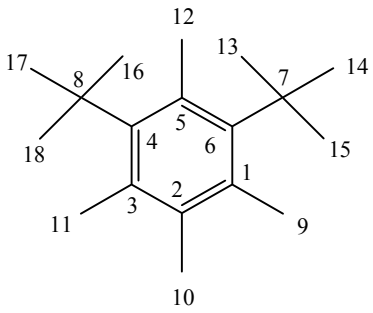
Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	-0.134	-0.239	8	0.099	0.240	15	0.022	0.245
2	0.096	-0.035	9	0.081	0.245	16	-0.137	-0.699
3	-0.134	-0.239	10	0.079	0.245	17	-0.144	0.239
4	-0.091	-0.239	11	0.080	0.245	18	-0.114	0.239
5	-0.079	-0.253	12	0.099	0.240	19	0.013	0.244
6	-0.091	-0.239	13	0.022	0.245	20	0.015	0.235
7	-0.155	-0.480	14	0.429	-0.472	21	0.015	0.235

- **Table S9:** Ortho-xylene (OX)



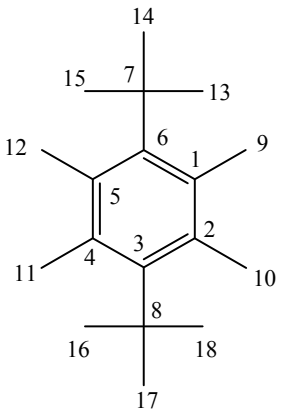
Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	-0.210	-0.233	7	-0.176	-0.708	13	0.051	0.247
2	-0.071	-0.247	8	-0.176	-0.708	14	0.054	0.249
3	-0.071	-0.247	9	0.114	0.239	15	0.054	0.249
4	-0.210	-0.233	10	0.077	0.244	16	0.051	0.247
5	0.106	-0.039	11	0.077	0.244	17	0.054	0.249
6	0.106	-0.039	12	0.114	0.239	18	0.054	0.249

- **Table S10:** Meta-xylene (MX)



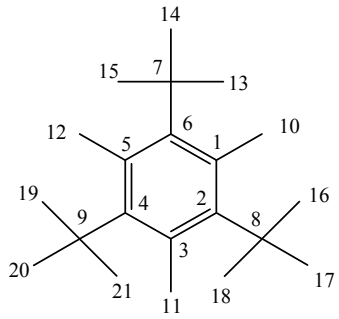
Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	-0.247	-0.250	7	-0.149	-0.708	13	0.042	0.248
2	-0.009	-0.231	8	-0.130	-0.708	14	0.041	0.246
3	-0.250	-0.250	9	0.115	0.240	15	0.044	0.253
4	0.215	-0.035	10	0.074	0.244	16	0.035	0.247
5	-0.327	-0.237	11	0.115	0.240	17	0.040	0.253
6	0.22	-0.035	12	0.134	0.235	18	0.037	0.247

- **Table S11:** Para-xylene (PX)



Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	-0.173	-0.233	7	-0.172	-0.707	13	0.048	0.247
2	-0.179	-0.233	8	-0.165	-0.707	14	0.050	0.252
3	0.166	-0.051	9	0.105	0.239	15	0.048	0.247
4	-0.179	-0.233	10	0.106	0.239	16	0.046	0.247
5	-0.171	-0.233	11	0.106	0.239	17	0.049	0.252
6	0.162	-0.051	12	0.105	0.239	18	0.046	0.247

- **Table S12:** 1,3,5-Trimethylbenzene (TMB)



Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
1	-0.379	-0.245	8	-0.171	-0.707	15	0.042	0.250
2	0.263	-0.025	9	-0.184	-0.707	16	0.047	0.250
3	-0.379	-0.245	10	0.145	0.234	17	0.049	0.251
4	0.253	-0.025	11	0.146	0.234	18	0.046	0.244
5	-0.371	-0.245	12	0.142	0.234	19	0.050	0.244
6	0.256	-0.025	13	0.042	0.244	20	0.052	0.251
7	-0.154	-0.707	14	0.044	0.251	21	0.051	0.251

Table S13: Prediction of liquid densities (g/l) at P = 1 bar using the new parameter set.

Solute	T/K	ρ^{calc}	AAD (%)	T/K	ρ^{calc}	AAD (%)	T/K	ρ^{calc}	AAD (%)
BZ	294	920.81	5.0	313	900.89	5.0	347	864.59	5.1
MB	293	891.78	2.6	311	873.63	2.5	345	840.36	2.5
EB	292	879.66	1.1	311	862.77	1.2	344	832.81	1.4
PB	291	876.55	1.3	309	861.21	1.4	343	832.87	1.6
BB	290	876.61	1.5	309	861.71	1.5	342	834.94	1.7
PeB	289	873.41	1.4	308	858.97	1.4	341	833.22	1.3
OX	291	896.16	1.6	309	879.67	1.5	343	850.61	1.4
MX	291	880.09	1.6	309	864.05	1.5	342	835.42	1.6
PX	291	875.86	1.5	309	860.23	1.5	342	831.99	1.6
TMB	289	889.19	2.3	308	874.50	2.4	340	847.92	2.6
		Overall	2.0		*Overall*	2.0		*Overall*	2.1

Table S14: Prediction of vaporization enthalpies (kJ/mol) at P = 1 bar using the new parameter set.

Solute	T/K	$\Delta_{vap}H^{exp}$	E^{Gas}	E^{Liq}	$\Delta_{vap}H^{sim}$	AAD (kJ/mol)
BZ	313	33.0	102.4	69.1	35.9	2.9
MB	311	37.4	100.0	64.9	37.7	0.3
EB	311	41.5	121.8	83.8	40.6	1.0
PB	309	46.6	129.5	87.2	44.9	1.7
BB	309	49.9	137.9	91.0	49.5	0.4
PeB	308	54.8	145.9	94.9	53.7	1.2
OX	309	42.9	97.2	58.6	41.2	1.7
MX	309	42.2	97.2	59.1	40.6	1.6
PX	309	41.7	97.2	59.4	40.4	1.3
TMB	308	46.9	94.6	52.6	44.6	2.3
					Overall	1.4

Table S15: Prediction of benzene dielectric constant (ε) using different parameter sets.

Model	ε^{calc}	$\varepsilon^{calc} \times \varepsilon_{\infty}$	ε^{exp}
TraPPE-EH	1.016	2.29	2.28
GROMOS-EH	1.046	2.36	
OPLS-AA	1.028	2.32	
New Model	1.013	2.28	

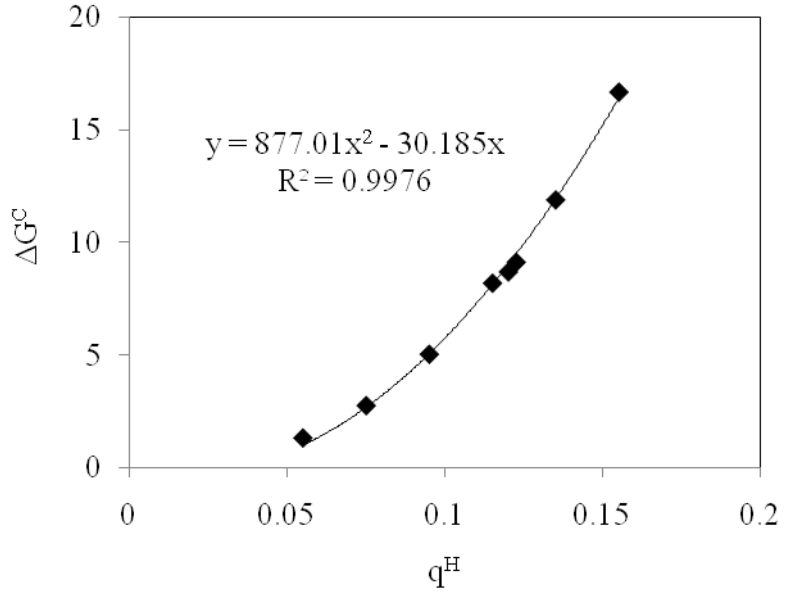


Figure S1: Correlation between ΔG^C (kJ/mol) and aromatic hydrogen point charges for BZ (the charge on the aromatic carbon is always symmetric to the hydrogen charge).

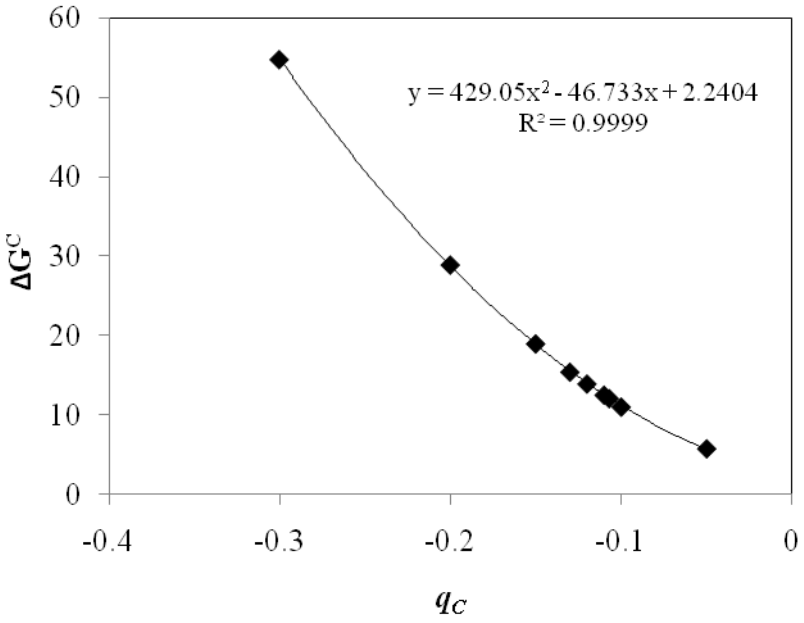


Figure S2: Correlations between ΔG^C (kJ/mol) for TMB and different point charges on the substituted aromatic carbon atom (remaining charges are kept equal to their corresponding values in BZ).

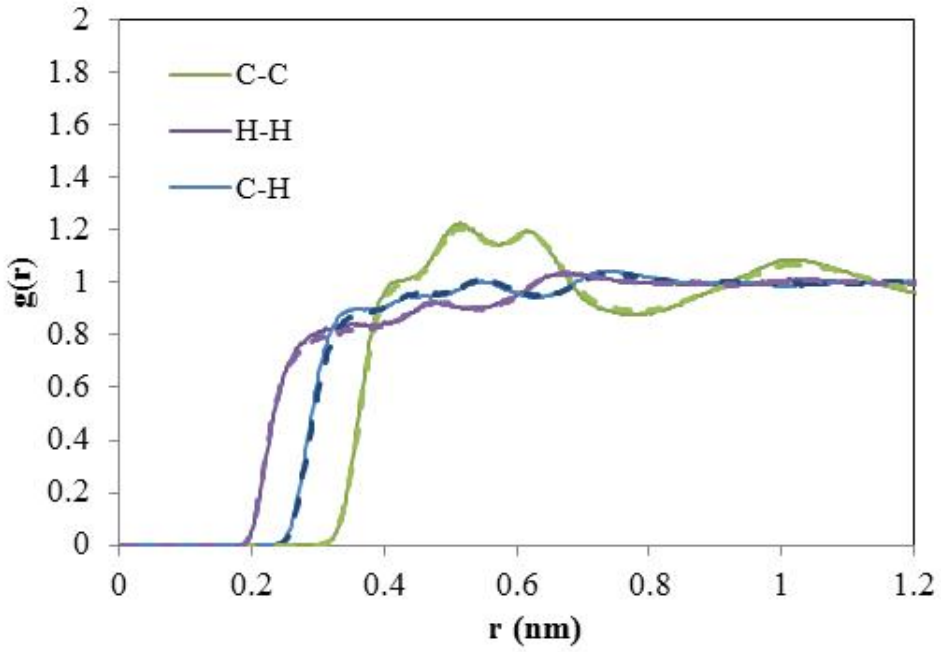


Figure S3: Benzene liquid structure: computed $C_{aro}-C_{aro}$ (aromatic carbon – aromatic carbon), $H_{aro}-H_{aro}$ (aromatic hydrogen – aromatic hydrogen) and $C_{aro}-H_{aro}$ (aromatic carbon – aromatic hydrogen) radial distribution functions at 298 K using the new charge set (solid lines) and the original TraPPE-EH parameters (dashed lines).

Tutorial: How to assign charges for **1,2,4-TMB** using the rule:

1) Assign each site (Carbon, Hydrogen or CH_x) to its corresponding position in the diagram of Figure 2.

2) For each site, determine the total number of substituents (N_j) on each position j (0 for the current C/H atoms, 1 for C/H atoms in ortho position, 2 for C/H atoms in meta position, and 3 for C/H atoms in para position). Recall that the maximum value of N is 1 for j=0,3 and 2 for j=1,2.

3) Compute the charge on each site by applying equation (4) and the charge increments of Table 4.

The table below shows the number of substituents and the total charge on each site of the 1,2,4-TMB molecule.

Atom	**N_0**	**N_1**	**N_2**	**N_3**	**q**
C_1	1	1	1	0	-0.1082
C_2	1	1	0	1	-0.1160
C_3	0	1	2	0	-0.1135
C_4	0	1	1	1	-0.1213
C_5	1	0	1	1	-0.1148
C_6	0	2	1	0	-0.1147
CH_7	1	1	1	0	0.1100
CH_8	1	1	0	1	0.1102

H_9	0	1	2	0	0.1193
H_{10}	0	1	1	1	0.1195
CH_{11}	1	0	1	1	0.1125
H_{12}	0	2	1	0	0.117
					$\sum = 0.0000$

Below are two examples of application of equation (4) to calculate the charge on the carbon atom at position 1 and on the CH_x pseudo-atom at position 7.

Example: $q_{C_1} = -0.1225 + 1*0.0087 + 1*0.0022 + 1*0.0034 - 0*0.0044 = -0.1082$

$q_{CH_7} = 0.1225 - 1*0.0096 - 1*0.0026 - 1*0.0003 - 0*0.0001 = 0.1100$