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}	$\Delta_{hyd}G^{sim}$	$\Delta_{\it hyd}G^{\it exp}$
BZ	4.55	0	4.55	-3.62
MB	5.56	0	5.56	-3.71
EB	6.66	0	6.66	-3.33
PB	7.1 ₁₀	0	7.1 ₁₀	-2.23
BB	7.99	0	7.99	-1.66
PeB	9.16	0	9.1 ₆	-0.96
	·		AAD	9.4 ₆

BZ*	5.55	-5.049	0.55	-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 energiesof 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	$\Delta G^{^{LJ}}$	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{_{hyd}}G^{\mathrm{exp}}$
DZ	()	0.0	1.4	2 (2
BZ	6.82	-8.21	-1.42	-3.62
MB	12.15	-12.248	-0.15	-3.71
EB	16.44	-11.708	4.74	-3.33
PB	19.44	-11.178	8.24	-2.23
BB	22.05	-11.188	10.85	-1.66
PeB	26.3 ₂	-11.098	15.22	-0.96
			AAD	8.8 ± 4.9

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

Solute	ΔG^{LJ}	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{\mathit{hyd}} G^{exp}$
BZ	7.65	-12.668	-5.25	-3.62
MB	7.94	-9.237	-1.44	-3.71
EB	8.76	-9.537	-0.86	-3.33
PB	9.06	-9.447	-0.56	-2.23
BB	9.97	-9.547	0.37	-1.66
PeB	10.78	-9 .49 ₇	1.28	-0.96
	<u>.</u>		AAD	2.1 ± 0.3

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

Solute	$\Delta G^{{\scriptscriptstyle L}{\scriptscriptstyle J}}$	ΔG^{C}	$\Delta_{hyd}G^{sim}$	$\Delta_{\mathit{hyd}} G^{\mathrm{exp}}$
BZ	1.76	0	1.76	-3.62
MB	2.53	0	2.53	-3.71
EB	3.33	0	3.33	-3.33
PB	4.03	0	4.03	-2.23
BB	4.18	0	4.1 ₈	-1.66
PeB	4.59	0	4.59	-0.96
			AAD	5.9 ± 0.4

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

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 S5: Benzene (BZ)

• **Table S6:** Toluene (MB)



Atom#	CHelpG	NPA	Atom#	CHelpG	NPA	Atom#	CHelpG	NPA
	0.010	0.040	6	0.00	0.000			
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

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

Solute T/K ρ^{mk} AAD (%) T/K ρ^{mk} AAD (%) T/K ρ^{mk} 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 5.1 MB 293 891.78 2.6 311 873.63 1.2 345 840.36 2.5 PB 292 879.66 1.1 311 862.77 1.2 344 832.81 1.4 PB 290 876.61 1.5 309 861.71 1.5 342 834.94 1.7 PB 290 876.61 1.5 309 861.71 1.5 343 833.22 1.6 PA 289 876.61 1.5 309 861.71 1.5 343 833.23 1.6 PA 289 876.70 1.5 343 <												
Solute T/K ρ^{aak} AAD (%) T/K ρ^{aak} AAD (%) T/K ρ^{aak} BZ 294 920.81 5.0 313 900.89 5.0 347 864.59 MB 293 891.78 2.6 311 873.63 2.5 345 840.36 MB 292 879.66 1.1 311 862.77 1.2 344 832.81 PB 291 876.55 1.3 309 861.21 1.4 343 832.87 PB 290 876.61 1.5 309 861.21 1.4 343 832.87 PB 290 876.61 1.5 309 861.71 1.5 343 833.28 PA 289 876.61 1.5 309 861.71 1.5 343 833.24 PA 289 876.61 1.5 349 833.22 834.94 PA 289 876.61 1.5 343	AAD (%)	5.1	2.5	1.4	1.6	1.7	1.3	1.4	1.6	1.6	2.6	2.1
Solute T/K ρ^{enfe} AAD (%) T/K ρ^{enfe} AAD (%) T/K BZ 294 920.81 5.0 313 900.89 5.0 347 BZ 293 891.78 2.6 311 875.63 2.5 345 MB 293 891.78 2.6 311 862.77 1.2 344 PB 291 876.55 1.3 309 861.21 1.4 343 PB 290 876.61 1.5 309 861.71 1.5 344 PB 290 876.61 1.5 309 861.71 1.4 343 PB 290 876.61 1.5 309 861.71 1.5 342 PA 291 876.55 1.5 309 861.71 1.5 343 PB 290 874.51 1.5 309 864.05 1.4 341 OX 291 880.09 1.6	$ ho^{calc}$	864.59	840.36	832.81	832.87	834.94	833.22	850.61	835.42	831.99	847.92	Overall
Solute T/K ρ^{cade} AAD (%) T/K ρ^{cade} AAD (%) BZ 294 920.81 5.0 313 900.89 5.0 BZ 293 891.78 2.6 311 873.63 2.5 MB 293 891.78 2.6 311 862.77 1.2 PB 291 876.55 1.1 311 862.77 1.2 PB 291 876.55 1.3 309 861.21 1.4 PB 290 876.61 1.5 309 861.71 1.5 PB 290 875.61 1.5 309 861.71 1.5 PB 290 876.61 1.5 309 861.71 1.5 MX 291 876.61 1.5 309 861.71 1.5 PeB 289 873.41 1.4 308 858.97 1.4 MX 291 880.09 1.6 309 864.05	T/K	347	345	344	343	342	341	343	342	342	340	
Solute T/K ρ^{catc} AAD (%) T/K ρ^{catc} BZ 294 920.81 5.0 313 900.89 BZ 293 891.78 2.6 311 873.63 MB 292 879.66 1.1 311 862.77 EB 292 879.66 1.1 311 862.77 PB 291 876.55 1.3 309 861.21 PB 290 876.61 1.5 309 861.21 PB 290 876.61 1.5 309 861.21 PC 289 873.41 1.4 308 858.97 PeB 289 873.61 1.5 309 861.61 MX 291 896.16 1.6 309 864.05 MX 291 880.09 1.6 309 864.05 MX 291 880.09 1.6 309 864.05 MX 291 889.19	AAD (%)	5.0	2.5	1.2	1.4	1.5	1.4	1.5	1.5	1.5	2.4	2.0
Solute T/K ρ^{catc} AAD (%) T/K BZ 294 920.81 5.0 313 BZ 294 920.81 5.0 313 MB 293 891.78 2.6 311 MB 293 891.78 2.6 311 EB 292 879.66 1.1 311 BB 291 876.55 1.3 309 PB 290 876.61 1.5 309 PB 290 873.41 1.4 308 PC 289 873.41 1.4 308 MX 291 896.16 1.6 309 MX 291 880.09 1.6 309 MX 291 880.09 1.6 309 PX 291 880.09 1.6 309 PX 291 889.19 2.3 309 PX 291 889.19 2.3 309 IMB <td>ho^{calc}</td> <td>900.89</td> <td>873.63</td> <td>862.77</td> <td>861.21</td> <td>861.71</td> <td>858.97</td> <td>879.67</td> <td>864.05</td> <td>860.23</td> <td>874.50</td> <td>Overall</td>	$ ho^{calc}$	900.89	873.63	862.77	861.21	861.71	858.97	879.67	864.05	860.23	874.50	Overall
Solute T/K ρ^{calc} AAD (%) BZ 294 920.81 5.0 BZ 293 891.78 5.0 MB 293 891.78 2.6 MB 293 891.78 2.6 MB 293 891.78 2.6 MB 293 879.66 1.1 PB 291 876.55 1.3 PB 290 876.61 1.5 PB 290 876.61 1.5 PA 291 896.16 1.6 MX 291 896.16 1.5 MX 291 880.09 1.5 PX 291 875.86 1.5 PX 291 875.86 1.5 TMB 289 889.19 2.3	T/K	313	311	311	309	309	308	309	309	309	308	
Solute T/K ρ^{calc} BZ 294 920.81 BZ 293 891.78 MB 293 891.78 MB 292 879.66 EB 292 876.61 PB 291 876.55 PB 291 876.55 PB 290 876.61 PB 291 876.55 PB 290 876.61 PB 290 876.61 PB 291 896.16 MX 291 896.16 MX 291 896.16 PX 291 896.16 PX 291 875.86 PX 291 875.86 TMB 289 889.19	AAD (%)	5.0	2.6	1.1	1.3	1.5	1.4	1.6	1.6	1.5	2.3	2.0
SoluteT/KBZ294BZ293MB293EB291PB291PB291PB291PB291PC291PA291PA291PA291PA291PA291PA291PA291PX291PX291PX291PX291PX291PX291PX291PX291PX291PX291	$ ho^{calc}$	920.81	891.78	879.66	876.55	876.61	873.41	896.16	880.09	875.86	889.19	Overall
Solute BZ MB MB EB EB BB BB BB BB MX MX MX MX TMB TMB	T/K	294	293	292	291	290	289	291	291	291	289	
	Solute	ΒZ	MB	EB	PB	BB	PeB	OX	MX	ΡX	TMB	

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

parameter set.

Solute	T/K	$\Delta_{vap}H^{ m exp}$	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
РХ	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	$oldsymbol{arepsilon}^{calc}$	$\mathcal{E}^{calc} imes \mathcal{E}_{\infty}$	\mathcal{E}^{exp}
TraPPE-EH	1.016	2.29	
GROMOS-EH	1.046	2.36	2.28
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_{I}	1	1	1	0	-0.1082
C_2	1	1	0	1	-0.1160
<i>C</i> ₃	0	1	2	0	-0.1135
C_4	0	1	1	1	-0.1213
C_5	1	0	1	1	-0.1148
<i>C</i> 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
					0.1105
H_{10}	0	l	l	I	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: $q_{C_1} = -0.1225 + 1*0.0087 + 1*0.0022 + 1*0.0034 - 0*0.0044 = -0.1082$

 $q_{_{CH_{7}}} = 0.1225 - 1*0.0096 - 1*0.0026 - 1*0.0003 - 0*0.0001 = 0.1100$