Supplemental Information

Polarizable empirical force field for the primary and secondary alcohol series based on the classical Drude model

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Table S1. Methanol vibrational spectra, cm^{-1}.

Exp.[1]	QM[2]	Assignment	Drude	Assignment	Diff., %[3]
200	332	COtorsion	306	COtorsion	53
1033	1022	COstr	1036	COstr	0
1060	1050	COstr; CH3rock	1098	CH3rock	4
1165	1136	CH3rock	1121	CH3rock	4
1345	1338	COHdef	1342	COHdef	0
1455	1452	CH3def	1438	CH3def	1
1477	1476	CH3def	1442	CH3def	2
1477	1489	CH3def	1611	CH3def	9

2844	2901	CH3str	2849	CH3str	0
2960	2964	CH3str	2914	CH3str	2
3000	3038	CH3str	2914	CH3str	3
3681	3580	OHstr	3654	OHstr	1

[1]NIST Chemistry WebBook (http://webbook.nist.gov/chemistry). [2]MP2/6-31G* level of theory; frequencies scaled by factor 0.9434. [3]Diff = [abs($\nu_{exp} - \nu_{emp}$)/ ν_{exp}]*100

Table S2. Ethanol vibrational spectra, cm^{-1}

Exp.[1]	QM[2]	Assignment	Drude	Assignment	Diff, %[3]
–	249	COtorsion	258	COtorsion	4
–	295	CCtorsion	292	CCtorsion	1
417	402	OCCsciss	418	OCCsciss	0
812	799	CH3rock, CH2rock	844	CH2rock, CH3rock	4
888	883	COstr, CH3rock, CCstr	886	CCstr, Costr, CH3rock	0
1028	1017	CCstr	1025	CH3rock, CCstr	0
1091	1079	COstr, CH3rock	1062	COstr	3
1161	1153	CH2rock, CH3rock	1058	CH3rock, CH2rock	9
1256	1237	HOCdef	1254	HOCdef	0
1275	1260	CH2twist	1249	CH2twist	2
1371	1372	CH3def	1421	CH3def	4
1412	1423	CH2wag	1402	CH2sciss, CH2wag	1

1446	1461	CH3def	1424	CH3def	2
1464	1477	CH3def	1429	CH3def	2
1490	1507	CH2sciss	1555	CH2wag, CH2sciss	4
2900	2887	CH2str	2853	CH2str	2
2910	2927	CH2str	2885	CH2str	1
2939	2941	CH3str	2904	CH3str	1
2984	3027	CH3str	2959	CH3str	1
2991	3037	CH3str	2960	CH3str	1
3653	3565	OHstr	3653	OHstr	0

[1]Matrix isolation[94]. [2]MP2/6-31G* level of theory; frequencies scaled by factor 0.9434. [3]Diff = $[abs(\nu_{exp} - \nu_{emp})/ \nu_{exp}]*100$

Table S3. Iso-propanol vibrational spectra, cm^{-1}

QM[1]	Assignment	Drude	Assignment	Diff, %[2]
238	CCtorsion	219	CCtorsion	8
275	CCtorsion	228	CCtorsion	17
293	COtorsion	257	COtorsion	12
348	CCCrock	352	CCCrock	1
411	OCCrock	403	OCCrock	2
457	CCCsciss	411	CCCsciss	10
799	CCstr	798	CCstr	0

900	CH3rock	912	CH3rock	1
918	CCstr, CH3rock	933	CH3rock, CCstr	2
950	COstr, CH3rock	955	CH3rock	1
1050	COHdef, OCHrock	1104	OCHrock	5
1130	CCstr	1113	CCstr	2
1163	CH3rock	1055	CH3rock	9
1277	COHdef	1275	COHdef	0
1334	CCHrock	1340	CCHrock	0
1371	OCHrock	1455	OCHrock	6
1376	CH3rock	1390	CH3rock	1
1388	CH3rock	1393	CH3rock	0
1460	CH3rock	1416	CH3rock	3
1462	CH3rock	1424	CH3rock	3
1473	CH3rock	1425	CH3rock	3
1481	CH3rock	1427	CH3rock	4
2919	CH3str	2898	CH3str	1
2922	CH3str	2900	CH3str	1
2956	CHstr	2909	CHstr	2
2998	CH3str	2957	CH3str	1
3006	CH3str	2958	CH3str	2
3027	CH3str	2959	CH3str	2

3028	CH3str	2960	CH3str	2
3532	OHstr	3656	OHstr	4

[1]MP2/6-31G* level of theory; frequencies scaled by factor 0.9434. [3]Diff = [abs(ν_{qm} – ν_{emp})/ ν_{qm}]*100

Table S4. Minimum distances and interaction energies of rare gases with methanol and ethanol.

	QM		Drude		CHARMM22	
MeOH+He	R_{min}	E_{int}	R_{min}	E_{int}	R_{min}	E_{int}
BIS	3.29	-0.09	3.15	-0.11	3.17	-0.10
180	3.18	-0.10	3.20	-0.08	3.21	-0.08
120	3.48	-0.08	3.15	-0.12	3.16	-0.11
ROH	2.50	-0.13	2.15	-0.12	2.17	-0.12
CH3	3.18	-0.15	3.34	-0.12	3.37	-0.09
MeOH+Ne						
BIS	3.19	-0.35	3.16	-0.24	3.22	-0.20
180	3.11	-0.39	3.21	-0.17	3.25	-0.16
120	3.29	-0.38	3.16	-0.26	3.21	-0.22
ROH	2.37	-0.61	2.09	-0.33	2.21	-0.24
CH3	3.22	-0.53	3.39	-0.24	3.42	-0.19
EtOH+He						
BIS	3.32	-0.13	3.12	-0.15	3.14	-0.16
180	3.18	-0.10	3.18	-0.08	3.18	-0.08
120	3.51	-0.10	3.12	-0.16	3.15	-0.16
ROH	2.52	-0.13	2.15	-0.12	2.16	-0.12

CH3	3.35	-0.12	3.33	-0.10	3.35	-0.10
CH2	3.59	-0.10	3.33	-0.13	3.44	-0.11
EtOH+Ne						
BIS	3.17	-0.58	3.13	-0.35	3.19	-0.32
180	3.11	-0.42	3.21	-0.18	3.23	-0.17
120	3.30	-0.50	3.14	-0.35	3.20	-0.33
ROH	2.36	-0.63	2.08	-0.33	2.21	-0.25
CH3	3.30	-0.58	3.38	-0.21	3.40	-0.21
CH2	3.46	-0.50	3.38	-0.27	3.49	-0.22

Interaction energies in kcal/mol and distances in Å.

Table S5. Free energies of solvation, kcal/mol, using the alcohol oxygen LJ parameters determined from the pure solvent simulations of the alcohols

Alcohol	LRC	Drude		Exp
		ΔGsolv	%diff	ΔGsolv
MeOH	-0.26	-5.20	2	-5.11
EtOH	-0.35	-5.66	13	-5.01
2-PrOH	-0.45	-6.06	27	-4.76
2-BuOH	-0.57	-6.11	34	-4.57
1-PrOH	-0.46	-5.38	11	-4.83
1-BuOH	-0.57	-5.72	21	-4.72
Average			18	

a) The long range correction is estimated for dispersion forces. In the polarizable model. b) Experimental results as reported in reference [92] and c) in reference.[93]

Table S6. Optimized internal parameters

BONDS	Parameter	K_b	b_0	Phase	Reused from
meoh	OH1–CT3	430.0	1.425		
meoh	OH1–H	536.5	0.970		
etoh	OH1–CT2	396.0	1.425		
pro2	OH2–CT1	350.0	1.440		
ANGLES		K_θ	θ_0		
meoh	H–OH1–CT3	58.2	106.00		
meoh	OH1–CT3–HA3	61.0	108.89		
etoh	H–OH1–CT2	49.0	106.00		
etoh	OH1–CT2–HA2	54.0	111.50		
etoh	OH1–CT2–CT3	66.0	112.50		
pro1	OH1–CT2–CT2	66.0	112.50		etoh
pro2	H–OH2–CT1	59.0	108.00		
pro2	OH2–CT1–CT3	66.0	113.10		
pro2	OH2–CT1–HA1	47.00	104.00		
buo2	OH2–CT1–CT2	59.30	113.10		pro2
DIHEDRALS		K_ϕ	n	δ	
meoh	HA3–CT3–OH1–H	0.179	3	0.0	
etoh	H–OH1–CT2–CT3	1.250	1	0.0	

	H–OH1–CT2–CT3	0.350	2	0.0
	H–OH1–CT2–CT3	0.360	3	0.0
etoh	H–OH1–CT2–HA2	0.140	2	0.0
	H–OH1–CT2–HA2	0.130	3	0.0
etoh	OH1–CT2–CT3–HA3	0.175	3	0.0
pro1	H–OH1–CT2–CT2	1.050	1	0.0
	H–OH1–CT2–CT2	0.370	2	0.0
	H–OH1–CT2–CT2	0.340	3	0.0
pro1	CT3–CT2–CT2–OH1	0.200	1	0.0
	CT3–CT2–CT2–OH1	0.410	2	0.0
	CT3–CT2–CT2–OH1	0.400	3	0.0
pro1	HA2–CT2–CT2–OH1	0.270	1	0.0
	HA2–CT2–CT2–OH1	0.050	2	0.0
	HA2–CT2–CT2–OH1	0.120	3	0.0
pro2	H–OH2–CT1–CT3	1.660	1	0.0
	H–OH2–CT1–CT3	0.120	2	0.0
	H–OH2–CT1–CT3	0.340	3	0.0
pro2	HA1–CT1–OH2–H	0.060	1	0.0
	HA1–CT1–OH2–H	0.060	2	0.0
pro2	OH2–CT1–CT3–HA3	0.075	3	0.0

buo1	CT2–CT2–CT2–OH1	0.200	1	0.0	pro1
	CT2–CT2–CT2–OH1	0.410	2	0.0	pro1
	CT2–CT2–CT2–OH1	0.400	3	0.0	pro1
buo2	CT3–CT2–CT1–OH2	0.200	1	0.0	pro1
	CT3–CT2–CT1–OH2	0.410	2	0.0	pro1
	CT3–CT2–CT1–OH2	0.400	3	0.0	pro1
buo2	H–OH2–CT1–CT2	1.660	1	0.0	pro2
	H–OH2–CT1–CT2	0.120	2	0.0	pro2
	H–OH2–CT1–CT2	0.340	3	0.0	pro2
buo2	OH2–CT1–CT2–HA2	0.075	3	0.0	pro2
buo2	CT3–CT1–CT2–CT3	0.200	5	0.0	alkane
	CT3–CT1–CT2–CT3	0.144	4	0.0	alkane
	CT3–CT1–CT2–CT3	0.084	3	0.0	alkane
	CT3–CT1–CT2–CT3	0.126	2	0.0	alkane

K_b, K_θ and K_ϕ are the force constants for the bond, valence angle and dihedral angles terms, respectively, b_0 and q_0 are the bond and valence angle equilibrium parameters, respectively, n is the dihedral angle multiplicity and $_d$ is the dihedral angle phase.

Table S7. Complete set of Lennard-Jones parameters (well depth and radius) utilized in this work in the polarizable model (CHARMM parameter file format)

Atom type	ε, kcal/mol	$R_{min}/2$, Å	1-4 ε, kcal/mol	1-4 $R_{min}/2$, Å
H (OH group)	-0.01	0.4	n/o	n/o
O (for all alcohols)	-0.15	1.765	n/o	n/o
O (alt. set for 1-propanol and 1-butanol)	-0.15	1.74	n/o	n/o
C (CH_3 methanol)	-0.11	2.04	-0.01	1.9
H (CH_3 methanol)	-0.035	1.34	n/o	n/o
C (CH_3 polarizable alkanes)	-0.078	2.04	-0.01	1.9
C (CH_2 polarizable alkanes)	-0.056	2.01	-0.01	1.9
C (CH polarizable alkanes)	-0.032	2.00	-0.01	1.9
H (CH_3 polarizable alkanes)	-0.024	1.34	n/o	n/o
H (CH_2 polarizable alkanes)	-0.035	1.34	n/o	n/o
H (CH polarizable alkanes)	-0.045	1.32	n/o	n/o
NBFIX OH1 OW	-0.18	3.58[a]	n/o	n/o
NBFIX OH2 OW	-0.21	3.60[a]	n/o	n/o

a) R_{min} values for the atom type pair used directly with NBFIX. n/o indicates parameter value is not optimized; the standard ε and $R_{min}/2$ terms are applied to the 1-4 interactions.

Table S8. Scan of partial atomic charges (q) on COH site and its influence on molecular volume and enthalpy of vaporization (percent difference with experiment, Diff)

MeOH #	qH	qLP	qC(O)	V_m, Å^3	Diff(ΔV_m), %	ΔH_{vap}, kcal/mol	Diff(ΔH_{vap}), %	Dipole, D
0	0.34	-0.25	-0.08	65.77	-2.2	8.93	-0.2	2.03
1	0.34	-0.24	-0.10	66.57	-1.0	8.59	-4.0	1.93
2	0.34	-0.23	-0.12	67.56	+0.5	8.24	-8.0	1.84
3	0.34	-0.22	-0.14	68.59	+2.0	7.88	-12.0	1.76
4	0.34	-0.21	-0.16	69.08	+2.7	7.64	-14.6	1.69
10	0.35	-0.25	-0.09	65.62	-2.4	9.26	+3.4	2.01
11	0.35	-0.24	-0.11	66.56	-1.0	8.88	-0.8	1.92
12	0.35	-0.23	-0.13	67.40	+0.2	8.58	-4.1	1.83
13	0.35	-0.22	-0.15	68.31	+1.6	8.24	-8.0	1.76
14	0.35	-0.21	-0.17	69.10	+2.8	7.95	-11.2	1.70
20	0.36	-0.25	-0.10	65.42	-2.7	9.62	+7.5	1.99
21	0.36	-0.24	-0.12	66.13	-1.6	9.31	+4.0	1.91
22	0.36	-0.23	-0.14	67.28	+0.1	8.92	-0.4	1.83
23	0.36	-0.22	-0.16	67.96	+1.1	8.64	-3.5	1.76
24	0.36	-0.21	-0.18	68.55	+2.0	8.34	-6.8	1.71
30	0.37	-0.25	-0.11	65.41	-2.7	10.02	+12.0	1.98
31	0.37	-0.24	-0.13	66.33	-1.3	9.67	+8.0	1.90
32	0.37	-0.23	-0.15	67.10	-0.2	9.31	+4.0	1.83
33	0.37	-0.22	-0.17	67.87	+1.0	9.00	+0.5	1.77
34	0.37	-0.21	-0.19	68.62	+2.1	8.69	-2.9	1.72
40	0.38	-0.25	-0.12	65.55	-2.5	10.39	+16.1	1.97
41	0.38	-0.24	-0.14	66.62	-0.9	10.03	+12.1	1.90
42	0.38	-0.23	-0.16	67.06	-0.3	9.71	+8.5	1.84

43	0.38	-0.22	-0.18	67.66	+0.6	9.43	+5.4	1.78
44	0.38	-0.21	-0.20	67.70	+0.7	9.22	+3.1	1.74
EtOH								
0	0.34	-0.25	0.00	96.42	-0.5	9.77	-3.4	2.18
1	0.34	-0.24	-0.02	96.99	+0.1	9.51	-5.9	2.04
2	0.34	-0.23	-0.04	98.10	+1.2	9.17	-9.3	1.95
3	0.34	-0.22	-0.06	98.63	+1.8	8.90	-12.0	1.82
4	0.34	-0.21	-0.08	99.88	+3.1	8.55	-15.4	1.76
10	0.35	-0.25	-0.01	96.09	-0.9	10.21	+1.0	2.10
11	0.35	-0.24	-0.03	96.70	-0.2	9.90	-2.0	2.02
12	0.35	-0.23	-0.05	97.49	+0.6	9.62	-4.8	1.92
13	0.35	-0.22	-0.07	98.03	+1.1	9.32	-7.9	1.87
14	0.35	-0.21	-0.09	98.50	+1.6	9.12	-9.8	1.75
20	0.36	-0.25	-0.02	95.42	-1.6	10.66	+5.4	2.08
21	0.36	-0.24	-0.04	96.37	-0.6	10.36	+2.5	2.07
22	0.36	-0.23	-0.06	96.60	-0.3	10.10	-0.1	1.93
23	0.36	-0.22	-0.08	97.77	+0.9	9.83	-2.7	1.80
24	0.36	-0.21	-0.10	97.93	+1.0	9.58	-5.2	1.77
30	0.37	-0.25	-0.03	95.15	-1.8	11.18	+10.6	2.13
31	0.37	-0.24	-0.05	95.77	-1.2	10.81	+6.9	2.06
32	0.37	-0.23	-0.07	96.36	-0.6	10.60	+4.9	1.90
33	0.37	-0.22	-0.09	97.28	+0.4	10.28	+1.7	1.84
34	0.37	-0.21	-0.11	97.95	+1.1	9.99	-1.2	1.76
40	0.38	-0.25	-0.04	95.22	-1.8	11.61	+14.8	2.09
41	0.38	-0.24	-0.06	95.71	-1.3	11.32	+11.9	1.99
42	0.38	-0.23	-0.08	96.50	-0.4	11.02	+9.0	1.95
43	0.38	-0.22	-0.10	97.06	+0.1	10.78	+6.6	1.83

44	0.38	-0.21	-0.12	97.40	+0.5	10.52	+4.1	1.79
2-PrOH								
0	0.34	-0.25	0.06	125.82	-1.5	10.33	-4.8	2.19
1	0.34	-0.24	0.04	126.20	-1.2	10.16	-6.4	2.08
2	0.34	-0.23	0.02	127.43	-0.3	9.84	-9.3	1.98
3	0.34	-0.22	0.00	127.55	-0.2	9.66	-11.0	1.89
4	0.34	-0.21	-0.02	129.11	+1.0	9.39	-13.5	1.80
10	0.35	-0.25	0.05	125.35	-1.9	10.85	+0.0	2.17
11	0.35	-0.24	0.03	125.61	-1.7	10.64	-1.9	2.07
12	0.35	-0.23	0.01	126.72	-0.8	10.38	-4.3	1.97
13	0.35	-0.22	-0.01	126.65	-0.9	10.23	-5.7	1.88
14	0.35	-0.21	-0.03	127.71	-0.1	10.03	-7.5	1.80
20	0.36	-0.25	0.04	124.18	-2.8	11.39	+5.0	2.15
21	0.36	-0.24	0.02	125.06	-2.1	11.18	+3.0	2.05
22	0.36	-0.23	0.00	125.81	-1.5	10.96	+1.0	1.96
23	0.36	-0.22	-0.02	126.07	-1.3	10.80	-0.5	1.88
24	0.36	-0.21	-0.04	126.91	-0.7	10.54	-2.9	1.80
30	0.37	-0.25	0.03	123.78	-3.1	11.97	+10.3	2.14
31	0.37	-0.24	0.01	124.75	-2.4	11.71	+7.9	2.04
32	0.37	-0.23	-0.01	125.19	-2.0	11.52	+6.2	1.96
33	0.37	-0.22	-0.03	125.41	-1.9	11.37	+4.8	1.88
34	0.37	-0.21	-0.05	125.60	-1.7	11.19	+3.1	1.81
40	0.38	-0.25	0.02	123.22	-3.6	12.54	+15.6	2.13
41	0.38	-0.24	0.00	123.92	-3.0	12.32	+13.6	2.04
42	0.38	-0.23	-0.02	125.06	-2.1	12.10	+11.5	1.95
43	0.38	-0.22	-0.04	125.30	-1.9	11.95	+10.2	1.88
44	0.38	-0.21	-0.06	125.33	-1.9	11.74	+8.2	1.81

Table S9. Scan of atomic polarizabilities (α) on COH site and its influence on molecular volume and enthalpy of vaporization (percent differences with experiment, Diff)

MeOH #	Cα	Oα	V_m, Å^3	Diff(ΔV_m), %	ΔH_{vap}, kcal/mol	Diff(ΔH_{vap}), %	Dipole, D
0	0.8	0.8	68.37	+1.7	8.34	-6.8	1.83
1	0.8	0.9	67.89	+1.0	8.60	-3.9	1.83
2	0.8	1.0	67.54	+0.5	8.85	-1.1	1.83
3	0.8	1.1	66.69	-0.8	9.22	+3.1	1.83
4	0.8	1.2	66.44	-1.2	9.67	+8.0	1.83
10	0.9	0.8	68.43	+1.8	8.34	-6.8	1.83
11	0.9	0.9	67.66	+0.6	8.63	-3.6	1.83
12	0.9	1.0	67.26	+0.1	8.91	-0.5	1.83
13	0.9	1.1	66.64	-0.9	9.30	+3.9	1.83
14	0.9	1.2	66.50	-1.1	9.66	+8.0	1.83
20	1.0	0.8	67.91	+1.0	8.38	-6.3	1.83
21	1.0	0.9	67.66	+0.6	8.63	-3.5	1.83
22	1.0	1.0	67.22	-0.0	8.92	-0.3	1.83
23	1.0	1.1	66.96	-0.4	9.26	+3.4	1.83
24	1.0	1.2	66.24	-1.5	9.68	+8.2	1.83
30	1.1	0.8	68.08	+1.3	8.40	-6.1	1.83
31	1.1	0.9	67.54	+0.5	8.67	-3.2	1.83
32	1.1	1.0	67.19	-0.1	8.95	+0.0	1.83
33	1.1	1.1	66.37	-1.3	9.35	+4.5	1.83
34	1.1	1.2	66.20	-1.5	9.69	+8.3	1.83
40	1.2	0.8	67.97	+1.1	8.42	-5.9	1.83
41	1.2	0.9	67.36	+0.2	8.70	-2.8	1.83

42	1.2	1.0	66.97	-0.4	8.98	+0.4	1.83
43	1.2	1.1	66.66	-0.8	9.33	+4.2	1.83
44	1.2	1.2	65.87	-2.0	9.78	+9.2	1.83
EtOH							
0	0.8	0.8	98.78	+1.9	9.22	-8.8	1.94
1	0.8	0.9	98.11	+1.2	9.59	-5.1	1.89
2	0.8	1.0	97.00	+0.1	10.10	-0.1	1.89
3	0.8	1.1	96.53	-0.4	10.61	+5.0	1.95
4	0.8	1.2	95.56	-1.4	11.23	+11.1	1.94
10	0.9	0.8	98.50	+1.6	9.24	-8.7	1.93
11	0.9	0.9	97.82	+0.9	9.64	-4.6	1.92
12	0.9	1.0	97.07	+0.2	10.10	-0.1	1.93
13	0.9	1.1	95.95	-1.0	10.61	+5.0	1.92
14	0.9	1.2	95.71	-1.3	11.19	+10.7	1.94
20	1.0	0.8	98.21	+1.3	9.25	-8.5	1.92
21	1.0	0.9	97.61	+0.7	9.64	-4.6	1.94
22	1.0	1.0	96.88	-0.0	10.11	-0.0	1.88
23	1.0	1.1	96.41	-0.5	10.60	+4.8	1.92
24	1.0	1.2	95.42	-1.5	11.24	+11.2	1.90
30	1.1	0.8	98.11	+1.2	9.25	-8.5	1.88
31	1.1	0.9	96.99	+0.1	9.69	-4.1	1.92
32	1.1	1.0	96.68	-0.3	10.11	-0.0	1.93
33	1.1	1.1	95.92	-1.0	10.63	+5.1	1.91
34	1.1	1.2	95.73	-1.2	11.22	+11.0	1.88
40	1.2	0.8	98.22	+1.3	9.25	-8.5	1.92
41	1.2	0.9	97.48	+0.6	9.65	-4.5	1.97
42	1.2	1.0	96.96	+0.0	10.10	-0.1	1.95

43	1.2	1.1	96.44	-0.5	10.59	+4.7	1.90
44	1.2	1.2	95.21	-1.8	11.22	+10.9	1.95
2-PrOH							
0	0.8	0.8	127.43	-0.3	10.06	-7.3	1.97
1	0.8	0.9	126.53	-1.0	10.52	-3.0	1.97
2	0.8	1.0	125.70	-1.6	11.03	+1.7	1.96
3	0.8	1.1	124.98	-2.2	11.53	+6.2	1.96
4	0.8	1.2	124.55	-2.5	12.16	+12.0	1.96
10	0.9	0.8	127.24	-0.4	10.10	-6.9	1.97
11	0.9	0.9	126.26	-1.2	10.59	-2.4	1.97
12	0.9	1.0	125.51	-1.8	11.03	+1.6	1.96
13	0.9	1.1	124.58	-2.5	11.53	+6.3	1.96
14	0.9	1.2	124.31	-2.7	12.19	+12.4	1.96
20	1.0	0.8	127.04	-0.6	10.07	-7.2	1.97
21	1.0	0.9	126.25	-1.2	10.55	-2.8	1.96
22	1.0	1.0	125.70	-1.6	10.96	+1.1	1.96
23	1.0	1.1	125.20	-2.0	11.44	+5.4	1.96
24	1.0	1.2	124.39	-2.7	12.19	+12.4	1.95
30	1.1	0.8	126.88	-0.7	10.06	-7.3	1.97
31	1.1	0.9	126.31	-1.2	10.49	-3.3	1.96
32	1.1	1.0	125.35	-1.9	11.02	+1.6	1.96
33	1.1	1.1	125.01	-2.2	11.52	+6.2	1.96
34	1.1	1.2	124.57	-2.5	12.14	+11.9	1.95
40	1.2	0.8	126.66	-0.9	10.10	-6.9	1.97
41	1.2	0.9	126.08	-1.3	10.56	-2.7	1.96
42	1.2	1.0	126.10	-1.3	10.97	+1.1	1.96
43	1.2	1.1	125.08	-2.1	11.57	+6.6	1.96

44	1.2	1.2	124.61	-2.5	12.16	+12.1	1.95

Table S10. Scan of atomic polarizabilities (α) on alkane CH_3 site and its influence on molecular volume and enthalpy of vaporization (percent differences with experiment, Diff)

EtOH #	$C_{Me}\alpha$	V_m, Å^3	Diff(ΔV_m), %	ΔH_{vap}, kcal/mol	Diff(ΔH_{vap}) %	Dipole, D
0	1.3	97.30	+0.4	10.07	-0.4	1.89
1	1.4	96.95	0.0	10.09	-0.2	1.91
2	1.5	96.85	-0.1	10.09	-0.2	1.92
2-PrOH						
0	1.3	125.88	-1.5	11.01	+1.5	1.94
1	1.4	125.48	-1.8	11.04	+1.7	1.96
2	1.5	126.11	-1.3	10.92	+0.6	1.97

Table S11. Component analysis of five independent hydration free energy calculations.

#	ΔG, kcal/mol	E_{rep}^{solv}, kcal/mol	E_{disp}^{solv}, kcal/mol	E_{elst}^{solv}, kcal/mol	E_{rep}^{gas}, kcal/mol	E_{disp}^{gas}, kcal/mol	E_{elst}^{gas}, kcal/mol
MeOH	additive						
1	-4.82	8.57	-7.36	5.61	0.00	-0.02	11.66
2	-4.81	8.80	-7.39	5.42	0.00	-0.02	11.66
3	-4.86	8.66	-7.41	5.54	0.00	-0.02	11.66
4	-4.66	8.84	-7.40	5.55	0.00	-0.02	11.66
5	-4.76	8.86	-7.41	5.44	0.00	-0.02	11.66
MeOH	polar						
1	-5.22	8.35	-7.42	5.48	0.00	-0.02	11.66
2	-4.68	8.75	-7.41	5.62	0.00	-0.02	11.66

3	-4.80	8.66	-7.39	5.57	0.00	-0.02	11.66
4	-4.94	8.54	-7.41	5.57	0.00	-0.02	11.66
5	-5.08	8.34	-7.40	5.62	0.00	-0.02	11.66
EtOH	additive						
1	-5.09	10.08	-8.35	-12.14	0.31	-0.30	-5.34
2	-5.09	10.04	-8.34	-12.11	0.30	-0.30	-5.33
3	-5.05	10.06	-8.33	-12.07	0.30	-0.30	-5.30
4	-4.82	10.35	-8.37	-12.15	0.30	-0.30	-5.35
5	-5.13	9.94	-8.32	-12.08	0.30	-0.30	-5.33
EtOH	polar						
1	-4.79	11.60	-9.46	-5.95	0.32	-0.34	1.00
2	-5.68	10.85	-9.52	-6.07	0.33	-0.34	0.95
3	-5.46	11.03	-9.44	-6.06	0.32	-0.34	1.02
4	-5.23	11.45	-9.42	-6.23	0.31	-0.34	1.05
5	-5.43	11.24	-9.48	-6.23	0.33	-0.34	0.98
1-PrOH	additive						
1	-5.04	12.26	-10.64	1.02	0.60	-0.59	7.66
2	-4.82	12.48	-10.69	0.98	0.66	-0.57	7.50
3	-5.10	12.15	-10.66	0.77	0.61	-0.57	7.32
4	-4.53	12.66	-10.60	0.99	0.59	-0.57	7.55
5	-5.04	12.34	-10.60	0.94	0.60	-0.58	7.70
1-PrOH	polar	LJ(O)=1.74					
1	-5.44	13.66	-12.00	-2.80	0.68	-0.73	4.35
2	-5.50	13.59	-12.05	-2.61	0.70	-0.73	4.46
3	-5.18	13.99	-12.15	-2.75	0.66	-0.72	4.34
4	-5.30	13.80	-12.02	-2.67	0.67	-0.72	4.46
5	-5.70	13.62	-12.16	-2.81	0.68	-0.72	4.39

1-PrOH	polar	LJ(O)=1.765					
1	-5.03	13.77	-12.13	-2.24	0.73	-0.72	4.42
2	-5.11	13.78	-12.17	-2.27	0.74	-0.73	4.43
3	-4.71	14.05	-12.18	-2.19	0.72	-0.73	4.39
4	-4.70	14.13	-12.18	-2.20	0.74	-0.73	4.43
5	-5.05	13.90	-12.20	-2.27	0.75	-0.74	4.47
1-BuOH	additive						
1	-5.01	14.77	-13.00	-1.57	1.12	-0.97	5.07
2	-5.05	14.56	-12.92	-1.63	1.08	-0.96	4.94
3	-5.01	14.61	-12.91	-1.57	1.05	-0.99	5.09
4	-5.41	14.67	-13.03	-1.66	1.24	-0.95	5.10
5	-4.85	14.76	-12.93	-1.38	1.18	-0.94	5.06
1-BuOH	polar	LJ(O)=1.74					
1	-5.56	16.41	-14.78	-2.92	1.43	-1.28	4.12
2	-5.93	16.43	-14.82	-3.07	1.54	-1.25	4.19
3	-5.34	16.86	-14.95	-2.99	1.41	-1.26	4.13
4	-5.75	16.57	-14.85	-3.18	1.38	-1.27	4.18
5	-5.80	16.46	-14.79	-3.09	1.46	-1.26	4.18
1-BuOH	polar	LJ(O)=1.765					
1	-5.29	16.56	-14.89	-2.63	1.43	-1.25	4.15
2	-5.08	16.78	-14.85	-2.60	1.51	-1.26	4.16
3	-4.99	16.56	-14.82	-2.47	1.39	-1.25	4.13
4	-5.43	16.38	-14.81	-2.52	1.58	-1.27	4.17
5	-4.97	16.86	-14.86	-2.54	1.52	-1.24	4.16
2-PrOH	additive						
1	-4.78	12.32	-10.22	-48.71	0.72	-0.64	-41.91
2	-4.56	12.56	-10.23	-48.69	0.74	-0.64	-41.89

3	-4.62	12.34	-10.15	-48.60	0.75	-0.64	-41.90
4	-4.71	12.32	-10.14	-48.66	0.75	-0.64	-41.88
5	-4.73	12.26	-10.15	-48.70	0.74	-0.64	-41.96
2-PrOH	polar						
1	-5.64	13.81	-11.70	-23.25	0.74	-0.73	-15.52
2	-5.35	13.81	-11.67	-23.05	0.71	-0.73	-15.54
3	-5.91	13.47	-11.66	-23.30	0.70	-0.73	-15.55
4	-5.77	13.78	-11.79	-23.28	0.73	-0.73	-15.53
5	-5.36	14.07	-11.74	-23.20	0.72	-0.73	-15.50
2-BuOH	additive						
1	-4.75	14.68	-12.56	-28.62	1.51	-1.10	-22.17
2	-4.39	14.89	-12.45	-28.60	1.52	-1.10	-22.19
3	-4.55	14.91	-12.53	-28.61	1.57	-1.10	-22.15
4	-4.67	14.66	-12.53	-28.53	1.55	-1.10	-22.17
5	-4.06	15.23	-12.49	-28.54	1.53	-1.10	-22.17
2-BuOH	polar						
1	-5.59	16.71	-14.50	-16.34	1.56	-1.28	-8.82
2	-5.55	16.45	-14.43	-16.18	1.46	-1.26	-8.81
3	-5.77	16.36	-14.49	-16.09	1.63	-1.27	-8.81
4	-5.23	16.86	-14.38	-16.18	1.65	-1.28	-8.84
5	-5.58	16.71	-14.50	-16.26	1.60	-1.27	-8.81

Energies in kcal/mol. Polarizable results based on the LJ parameters optimized based on the pure solvent properties of the alcohols.