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Supporting Information for

Structural properties of methanol - water binary mixtures within the quantum cluster equilibrium model

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Table S1 The a_{mf} - b_{xv} parameter pairs for the methanol – water binary mixture with inclusion of cubic *c8* clusters.

	B3LYP-D3			M06-2X		
x(MeOH)	a_{mf} / Jm^3mol^{-1}	b_{xv}	MAE[a] / dm^3 mol^{-1}	a_{mf} / Jm^3mol^{-1}	b_{xv}	MAE[a] / dm^3 mol^{-1}
0.0000	0.1868	1.1206	2.14E-05	0.1858	1.1207	2.45E-05
0.0588	0.1987	1.1045	3.47E-05	0.1977	1.1042	3.47E-05
0.1232	0.2115	1.0878	6.57E-05	0.2105	1.0871	6.33E-05
0.1942	0.2258	1.0728	9.97E-05	0.2246	1.0714	9.64E-05
0.2726	0.2421	1.0615	1.44E-04	0.2409	1.0595	1.42E-04
0.3599	0.2602	1.0531	1.76E-04	0.2595	1.0505	1.77E-04
0.4575	0.2822	1.0481	2.24E-04	0.2801	1.0456	2.27E-04
0.5675	0.3070	1.0465	2.67E-04	0.3018	1.0435	2.75E-04
0.6922	0.3345	1.0479	3.24E-04	0.3288	1.0446	3.42E-04
0.8350	0.3670	1.0520	3.83E-04	0.3538	1.0487	4.16E-04
0.9175	0.3876	1.0542	4.38E-04	0.3760	1.0540	4.77E-04
1.0000	0.4102	1.0583	5.30E-04	0.3962	1.0605	5.42E-04

[a] Mean absolute error between calculated and experimental isobars

Table S2 The a_{mf} - b_{xv} parameter pairs for the methanol – water binary mixture with cubic *c8* clusters excluded from the cluster set.

	B3LYP-D3			M06-2X		
x(MeOH)	a_{mf} / Jm^3mol^{-1}	b_{xv}	MAE[a] / dm^3 mol^{-1}	a_{mf} / Jm^3mol^{-1}	b_{xv}	MAE[a] / dm^3 mol^{-1}
0.0000	0.1870	1.1216	1.32E-05	0.1860	1.1220	1.40E-05
0.0588	0.1989	1.1051	1.86E-05	0.1978	1.1049	2.45E-05
0.1232	0.2116	1.0881	4.60E-05	0.2105	1.0874	1.93E-05
0.1942	0.2258	1.0726	7.81E-05	0.2246	1.0714	7.94E-05
0.2726	0.2412	1.0604	1.22E-04	0.2400	1.0592	1.25E-04
0.3599	0.2607	1.0518	1.54E-04	0.2583	1.0494	1.61E-04
0.4575	0.2819	1.0470	2.01E-04	0.2799	1.0443	2.13E-04
0.5675	0.3069	1.0453	2.46E-04	0.3035	1.0427	2.66E-04
0.6922	0.3354	1.0472	3.05E-04	0.3296	1.0439	3.37E-04
0.8350	0.3690	1.0529	3.71E-04	0.3572	1.0486	4.19E-04
0.9175	0.3878	1.0563	4.30E-04	0.3744	1.0540	4.81E-04
1.0000	0.4102	1.0583	5.30E-04	0.3962	1.0605	5.42E-04

[a] Mean absolute error between calculated and experimental isobars

Table S3 Gibbs free energy of interaction per hydrogen bond and cluster populations at T = 298K for x(MeOH) = 0.0 (neat water), 0.36, and 1.0 (neat MeOH), computed with B3LYP-D3.

Name of cluster	ΔG^{298} / H-bond	Populations (%) at x=0.0	at x=0.3599	at x=1.0
m1	0.00	0.00	0.01	0.04
w1	0.00	0.03	0.02	0.00
m2	16.89	0.00	0.00	0.00
m1w1	12.06	0.00	0.00	0.00
w1m1	11.67	0.00	0.00	0.00
w2	11.06	0.01	0.00	0.00
m3r	6.57	0.00	0.00	0.01
m2w1r	5.49	0.00	0.00	0.00
m1w2r	5.76	0.00	0.00	0.00
w3r	5.99	0.01	0.00	0.00
m4r	4.49	0.00	0.07	1.21
m3w1r	3.33	0.00	0.14	0.00
m2w2r	4.20	0.00	0.07	0.00
m1w3r	2.82	0.00	0.17	0.00
w4r	3.68	0.35	0.09	0.00
m5r	4.30	0.00	1.59	46.06
m4w1r	3.85	0.00	1.17	0.00
m3w2r	4.25	0.00	0.89	0.00
m2w3r	4.51	0.00	0.79	0.00
m1w4r	4.58	0.00	0.94	0.00
w5r	4.15	3.83	0.63	0.00
m6r	5.99	0.00	1.04	50.24
m5w1r	5.92	0.00	3.42	0.00
m4w2r	5.55	0.00	1.89	0.00
m3w3r	5.10	0.00	1.36	0.00
m2w4r	5.46	0.00	0.81	0.00
m1w5r	4.96	0.00	0.52	0.00
w6r	5.07	5.59	0.59	0.00
m7r	6.09	0.00	0.03	2.43
m6w1r	5.80	0.00	0.02	0.00
m5w2r	6.14	0.00	0.01	0.00
m4w3r	5.79	0.00	0.01	0.00
m3w4r	6.07	0.00	0.00	0.00
m2w5r	6.54	0.00	0.02	0.00
m1w6r	5.33	0.00	0.07	0.00
w7r	7.06	3.52	0.24	0.00

m6w1bc	5.30	0.00	0.01	0.00
m5w2bc	4.73	0.00	0.01	0.00
m4w3bc	4.68	0.00	0.00	0.00
m3w4bc	5.18	0.00	0.01	0.00
m2w5bc	4.38	0.00	0.03	0.00
m1w6bc	4.07	0.00	0.03	0.00
w7bc	3.81	0.31	0.02	0.00
m4w1s	8.68	0.00	0.00	0.00
m3w2s	8.65	0.00	0.00	0.00
m2w3s	7.99	0.00	0.00	0.00
m1w4s	7.13	0.00	0.00	0.00
w5s	7.09	0.00	0.00	0.00
m5w1s	6.93	0.00	0.01	0.00
m4w2s	6.96	0.00	0.01	0.00
m3w3s	5.93	0.00	0.00	0.00
m2w4s	5.88	0.00	0.00	0.00
m1w5s	6.11	0.00	0.00	0.00
w6s	6.22	0.03	0.00	0.00
m8w1s	5.54	0.00	0.04	0.00
m7w2s	5.73	0.00	0.05	0.00
m6w3s	5.92	0.00	1.29	0.00
m5w4s	6.19	0.00	0.52	0.00
m4w5s	6.05	0.00	0.14	0.00
m3w6s	6.07	0.00	1.31	0.00
m2w7s	5.75	0.00	0.36	0.00
m1w8s	5.38	0.00	0.34	0.00
w9s	5.49	11.93	0.34	0.00
m10w1s	6.08	0.00	0.12	0.00
m9w2s	7.55	0.00	0.31	0.00
m8w3s	7.81	0.00	0.14	0.00
m7w4s	7.57	0.00	0.09	0.00
m6w5s	7.32	0.00	0.18	0.00
m5w6s	7.40	0.00	0.13	0.00
m4w7s	7.56	0.00	0.65	0.00
m3w8s	7.18	0.00	0.24	0.00
m2w9s	6.35	0.00	0.26	0.00
m1w10s	6.10	0.00	0.15	0.00
w11s	6.23	5.38	0.06	0.00
m3w1r-m1	6.78	0.00	0.00	0.00
m5r-w1	6.88	0.00	0.00	0.00
m3w1r-2m1(1,1)	9.44	0.00	0.00	0.00

m3w1r-2m1(1,3)	10.12	0.00	0.00	0.00
m2·mw·m2	3.98	0.00	0.10	0.00
mw·mw·m2	4.79	0.00	0.17	0.00
mw·mw·mw	4.38	0.00	0.09	0.00
w2·mw·mw	3.76	0.00	0.13	0.00
mw·w2·mw	4.78	0.00	0.05	0.00
w2·mw·w2	3.99	0.00	0.12	0.00
w2·w2·w2	4.43	0.65	0.07	0.00
mw·w2·w2	4.32	0.00	0.06	0.00
m2·w2·mw	5.21	0.00	0.26	0.00
m2·w2·m2	4.45	0.00	0.05	0.00
m5w3c	2.19	0.00	1.72	0.00
m4w4c	1.43	0.00	9.19	0.00
m3w5c	1.33	0.00	30.46	0.00
m2w6c	1.68	0.00	11.84	0.00
m1w7c	1.73	0.00	19.11	0.00
w8c	2.26	68.37	3.03	0.00
m4w4c-m1	2.96	0.00	0.05	0.00

Figure S1 Number of clusters corresponding to a specific molar fraction x(MeOH).

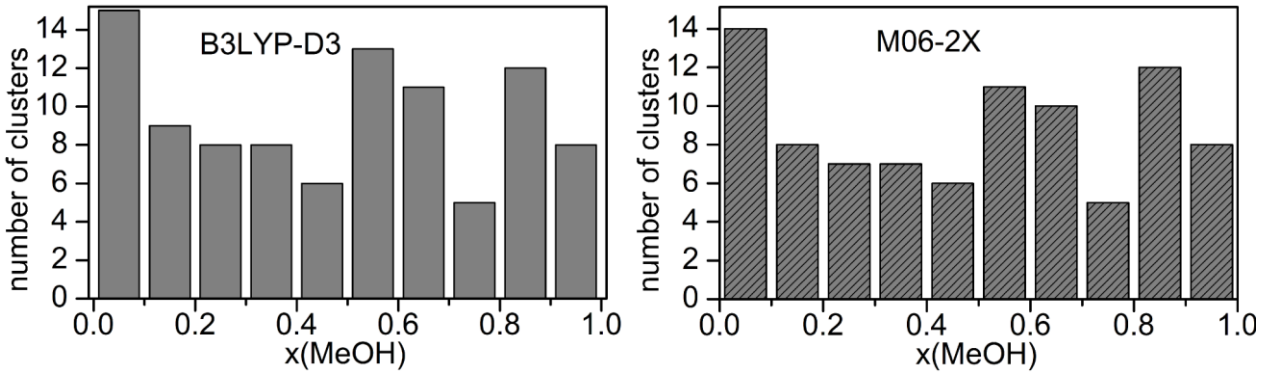


Figure S2 Comparison of B3LYP-D3/QZVP//TZVP and M06-2X/aug-cc-pVTZ interaction energies with MP2(fc)-CP/6-311++G(d,p) results[37] for the methanol ring clusters.

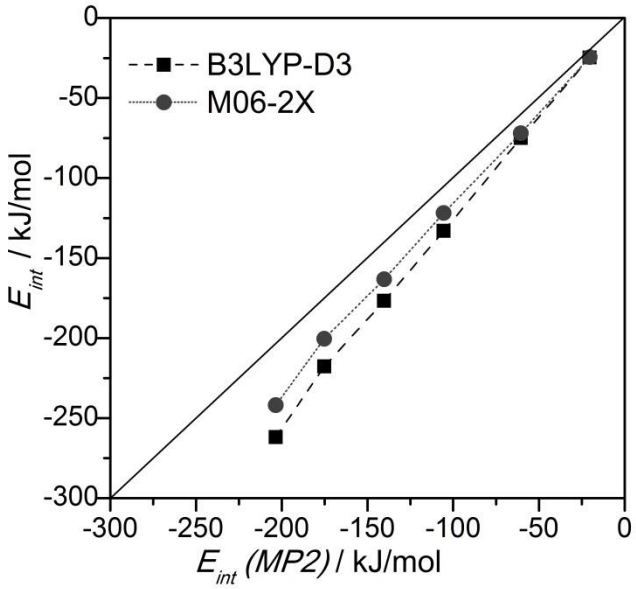


Figure S3 Comparison of B3LYP-D3/QZVP//TZVP with M06-2X/aug-cc-pVTZ interaction energies.

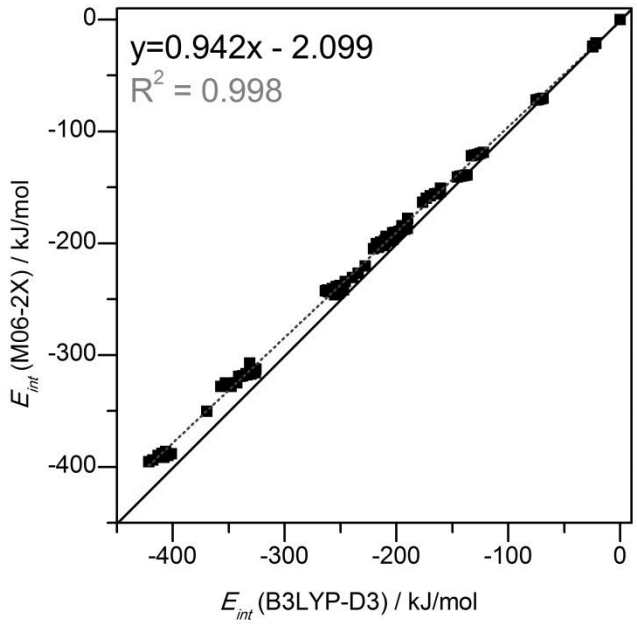


Figure S4 Population (%) of ■…pure methanol clusters, ●…pure water cluster, ▲…mixed MeOH–water clusters at 298 K based on M06-2X calculations.

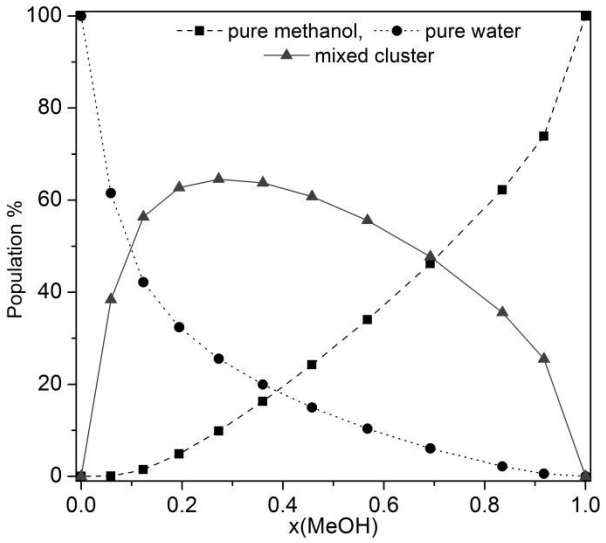


Figure S5 Plot of individual cluster distributions including *c8* cubic clusters (for clarity, only clusters > 10% are shown) at 298K based on M06-2X calculations.

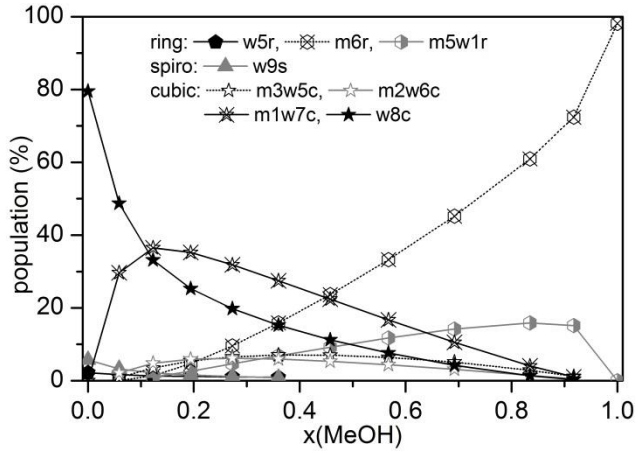
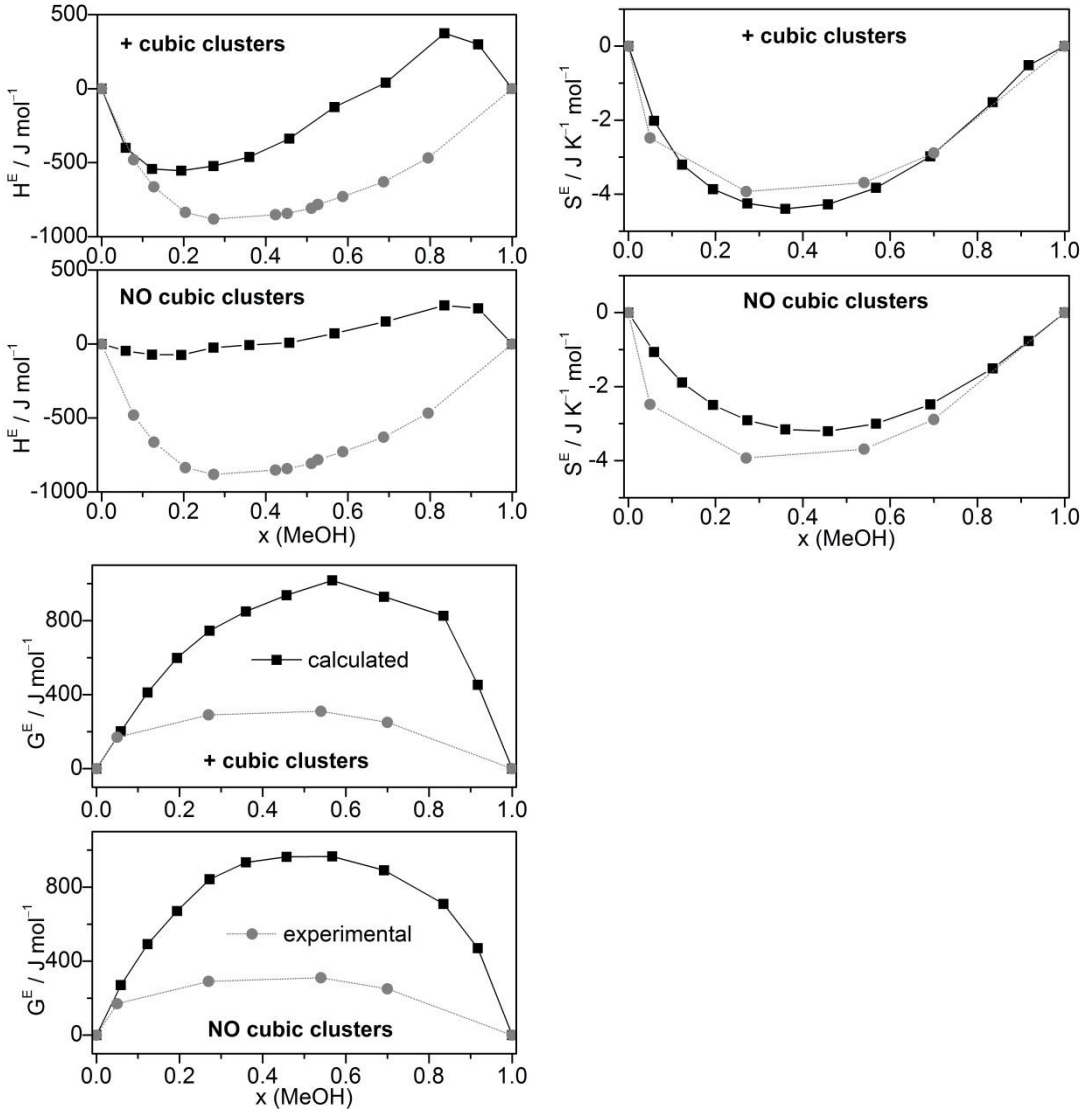


Figure S6 Comparison of experimental and calculated excess enthalpies H^E, entropies S^E, and Gibbs free energies G^E of mixing, based on M06-2X calculations, for the full cluster set as well as the cluster set without the cubic *c8* clusters at different molar ratios.[a]



[a]experimental values for H^E are taken from refs. [89-90], those for S^E and G^E from ref. [56].

Figure S7 Comparison of experimental[92-93] and B3LYP-D3 calculated excess heat capacities of mixing C_p^E at T = 298.15K.

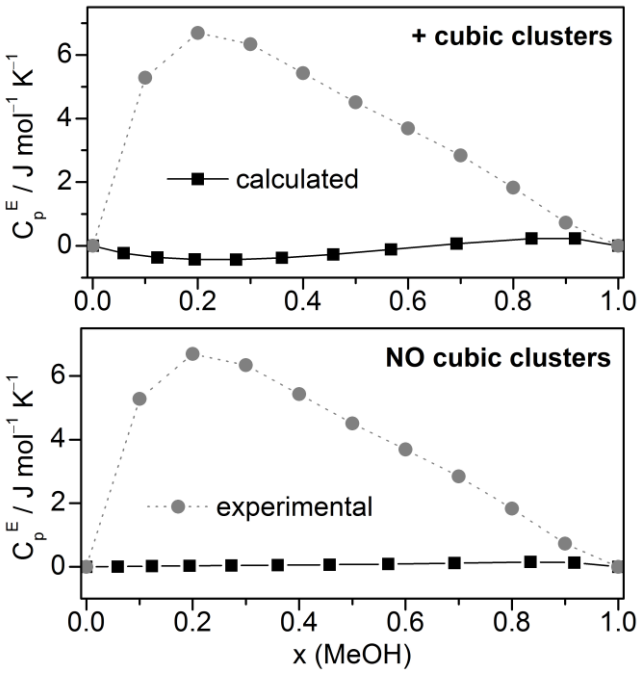


Figure S8 Comparison of M06-2X calculated and experimental heat capacities C_p [67, 92-93] and excess heat capacities of mixing C_p^E [92-93] at T = 298.15K.