Supporting Information

Calculation of Vapor – Liquid – Liquid Equilibria at Atmospheric and High Pressures

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Table S1. Coefficients of the NRTL equation for the systems (1) – (7) and (12) – (31).

	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	α_{12}	α_{13}	α_{23}
1	631.44	90.340	2299.3	1200.0	465.26	830.95	0.4902	0.2660	0.5169
2	793.08	-233.95	1146.1	1072.8	581.23	780.49	0.1269	0.2386	0.5044
3	608.01	22.563	2898.8	1319.5	579.92	701.31	0.4033	0.2436	0.4993
4	577.07	80.315	2775.7	1240.2	678.50	706.59	0.4794	0.2567	0.4982
5	590.73	69.080	1820.0	1826.6	363.40	369.11	0.4692	0.2991	0.5020
6	597.54	51.796	2290.0	1362.1	440.80	527.20	0.4387	0.2997	0.5345
7	1589.3	97.527	1765.4	2166.1	257.42	805.01	0.3629	0.2451	0.5465
12	-152.96	451.28	25.036	619.45	478.62	1249.1	0.0500	0.4034	0.3646
13	1276.2	277.79	1838.4	13784.0	714.16	-473.72	0.4526	0.1797	0.1005
14	997.19	333.69	1368.5	178.70	991.90	-529.28	0.5686	0.3424	0.2882
15	1114.8	-432.35	1254.2	399.07	31.394	9.7892	0.1266	0.4872	0.1500
16	584.88	67.730	1156.2	392.58	-51.932	1886.9	0.4611	0.5183	0.7795
17	-86.830	428.72	599.12	1512.8	160.00	788.61	0.0500	0.2912	0.4939
18	256.17	159.20	853.68	1560.0	163.64	911.93	0.2674	0.2893	0.4690
19	2027.7	-1206.3	1078.5	645.19	147.53	389.52	0.0501	0.2958	0.3432
20	569.12	333.77	1077.7	141.25	-492.40	1147.7	0.5040	0.3105	0.1861
21	595.26	53.217	975.19	636.82	-302.29	547.51	0.4400	0.4353	0.0447
22	-497.57	653.55	177.51	1484.7	246.40	1169.8	0.0500	0.2228	0.4908
23	981.30	-269.28	155.18	1299.9	1.2087	261.45	0.3759	0.1746	0.5477
24	2123.4	-1265.8	1435.6	1106.2	1813.3	-855.68	0.0500	0.1915	0.1170
25	-709.42	1039.8	220.78	1410.4	-1588.4	4256.5	0.1023	0.3648	0.0502
26	-140.69	351.83	233.53	1248.3	771.67	2027.0	0.0576	0.4302	0.3088
27	180.82	-167.15	443.35	852.96	702.14	1262.8	0.1500	0.4099	0.3754
28	1291.8	-453.67	1124.0	149.37	-87.138	220.85	0.4258	0.2741	0.4932
29	264.76	-48.577	218.09	890.50	422.37	1235.7	0.1000	0.5566	0.3130
30	578.17	-321.11	226.69	868.21	478.74	1047.7	0.0500	0.5606	0.3576
31	-889.99	1221.9	204.64	1574.4	183.01	827.98	0.0509	0.2226	0.5429

Table S2. Mean deviations of the VLLE prediction for water – ethanol – two hydrocarbons systems. The results of calculation for the NRTL-VLL model were taken from work[14].

hydrocarbons		NRTL-VLL	TC-L	TC-D	PSRK	LCVM
cyclohexane isooctane (8)	ΔXaq	0.0083	0.0123	0.0108	0.0121	0.0143
	$\Delta Xorg$	0.0077	0.0337	0.0349	0.0190	0.0226
	ΔY	0.0077	0.0143	0.0116	0.0163	0.0156
	ΔT	0.15	0.55	0.42	1.17	1.49
cyclohexane toluene (9)	ΔXaq	0.0078	0.0155	0.0188	0.0139	0.0172
	$\Delta Xorg$	0.0088	0.0384	0.0586	0.0434	0.0529
	ΔY	0.0098	0.0204	0.0185	0.0216	0.0201
	ΔT	0.24	1.04	0.31	0.93	1.06
cyclohexane n-heptane (10)	ΔXaq	0.0109	0.0109	0.0086	0.0159	0.0170
	$\Delta Xorg$	0.0075	0.0224	0.0253	0.0141	0.0172
	ΔY	0.0121	0.0178	0.0158	0.0223	0.0216
	ΔT	0.17	0.54	0.32	1.09	1.37
n-hexane toluene (11)	ΔXaq	0.0075	0.0121	0.0160	0.0118	0.0148
	$\Delta Xorg$	0.0097	0.0400	0.0511	0.0348	0.0424
	ΔY	0.0099	0.0268	0.0241	0.0296	0.0287
	ΔT	0.33	1.56	0.89	1.68	1.93

Table S3. Mean deviations of the VLE prediction for water – ethanol – hydrocarbon systems and their binary subsystems.

		system						
		1	2	3	4	5	6	7
water alcohol hydrocarbon	Δy_1	0.0109	0.0087	0.0083	0.0167	0.0094	0.0036	0.0367
	Δy_2	0.0238	0.0168	0.0082	0.0166	0.0112	0.0034	0.0327
	Δy_3	0.0283	0.0214	0.0106	0.0154	0.0136	0.0025	0.0314
	$\Delta T/ref$	0.54 [23]	1.07 [24]	0.26 [25]	0.78 [1]	0.15 [26]	0.09 [27]	1.5 [28]
water alcohol	Δy	0.0061	0.0103	0.0025	0.0013	0.0015	0.0016	0.0343
	ΔT	0.31 [S1]	0.34 [S1]	0.19 [S1]	0.03 [S1]	0.04 [S1]	0.06 [S1]	1.25 [S2]
alcohol hydrocarbon	Δy	0.0145	0.0087	0.0059	-	0.0065	0.0063	0.0163
	ΔT	0.72 [S3]	0.22 [S4]	0.57 [S5]	-	0.59 [S6]	0.20 [S7]	1.24 [S8]

Table S4. Mean deviations of the VLE prediction for systems 12, 24 and their binary subsystems.

system					
12			24		
water ethanol ethyl acetate	Δy_1 Δy_2 Δy_3 ΔT	0.0096 0.0119 0.0048 0.34 [5]	water ethanol ethyl benzoate	Δy_1 Δy_2 Δy_3 ΔP	0.0131 0.0137 0.0033 2.98 [39]
water ethanol	Δy ΔT	0.0020 0.09 [S1]	water ethanol	Δy ΔT	0.0035 0.20 [S1]
ethanol ethyl acetate	Δy ΔT	0.0048 0.24 [S9]	ethanol ethyl benzoate	Δy ΔP	0.0170 11.6 [39]

Table S5. Mean deviations of the VLE prediction for systems 12-23 and 25-31 and their binary subsystems.

	system					
	13		14		15	
Δy ΔT	water n-butanol	0.0158 0.64 [S2]	water n-propanol	0.0131 0.60 [S10]	water ethanol	0.0031 0.19 [S1]
Δy ΔT	n-butanol n-butyl acetate	0.0045 0.34 [S11]	n-propanol n-pentanol	0.0073 0.97 [S2]	ethanol n-butanol	0.0008 0.24 [S12]
	system					
	16		17		18	
Δy ΔT	water ethanol	0.0011 0.07 [S1]	water isopropanol	0.0050 0.11 [S13]	water n-propanol	0.0064 0.29 [S10]
Δy ΔT	ethanol *sec*-butanol	0.0067 0.38 [S14]	isopropanol diisopropyl ether	0.0156 0.35 [S15]	n-propanol dipropyl ether	0.0024 0.30 [S16]
	system					
	19		20		21	
Δy ΔT	water ethanol	0.0033 0.19 [S1]	water acetone	0.0017 0.13 [S17]	water ethanol	0.0016 0.06 [S1]
Δy ΔT	ethanol diethyl ether	0.0206 1.42 [S18]	- -	- -	ethanol MEK	0.0051 0.43 [S19]
	system					
	22		23		25	
Δy ΔT	water *sec*-butanol	0.0103 0.58 [S20]	water methanol	0.0061 0.32 [S21]	n-pentanol n-pentyl acetate	0.0041 1.01 [S22]
Δy ΔP	*sec*-butanol methyl isobutyl ketone	0.0035 0.64 [S23]	- -	- -	- -	- -
	system					
	26		27		28	
Δy $\Delta T/\Delta P$	water n-butanol	0.0146 0.57 K [S2]	methyl acetate methyl propionate	0.0106 0.29 K [6]	PGME PGMEA	0.0092 1.75 % [4]
Δy ΔT	n-butanol n-butyl propionate	0.0144 0.42 [S24]	- -	- -	- -	- -
	system					
	29		30		31	
Δy ΔT	water isopropanol	0.0067 0.22 [S13]	water isopropanol	0.0062 0.16 [S13]	water isopropanol	0.0044 0.29 [S13]
Δy	isopropanol	0.0095	isopropanol	0.0116	isopropanol	0.0039

$\Delta P/\Delta T$	isopropyl acetate	1.52 % [42]	ethyl acetate	1.02 % [43]	isopropyl propionate	0.30 K [44]

Table S6. Mean deviations of the VLLE prediction for miscellaneous systems. The experimental data refers to constant temperature.

system (no)		NRTL-VLL	TC-L	TC-D	PSRK	LCVM
methyl propionate methanol water (23)	ΔXaq	0.0209	0.0128	0.0127	0.0129	0.0188
	$\Delta Xorg$	0.0208	0.0827	0.0688	0.0388	0.0437
	ΔY	0.0366	0.0608	0.0555	0.0563	0.0543
	ΔP	2.64	5.44	4.64	0.97	4.29
water ethanol ethyl benzoate (24)	ΔXaq	0.0084	0.0401	0.0467	0.0545	0.0570
	$\Delta Xorg$	0.0143	0.0664	0.0791	0.0868	0.0816
	ΔY	0.0148	0.0493	0.0603	6.24	0.0431
	ΔP	3.92	6.40	8.91	0.537	2.20
n-pentanol n-pentyl acetate water (25)	ΔXaq	0.0021	0,0013	0,0018	0.0035	0.0074
	$\Delta Xorg$	0.0121	0,0174	0,0102	0.0406	0.1081
	ΔY	0.0166	0.0070	0,0070	0.0084	0.0106
	ΔP	3.59	3,14	3,00	3.13	1.54
n-butanol n-butyl propionate water (26)	ΔXaq	0.0012	0.0023	0.0027	0.0067	0.0179
	$\Delta Xorg$	0.0139	0.0259	0.0289	0.0211	0.0819
	ΔY	0.0127	0.0193	0.0190	0.0259	0.0214
	ΔP	1.68	3.37	3,23	5.24	3.84
methyl acetate methyl propionate water (27)	ΔXaq	0.0032	0.0023	0.0027	0.0044	0.0149
	$\Delta Xorg$	0.0109	0.0153	0.0212	0.0275	0.0466
	ΔY	0.0239	0.0276	0.0277	0.0336	0.0350
	ΔP	1.18	0.97	0.91	4.12	6.97
water PGME PGMEA (28)	ΔXaq	0.0121	0.0289	0.0467	-	-
	$\Delta Xorg$	0.0061	0.0347	0.1168	-	-
	ΔY	0.0183	0.0163	0.0566	-	-
	ΔP	2.45	0.63	4.85	-	-
isopropanol isopropyl acetate water (29)	ΔXaq	0.0104	0.0043	0.0069	0.0057	0.0202
	$\Delta Xorg$	0,0115	0.0153	0.0377	0.0289	0.0665
	ΔY	0.0096	0.0103	0.0114	0.0095	0.0201
	ΔP	1.14	2.44	2,89	1.18	5.54
isopropanol ethyl acetate water (30)	ΔXaq	0.0104	0.0054*	0.0070	0.0061*	0.0225*
	$\Delta Xorg$	0.0100	0.0127	0.0415	0.0375	0.0597
	ΔY	0.0128	0.0141	0.0158	0.0183	0.0185
	ΔP	1.74	1.18	1,68	4.44	8.02
isopropyl propionate isopropanol water (31)	ΔXaq	0.0129	0.0039	0.0069	0.0062	0.0124
	$\Delta Xorg$	0.0122	0,0492	0.0630	0.0221	0.0304
	ΔY	0.0228	0,0414	0.0387	0.0291	0.0305
	ΔP	1.21	10.89	10.41	0.76	4.54

* - model did not calculate the VLLE for all the experimental points.

Table S7. Parameters of the NRTL equation for the systems (32) – (37).

	system					
	32	33	34	35	36	37
A_{12}	2204.8	791.17	1975.7	2355.9	-94.593	4790.7
A_{21}	144.66	6361.7	1111.4	9846.0	518.83	129.63
A_{13}	2033.2	975.08	1462.9	-251.06	-700.95	920.00
A_{31}	2134.3	341.43	4034.8	993.19	3146.0	413.37
A_{14}	-	-	724.16	2060.2	1791.1	14950.
A_{41}	-	-	-227.43	-292.60	2943.2	1865.7
A_{23}	311.85	7763.1	1062.7	5977.6	-939.78	4292.4
A_{32}	1071.8	3291.4	-566.82	773.77	-816.21	14990.
A_{24}	-	-	-277.35	869.76	27.148	14996.
A_{42}	-	-	1908.1	-617.48	5316.7	8464.1
A_{34}	-	-	9998.5	9985.9	4471.6	2981.9
A_{43}	-	-	3071.1	3939.5	12526.0	2517.9
α_{12}	0.3085	0.2475	0.6779	0.4280	0.0501	0.1958
α_{13}	0.2902	0.5902	0.3261	0.2645	0.6557	0.1353
α_{14}	-	-	0.1242	0.1678	0.0750	0.1013
α_{23}	0.3098	0.3678	0.1209	0.3061	0.3150	0.1806
α_{24}	-	-	0.1200	0.2948	0.1316	0.0601
α_{34}	-	-	0.4013	0.3712	0.0995	0.2076

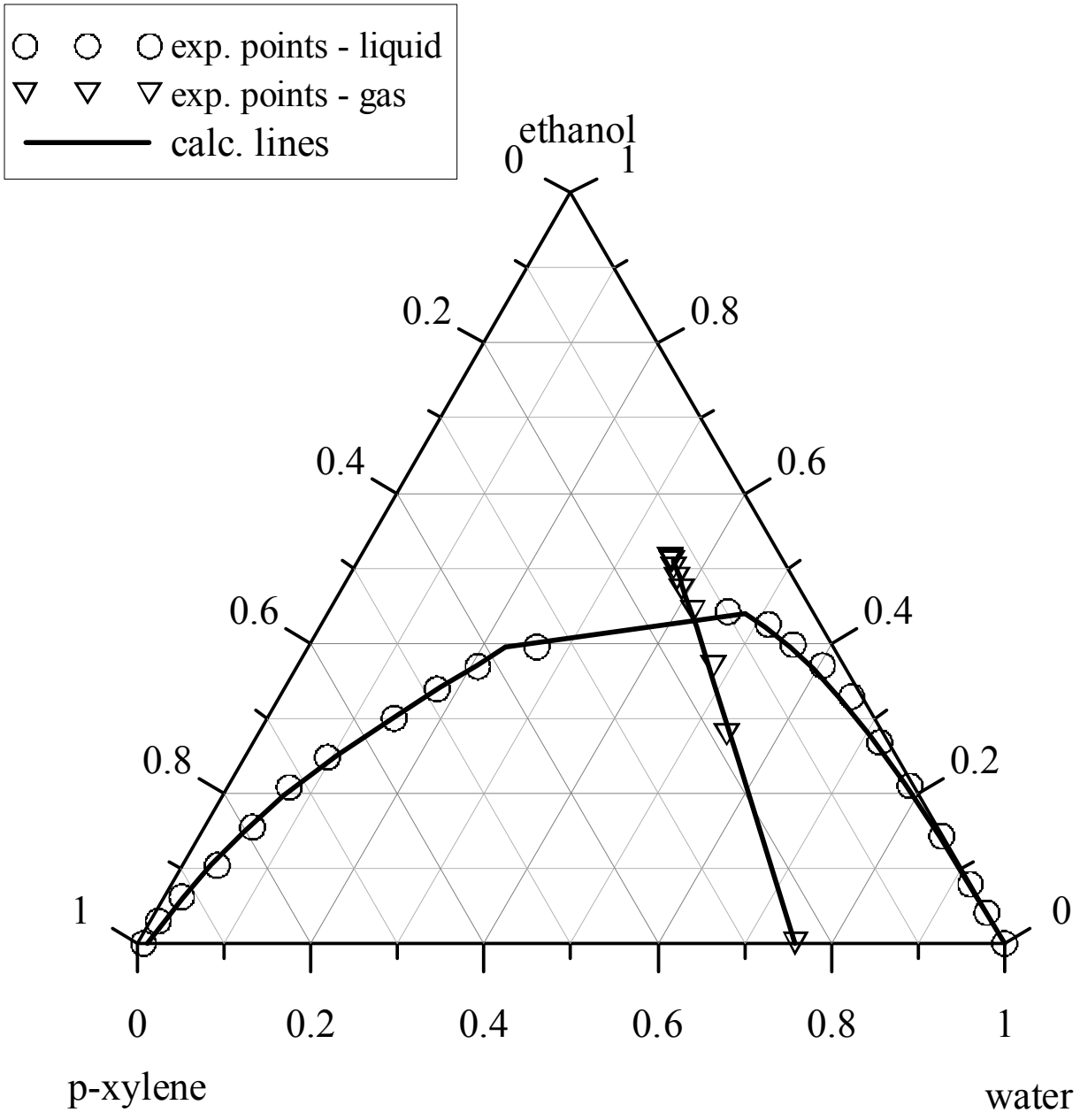

Figure S1. Experimental and calculated VLLE for water – ethanol – p-xylene system.

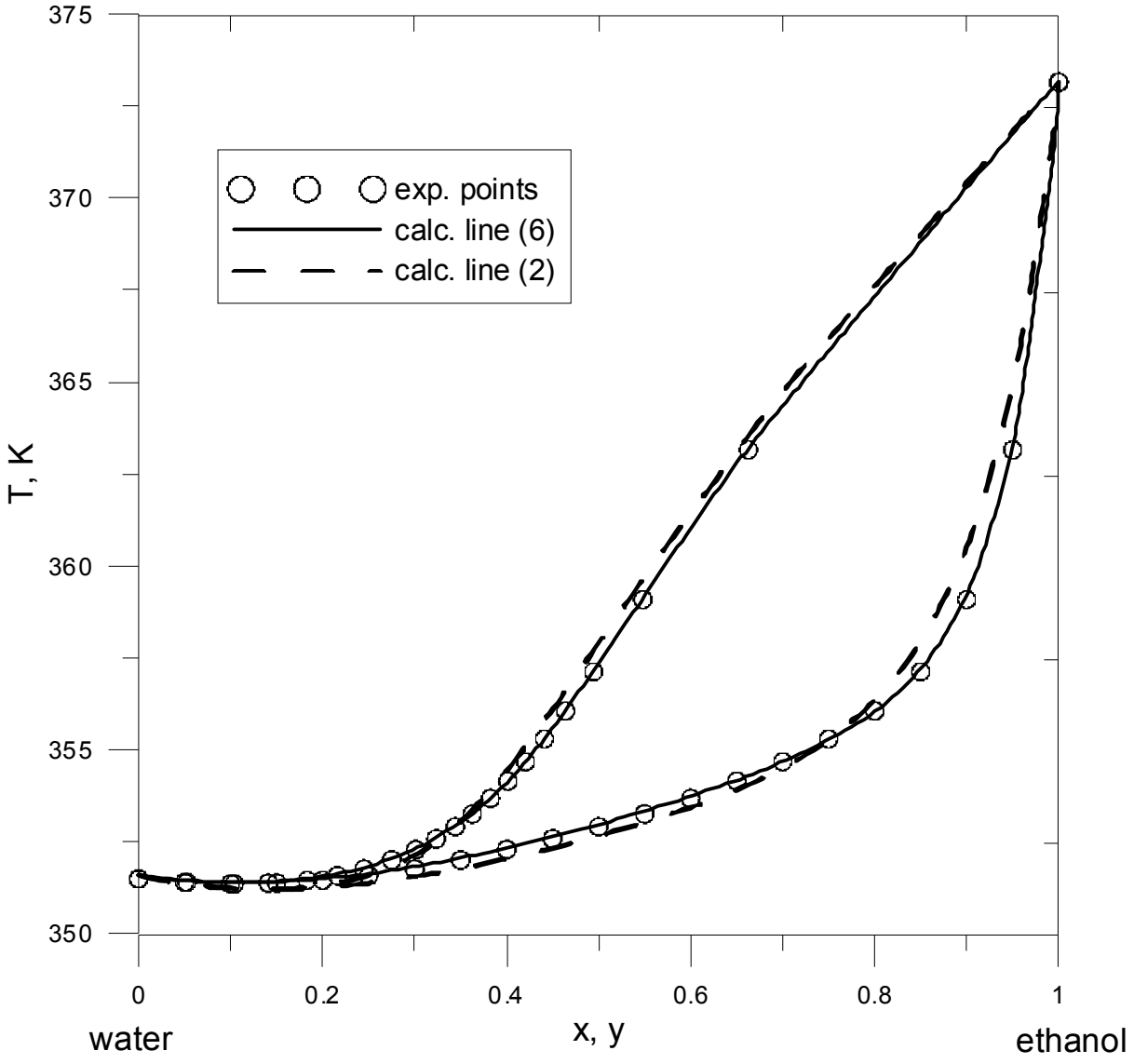

Figure S2. Experimental and calculated VLE for the water – ethanol mixture. Calculations were performed using parameters for ternary systems 2 and 6.

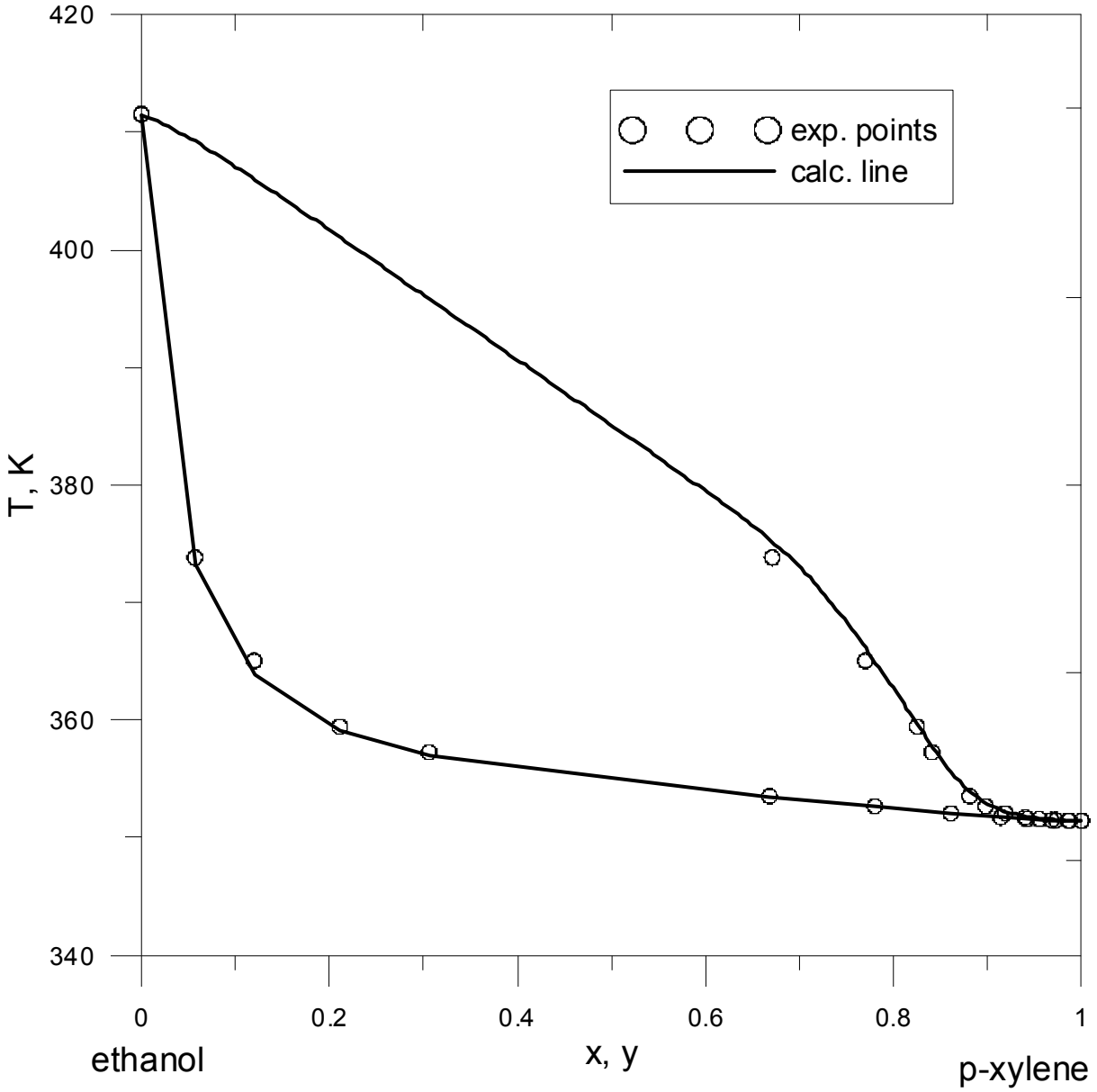

Figure S3. Experimental and calculated VLE for the ethanol - p-xylene mixture. Calculations were performed using parameters for ternary systems 6.

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