

supporting information for

**Synthesis of Methyl Benzoate Intensified by *p*-Toluenesulfonic Acid-
based Deep Eutectic Solvents**

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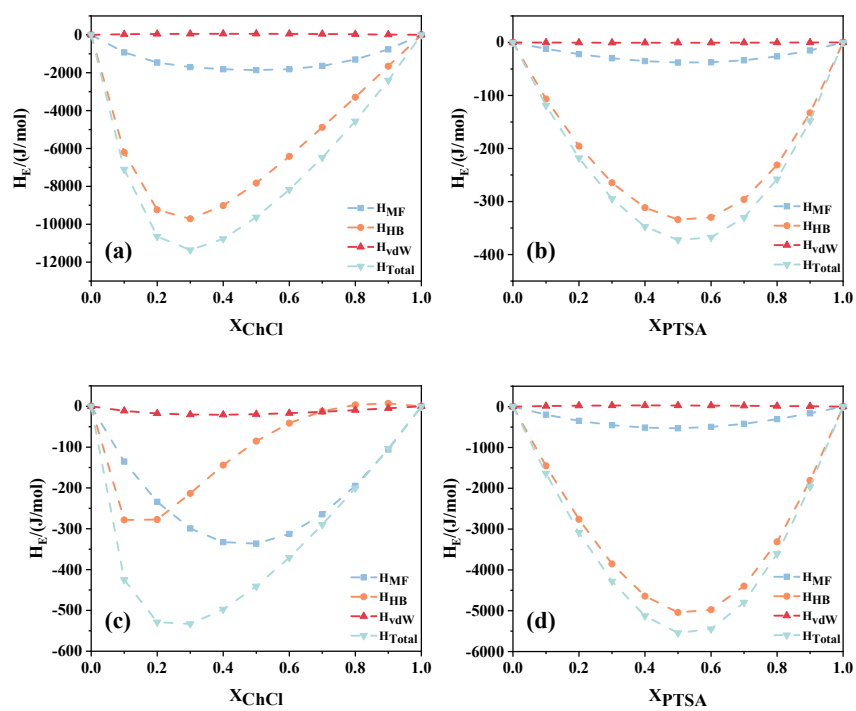


Figure S1. Excess enthalpy for the binary mixtures of ChCl (1) + BA (2) (a), PTSA (1) + BA (2) (b), ChCl (1) + MT (2) (c), and PTSA (1) + MT (2) (d) calculated by the COSMO-RS model at 298.15 K

Table S1. The activity of the components at 343.15K based on the UNIFAC method

	t (min)	BA	MT	MB	Water
343.15K	0	0.370676	0.681917	0	0
	5	0.326909	0.645186	0.071496	0.104937
	10	0.289625	0.61313	0.135137	0.193017
	15	0.274395	0.599825	0.161862	0.228704
	20	0.2615	0.588463	0.184821	0.258804
	25	0.20945	0.541671	0.280574	0.37945
	30	0.187726	0.521695	0.321987	0.429508
	50	0.15461	0.49073	0.386727	0.505649
	70	0.11542	0.453291	0.465781	0.595729
	90	0.099019	0.437371	0.499621	0.633498
	120	0.089291	0.42786	0.519892	0.655933
	180	0.066283	0.405166	0.568419	0.709143
	240	0.067396	0.40627	0.566053	0.706563
	300	0.058967	0.397892	0.584014	0.726115
K			18.07		

Table S2. The activity of the components at 353.15K based on the UNIFAC method

	t (min)	BA	MT	MB	Water
353.15K	0	0.370963	0.684604	0	0
	5	0.270558	0.598097	0.169007	0.238285
	10	0.206362	0.540234	0.285917	0.386766
	15	0.184624	0.520183	0.327027	0.436607
	20	0.166933	0.503697	0.361033	0.477057
	25	0.139622	0.477957	0.414468	0.539371
	30	0.131931	0.470646	0.429716	0.556903
	50	0.088848	0.4292098	0.516657	0.655102
	70	0.068045	0.408926	0.559509	0.7026
	90	0.05081	0.391997	0.595401	0.742035
	120	0.051424	0.392602	0.594118	0.74063
	180	0.040354	0.381676	0.617336	0.766012
	240	0.029985	0.3714056	0.639199	0.789832
	300	0.022146	0.3636190	0.655798	0.807875
K			65.79		

Table S3. The activity of the components at 363.15K based on the UNIFAC method

	t (min)	BA	MT	MB	Water
363.15K	0	0.372911	0.685397	0	0
	5	0.288427	0.612118	0.140691	0.201721
	10	0.163778	0.498381	0.368023	0.489432
	15	0.147739	0.483288	0.398856	0.52592
	20	0.131919	0.468309	0.429585	0.561842
	25	0.116645	0.453764	0.459540	0.596477
	30	0.098535	0.436418	0.495406	0.637508
	50	0.070638	0.409508	0.551329	0.700684
	70	0.03848	0.378247	0.616685	0.773583
	90	0.03223	0.372146	0.629485	0.787774
	120	0.022764	0.362895	0.648920	0.809282
	180	0.017064	0.357317	0.660652	0.822246
	240	0.012314	0.352665	0.670443	0.833057
	300	0.00961	0.350016	0.676022	0.839214
	K			168.67	

Table S4. The activity of the components at 1:1(MT/BA) based on the UNIFAC method

	t (min)	BA	MT	MB	Water
	0	0.529034	0.534071	0	0
	5	0.385887	0.392539	0.214295	0.4336865
	10	0.345269	0.351058	0.278861	0.556596
	15	0.316528	0.321477	0.325407	0.643787
	20	0.29102	0.29512	0.367250	0.721405
	25	0.273805	0.277302	0.395747	0.773945
MT/BA	30	0.220200	0.253903	0.433436	0.843155
1:1	50	0.211422	0.212834	0.500382	0.965687
	70	0.183463	0.184175	0.547765	1.052454
	90	0.166440	0.166861	0.576688	1.105576
	120	0.163955	0.164344	0.580912	1.113350
	180	0.139688	0.13993	0.622168	1.189548
	240	0.140851	0.141093	0.620192	1.185884
	300	0.130225	0.130504	0.638242	1.219400
K			45.79		

Table S5. The activity of the components at 3:1(MT/BA) based on the UNIFAC method

	t (min)	BA	MT	MB	Water
	0	0.284804	0.762384	0	0
	5	0.211361	0.70358	0.135440	0.151085
	10	0.182656	0.679803	0.191827	0.208520
	15	0.132802	0.637362	0.294491	0.306485
	20	0.126029	0.63148	0.308906	0.319641
	25	0.115441	0.622228	0.331664	0.340140
MT/BA	30	0.092372	0.601824	0.382201	0.384552
3:1	50	0.054659	0.56773	0.467611	0.456527
	70	0.043349	0.557325	0.493892	0.477989
	90	0.034078	0.548732	0.515663	0.495548
	120	0.026741	0.541892	0.533036	0.509426
	180	0.017858	0.533563	0.554238	0.526209
	240	0.012646	0.528652	0.566763	0.536048
	300	0.008953	0.525162	0.575676	0.543016
K			66.48		

Table S6. The activity of the components at 50 wt% based on UNIFAC method

	t (min)	BA	MT	MB	Water
	0	0.371467	0.68414	0	0
	5	0.279794	0.605317	0.153550	0.218077
	10	0.206878	0.539725	0.285729	0.387082
	15	0.17504	0.510273	0.346148	0.460094
	20	0.170901	0.506408	0.35412	0.469565
	25	0.158357	0.494646	0.378439	0.498238
DES	30	0.159021	0.49527	0.377147	0.496723
dosage 50	50	0.086979	0.426355	0.52117	0.661137
wt%	70	0.076739	0.41638	0.54221	0.684537
	90	0.078916	0.418505	0.537726	0.67956
	120	0.079388	0.418965	0.536755	0.678481
	180	0.077029	0.416663	0.541612	0.683873
	240	0.079388	0.418965	0.536755	0.678481
	300	0.079388	0.418965	0.536755	0.678481
K			10.95		

Table S7. The activity of the components at 150 wt% based on UNIFAC method

	t (min)	BA	MT	MB	Water
	0	0.371266	0.684325	0	0
	5	0.315919	0.637221	0.091029	0.132511
	10	0.281458	0.607159	0.150316	0.213637
	15	0.203263	0.5368	0.292197	0.394785
	20	0.164863	0.501157	0.365495	0.482736
	25	0.136699	0.474571	0.420692	0.547024
DES	30	0.120922	0.45952	0.452119	0.583002
dosage 150	50	0.057577	0.398026	0.58166	0.727650
wt%	70	0.050386	0.390948	0.596673	0.744127
	90	0.037506	0.378225	0.623705	0.773690
	120	0.018533	0.359388	0.663823	0.817373
	180	0.014363	0.355234	0.672685	0.826998
	240	0.014004	0.354876	0.67345	0.827828
	300	0.012567	0.353443	0.676508	0.831149
K			126.60		

Table S8. The activity of the components at 343.15K based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
	0	0.231324	0.614832	0	0
	5	0.196731	0.592142	0.091211	0.079679
	10	0.168646	0.571463	0.167586	0.150160
	15	0.157554	0.562639	0.198399	0.179646
	20	0.148340	0.554992	0.224302	0.204925
	25	0.112846	0.522405	0.326999	0.309889
	30	0.098863	0.507958	0.368908	0.355062
343.15K	50	0.078521	0.484929	0.431613	0.425426
	70	0.056012	0.456053	0.503826	0.510930
	90	0.047106	0.443431	0.533360	0.547391
	120	0.041970	0.435793	0.550675	0.569192
	180	0.030257	0.417271	0.591010	0.621255
	240	0.030809	0.418181	0.589080	0.618721
	300	0.026662	0.411245	0.603649	0.637949
K			35.12		

Table S9. The activity of the components at 353.15K based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
353.15K	0	0.240539	0.621395	0	0
	5	0.161759	0.563954	0.198832	0.186118
	10	0.116286	0.522493	0.320613	0.313736
	15	0.101826	0.507556	0.360725	0.358424
	20	0.090424	0.495054	0.392909	0.395320
	25	0.073479	0.475136	0.441735	0.453170
	30	0.068854	0.469389	0.455289	0.469650
	50	0.044165	0.436078	0.529519	0.563387
	70	0.032999	0.419308	0.564277	0.609441
	90	0.024126	0.405077	0.592506	0.647939
	120	0.024436	0.405588	0.591510	0.646564
	180	0.018913	0.396295	0.609373	0.671434
	240	0.013869	0.387476	0.625901	0.694825
	300	0.010140	0.380737	0.638264	0.712565
K			117.80		

Table S10. The activity of the components at 363.15K based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
363.15K	0	0.250731	0.625006	0	0
	5	0.182120	0.575041	0.161237	0.154299
	10	0.092606	0.490436	0.385632	0.401784
	15	0.082220	0.478560	0.413058	0.435206
	20	0.072246	0.466622	0.439739	0.468486
	25	0.062874	0.454886	0.465140	0.500898
	30	0.052094	0.440702	0.494782	0.539668
	50	0.036211	0.418292	0.539385	0.600039
	70	0.019005	0.391631	0.589128	0.670470
	90	0.015800	0.386348	0.598579	0.684248
	120	0.011033	0.378287	0.612753	0.705158
	180	0.008213	0.373398	0.621208	0.717775
	240	0.005892	0.369304	0.628206	0.728302
	300	0.004583	0.366966	0.632170	0.734299
K			276.00		

Table S11. The activity of the components at 1:1(MT/BA) based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
	0	0.409790	0.427426	0	0
	5	0.271177	0.345022	0.234862	0.315022
	10	0.235039	0.318139	0.298672	0.413953
	15	0.210434	0.298091	0.342921	0.486564
	20	0.189296	0.279559	0.381524	0.552820
	25	0.175415	0.266648	0.407206	0.598496
MT/BA	30	0.157671	0.249190	0.440456	0.659635
1:1	50	0.127806	0.217036	0.497629	0.770410
	70	0.107885	0.193313	0.536747	0.850638
	90	0.096197	0.178404	0.560120	0.900419
	120	0.094519	0.176197	0.563504	0.907744
	180	0.078513	0.154247	0.596163	0.980042
	240	0.079264	0.155316	0.594614	0.976546
	300	0.072459	0.145486	0.608708	1.008603
K			58.24		

Table S12. The activity of the components at 3:1(MT/BA) based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
	0	0.166254	0.722473	0	0
	5	0.116262	0.679117	0.161771	0.121325
	10	0.097968	0.660833	0.223563	0.170728
	15	0.067969	0.627154	0.328623	0.259154
	20	0.064073	0.622383	0.342654	0.271419
	25	0.058072	0.614829	0.364462	0.290710
MT/BA	30	0.045376	0.597958	0.411431	0.333232
3:1	50	0.025773	0.569131	0.486472	0.404132
	70	0.020180	0.560180	0.508522	0.425710
	90	0.015696	0.552735	0.526431	0.443501
	120	0.012211	0.546774	0.540496	0.457643
	180	0.008069	0.539477	0.557394	0.474838
	240	0.005679	0.535153	0.567240	0.484962
	300	0.004002	0.532071	0.574185	0.492151
K			132.70		

Table S13. The activity of the components at 50 wt% based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
	0	0.241011	0.620788	0	0
	5	0.168662	0.568702	0.181809	0.169369
	10	0.116653	0.521916	0.320409	0.313901
	15	0.095622	0.499885	0.378913	0.379636
	20	0.092966	0.496947	0.386421	0.388295
	25	0.085028	0.487938	0.409027	0.414688
DES	30	0.085444	0.488418	0.407838	0.413287
dosage 50	50	0.043146	0.433621	0.533223	0.568981
wt%	70	0.037608	0.425398	0.550375	0.591637
	90	0.038776	0.427155	0.546743	0.586810
	120	0.039029	0.427535	0.545955	0.585764
	180	0.037764	0.425632	0.549892	0.590993
	240	0.039029	0.427535	0.545955	0.585764
	300	0.039029	0.427535	0.545955	0.585764
K			19.17		

Table S14. The activity of the components at 150 wt% based on the COSMO-RS method

	t (min)	BA	MT	MB	Water
	0	0.240822	0.621031	0.000000	0.000000
	5	0.196278	0.590439	0.110688	0.100575
	10	0.169896	0.570073	0.178228	0.165746
	15	0.114206	0.519836	0.326817	0.320796
	20	0.089119	0.493006	0.397057	0.400449
	25	0.071719	0.472388	0.447278	0.460243
DES	30	0.062352	0.460485	0.474900	0.494218
dosage 150	50	0.027570	0.410112	0.581787	0.633715
wt%	70	0.023914	0.404133	0.593487	0.649825
	90	0.017515	0.393291	0.614213	0.678801
	120	0.008447	0.377015	0.644182	0.721733
	180	0.006511	0.373389	0.650677	0.731204
	240	0.006345	0.373076	0.651236	0.732021
	300	0.005683	0.371821	0.653466	0.735289
K			227.39		

Table S15. The experimental and calculated MB yield at different temperatures based on the UNIFAC method

	MB yield					
	343.15K		353.15K		363.15K	
	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}
0	0	0	0	0	0	0
5	0.1128	0.1018	0.2623	0.1777	0.2205	0.2128
10	0.21	0.1887	0.4336	0.3121	0.5536	0.3659
15	0.25	0.2633	0.4922	0.4168	0.597	0.4803
20	0.284	0.3277	0.5401	0.5001	0.6399	0.5679
25	0.4225	0.3840	0.6144	0.5675	0.6814	0.6370
30	0.4809	0.4328	0.6354	0.6226	0.7307	0.6919
50	0.5706	0.5766	0.7536	0.7654	0.8068	0.8285
70	0.6778	0.6662	0.811	0.84	0.8947	0.8955
90	0.723	0.7234	0.8587	0.8812	0.9118	0.9303
120	0.7499	0.7744	0.857	0.9128	0.9377	0.9555
180	0.8138	0.8169	0.8877	0.9335	0.9533	0.9705
240	0.8107	0.8301	0.9165	0.9377	0.9663	0.9735
300	0.8342	0.8340	0.9383	0.9389	0.9737	0.9738

Table S16. The experimental and calculated MB yield at different ratios based on the UNIFAC method

	MB yield			
	1:1		3:1	
	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}
0	0	0	0	0
5	0.2688	0.1449	0.2464	0.1752
10	0.3456	0.2517	0.3448	0.3118
15	0.4	0.3334	0.5186	0.4200
20	0.4483	0.3977	0.5425	0.5076
25	0.4809	0.4495	0.58	0.5787
30	0.5237	0.4918	0.6623	0.6378
50	0.599	0.6026	0.7986	0.7909
70	0.6519	0.6620	0.8399	0.8701
90	0.6841	0.696	0.8739	0.9127
120	0.6888	0.7249	0.9009	0.9437
180	0.7347	0.7462	0.9337	0.9626
240	0.7325	0.7518	0.953	0.9658
300	0.7526	0.7532	0.9667	0.9666

Table S17. The experimental and calculated MB yield at different DES dosages based on the UNIFAC method

	MB yield			
	DES 50 wt%		DES 150 wt%	
	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}
0	0	0	0	0
5	0.2389	0.1711	0.1436	0.1793
10	0.433	0.3003	0.2341	0.3149
15	0.5188	0.3996	0.4424	0.4203
20	0.53	0.4771	0.5461	0.5045
25	0.564	0.5378	0.6227	0.5724
30	0.5622	0.5858	0.6658	0.6283
50	0.7591	0.6984	0.8401	0.7746
70	0.7873	0.7456	0.86	0.8527
90	0.7813	0.7657	0.8957	0.8972
120	0.78	0.7768	0.9484	0.9323
180	0.7865	0.7810	0.96	0.9573
240	0.78	0.7813	0.961	0.9633
300	0.78	0.7813	0.965	0.9648

Table S18. The experimental and calculated MB yield at different temperatures based on the COSMO-RS method

	MB yield					
	343.15K		353.15K		363.15K	
	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}
0	0	0	0	0	0	0
5	0.1128	0.1039	0.2623	0.1852	0.2205	0.2149
10	0.21	0.1911	0.4336	0.3212	0.5536	0.3644
15	0.25	0.2645	0.4922	0.4252	0.597	0.4740
20	0.284	0.3274	0.5401	0.5067	0.6399	0.5577
25	0.4225	0.3819	0.6144	0.5720	0.6814	0.6235
30	0.4809	0.4289	0.6354	0.6252	0.7307	0.6760
50	0.5706	0.5668	0.7536	0.7633	0.8068	0.8087
70	0.6778	0.6530	0.811	0.8363	0.8947	0.8772
90	0.723	0.7094	0.8587	0.8778	0.9118	0.9153
120	0.7499	0.7612	0.857	0.9109	0.9377	0.9456
180	0.8138	0.8082	0.8877	0.9344	0.9533	0.9669
240	0.8107	0.8247	0.9165	0.9401	0.9663	0.9720
300	0.8342	0.8307	0.9383	0.9413	0.9737	0.9732

Table S19. The experimental and calculated MB yield at different ratios based on the COSMO-RS method

	MB yield			
	1:1		3:1	
	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}
0	0	0	0	0
5	0.2688	0.1433	0.2464	0.1780
10	0.3456	0.2501	0.3448	0.3131
15	0.4	0.3324	0.5186	0.4184
20	0.4483	0.3971	0.5425	0.5024
25	0.4809	0.4493	0.58	0.5707
30	0.5237	0.4918	0.6623	0.6266
50	0.599	0.6028	0.7986	0.7745
70	0.6519	0.6620	0.8399	0.8536
90	0.6841	0.6962	0.8739	0.8991
120	0.6888	0.7243	0.9009	0.9344
180	0.7347	0.7451	0.9337	0.9590
240	0.7325	0.7506	0.953	0.9650
300	0.7526	0.7520	0.9667	0.9662

Table S20. The experimental and calculated MB yield at different DES dosages based on the COSMO-RS method

	MB yield			
	DES 50wt%		DES 150wt%	
	Y_{exp}	Y_{cal}	Y_{exp}	Y_{cal}
0	0	0	0	0
5	0.2389	0.1720	0.1436	0.1808
10	0.433	0.2993	0.2341	0.3137
15	0.5188	0.3957	0.4424	0.4155
20	0.53	0.4702	0.5461	0.4957
25	0.564	0.5285	0.6227	0.5606
30	0.5622	0.5750	0.6658	0.6138
50	0.7591	0.6867	0.8401	0.7548
70	0.7873	0.7363	0.86	0.8323
90	0.7813	0.7591	0.8957	0.8789
120	0.78	0.7729	0.9484	0.9185
180	0.7865	0.7789	0.96	0.9507
240	0.78	0.7798	0.961	0.9606
300	0.78	0.7798	0.965	0.9636