Supporting Information

Deep deterpenation of citrus essential oils intensified by in situ formation of a deep eutectic solvent in associative extraction

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Table S1. Three COSMO-RS interactions of ions with linalool and limonene

Ion	Interaction energies (Linalool)			Interaction energies (Limonene)		
	HB	Misfit	VDW	HB	Misfit	VDW
Ch^+	-18.066	14.278	-29.097	-0.391	17.929	-30.726
TEA^+	-1.295	14.483	-37.383	-0.047	13.630	-38.677
$TPrA^+$	-1.132	15.918	-52.957	-0.041	13.981	-54.286
TBA^+	-0.951	17.779	-69.260	-0.036	14.983	-70.732
$TPeA^+$	-0.988	19.650	-85.550	-0.036	16.097	-87.186
Cl^-	-75.605	13.753	-11.898	0	38.071	-12.003
Br^-	-43.041	18.058	-12.906	0	34.575	-13.573

Table S2. Influence of mass ratio of TBAC/linalool on the performance of associative extraction at the settling temperature of 45 ºC

Mass ratio (TBAC/linalool)	β_{LM}	β_{LN}	S_{LN}	η_{LN} (%)
1.81	0.403	5.10	12.7	47.3
3.99	0.235	9.33	39.7	68.6
9.97	0.185	10.85	58.6	88.1
14.77	0.144	11.94	82.9	92.0
20.03	0.141	13.12	93.0	94.9
24.84	0.143	12.98	90.8	95.8
29.62	0.148	12.72	85.9	96.6

Table S3. Influence of settling temperature on the performance of associative extraction with the mass ratio of TBAC/linalool fixed at 20

Settling temperature (ºC)	β_{LM}	β_{LN}	S_{LN}	η_{LN} (%)
30	0.136	14.13	103.9	96.0
35	0.138	13.80	100.0	95.7
40	0.140	13.45	96.1	95.4
45	0.141	13.12	93.0	94.9
50	0.143	12.80	89.5	94.6
55	0.144	12.48	86.7	94.4

Table S4. Interaction of limonene with various organic solvents

Organic solvent	Interaction energies (kJ/mol)			
	HB	Misfit	VDW	Total
Octane	0	3.340	-41.005	-37.222
Heptane	0	3.344	-41.016	-37.229
Hexane	0	3.352	-41.027	-37.233
Pentane	0	3.366	-41.045	-37.237
Ethylbenzene	0	6.955	-40.828	-33.457
1,4-dimethylbenzene	0	6.885	-40.802	-33.501
1,3-dimethylbenzene	0	6.901	-40.804	-33.486
1,2-dimethylbenzene	0	7.156	-40.792	-33.221
Toluene	0	7.534	-40.786	-32.840
Benzene	0	8.429	-40.753	-31.915
Dipropylcarbonate	0	8.662	-39.497	-30.435
Diethylcarbonate	0	10.091	-39.300	-28.817
Dimethylcarbonate	-0.00059	12.780	-38.785	-25.620
Propylacetate	-0.00017	9.595	-39.563	-29.572
Ethylacetate	-0.00012	10.583	-39.453	-28.478
Methylacetate	-0.00038	12.038	-39.208	-26.782

Table S5. Performance of the first-step of reextraction with different ratios of n-hexane to extract E at 30 ºC

Ratio	n-Hexane phase		DES phase		β'_{LM}	β'_{LN}	S'_{LM}	k[e] (g/g)	δ_{LN}[f] (%)	η'_{LM} (%)
	w_{LM}^{HEX}[a]	w_{LN}^{HEX}[b]	w_{LM}^{DES}[c]	w_{LN}^{DES}[d]						
0.2	0.3352	0.0015	0.0384	0.0437	8.73	0.034	256.8	0.5055	1.14	74.6
0.4	0.2256	0.0014	0.0213	0.0442	10.59	0.032	330.9	0.2920	1.50	86.1
0.6	0.1692	0.0013	0.0150	0.0442	11.28	0.029	389.0	0.2041	2.37	90.1
0.8	0.1354	0.0012	0.0115	0.0442	11.77	0.027	435.9	0.1570	2.80	92.6
1.0	0.1126	0.0011	0.0095	0.0443	11.85	0.025	474.0	0.1273	3.13	93.9

[a] w_{LM}^{HEX}: the mass fraction of limonene in n-hexane phase

[b] w_{LN}^{HEX}: the mass fraction of linalool in n-hexane phase

[c] w_{LM}^{DES}: the mass fraction of limonene in DES phase

[d] w_{LN}^{DES}: the mass fraction of linalool in DES phase

[e] Extraction capability for n-hexane: $k = \frac{\text{Amount of limonene extracted}}{\text{Amount of n-hexane used}}$ (g/g)

[f] Loss ratio of linalool: $\delta_{LN} = \frac{\text{Amount of extracted linalool in n-hexane phase}}{\text{Initial amount of linalool in extract E}} \times 100\%$

Table S6. Performance of n-hexane as anti-extractant for multistage cross-flow reextraction

Stage no.	n-Hexane phase		DES phase		β'_{LM}	β'_{LN}	S'_{LM}	k (g/g)	δ_{LN} (%)	η'_{LM} (%)
	w_{LM}^{HEX}	w_{LN}^{HEX}	w_{LM}^{DES}	w_{LN}^{DES}						
1	0.3352	0.0015	0.0384	0.0437	8.73	0.034	256.8	0.5055	1.14	74.6
2	0.1177	0.0009	0.0120	0.0447	9.81	0.020	490.5	0.1336	0.47	69.6
3	0.0389	0.0006	0.0039	0.0450	9.97	0.013	766.9	0.0407	0.28	67.8
4	0.0133	-	0.0013	0.0452	10.23	-	-	0.0135	-	67.6
5	0.0065	-	-	0.0453	-	-	-	0.0065	-	-

Table S7. Second-step of reextraction performance with different ratios of water/R1 (fixed n-hexane/R1 ratio of 0.2)

Mass ratio (water/R1)	Mass fraction of linalool (%)	
	In aqueous phase	In hexane phase
0.2	3.49	1.73
0.4	2.67	3.93
0.6	1.96	6.64
0.8	1.21	10.50
1.0	0.82	12.74
1.2	0.59	14.02
1.5	0.30	15.98
2.0	0.17	16.81

Table S8. Second-step of reextraction performance with different ratios of n-hexane/R1 (fixed water/R1 ratio of 2)

Mass ratio (n-hexane/R1)	Mass fraction of linalool (%)	
	In aqueous phase	In hexane phase
0.2	0.17	16.81
0.4	0.12	9.43
0.6	0.10	6.58
0.8	0.09	5.05
1.0	0.08	4.12

Table S9. Operation conditions of deep deterpenation process for citrus essential oil

Process	Extractant	Time			Vacuum Pressure	Temperature			Mass ratio
		Stirring	Settling	Vacuum distillation		Stirring	Settling	Vacuum distillation	
Extraction	TBAC	2 h	3 h	-	-	65°C	30°C	-	20:1 TBAC:linalool
First-step reextraction	n-hexane	2 h	3 h	-	-	30°C	30°C	-	0.2:1 n-hexane:E
Second reextraction	n-hexane	2 h	3 h	-	-	25°C	25°C	-	1:2:1 n-hexane:water:R1
Vacuum distillation (V1&V2)	-	-	-	20 min	3 kPa	-	-	30°C	-
Vacuum distillation (V3)	-	-	-	6 h	3 kPa	-	-	60°C	-