Supplementary Material

Evaluation of ionic liquids for the sustainable fractionation of essential oils

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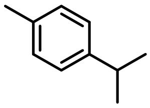
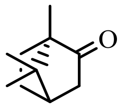
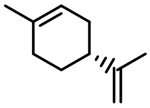
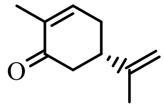
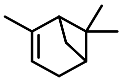
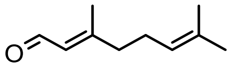
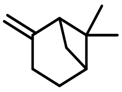
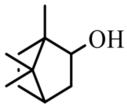
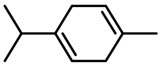
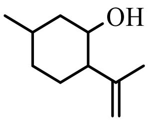
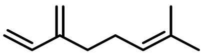
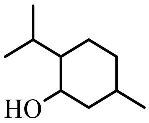
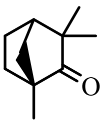
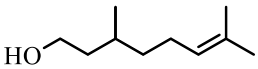
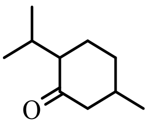
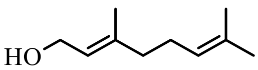
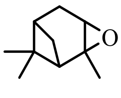
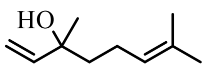
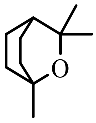
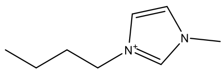
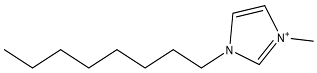
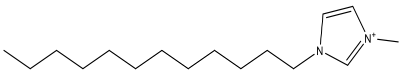
Section SM.1 – Chemicals list and properties

Table S1. Name, chemical structure, supplier, boiling point (T_b),[a,b] and purity[c] of the studied terpenes.

Compound	Chemical structure	Compound	Chemical structure
p-cymene Aldrich T_b = 450.28 K[a] $wt \geq 0.990$		(1*R*)-(+)-camphor Aldrich T_b = 480.55 K[b] $wt \geq 0.980$	
R-(+)-limonene Aldrich T_b = 449.65 K[a] $wt \geq 0.970$		*S*-(+)-carvone Merck T_b = 503.65 K[b] $wt \geq 0.980$	
α-pinene Aldrich T_b = 430.00 K[a] $wt \geq 0.980$		citronellal Acros T_b = 479.15 K[b] $wt \geq 0.930$	
β-pinene Aldrich T_b = 439.20 K[a] $wt \geq 0.990$		(−)-borneol Fluka T_b = 485.15 K[b] $wt \geq 0.990$	
γ-terpinene Acros T_b = 456.20 K[a] $wt \geq 0.970$		(−)-isopulegol SAFC T_b = 470.15 K[b] $wt \geq 0.980$	
myrcene Acros T_b = 440.15 K[b] $wt \geq 0.990$		L-(−)-menthol Acros T_b = 488.55 K[b] $wt \geq 0.997$	
(1*R*)-(−)-fenchone Aldrich T_b = 466.65 K[b] $wt \geq 0.980$		β-citronellol Aldrich T_b = 497.65 K[b] $wt \geq 0.950$	
(−)-menthone Fluka T_b = 490.79 K[a] $wt \geq 0.990$		geraniol Aldrich T_b = 502.15 K[b] $wt \geq 0.980$	
α-pinene oxide Aldrich T_b = 447.15 K[b] $wt \geq 0.970$		linalool Aldrich T_b = 471.65 K[b] $wt \geq 0.970$	
eucalyptol Aldrich T_b = 449.55 K[b] $wt \geq 0.990$			

[a]The boiling temperature was obtained from Yaws.[1]
[b]The boiling temperature was obtained from ChemSpider.[2]
[c]As declared by the supplier.

Table S2. Chemical structure of the cation, and name, source, molar mass, melting temperature and mass fraction purity of the studied ionic liquids.

	1-butyl-3-methylimidazolium chloride, [C_4mim]Cl (*Mw* = 174.671 g·mol^{-1}; T_m = 341.95 K[3,a]) Acquired from Iolitec; *wt* ≥ 0.99
	1-octyl-3-methylimidazolium chloride, [C_8mim]Cl (*Mw* = 230.777 g·mol^{-1}; T_m = 285.41 K[3,b]) Acquired from Iolitec; *wt* ≥ 0.99
	1-dodecyl-3-methylimidazolium chloride [C_{12}mim]Cl (*Mw* = 286.884 g·mol^{-1}; T_m = 369.78 K[3,c]) Acquired from Iolitec; *wt* ≥ 0.98

[a]The IL presents a glass transition at 197.35 K.[3]

[b]The IL presents a glass transition at 210.85 K.[3]

[c]The IL presents a liquid crystal transition at 310.15 K.[3]

[d]As declared by the supplier.

Section SM.2 – Detailed experimental procedure

The experiments were performed in a Varian 3380 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a 1041 on-column injector in the temperature range between (373.2-453.2) K. Before the experiments, each column was kept at 393.2 K for at least 6 hours under a continuous helium flow to remove any remaining residual contaminant. During the experiments, the injector and detector temperatures were set at 553.2 K and 573.2 K, respectively, and the column temperature was controlled by the GC oven (±0.1 K), varying between (373.2-453.2) K. The atmospheric pressure, the outlet temperature, and the exit flow rate were measured by an Agilent Precision Gas Flow Meter (model 5067-0223), and a Swagelok S model pressure transducer (accuracy of 0.25% BFSL) was used to determine the inlet pressure. To ensure that the terpenes were at infinite dilution state, injection volumes between (0.2-0.4) µL were introduced into the GC column. For α-pinene and eucalyptol, the activity coefficients were independently measured in two columns for the three stationary phases, achieving an average coefficient of variation of 2.1% between different runs. To ensure the reliability of the results, at least two independent measurements were carried out for each solute.

Section SM.3 – Thermodynamic background

Table S3. Summary of all the parameters used in the calculations of the vapor pressures and densities of the pure terpenes.

Solute	Vapor pressure (Pa)[a,b]				Density (kmol m^{-3})[c]			
	A	B (K)	C (K)	References	A	B	C	References
p-cymene	19.730	2993.090	-95.570	[4,d]	-7.333E-07	-6.876E-03	8.358	[5,6]
R-(+)-limonene	9.346	1712.777	-55.513	[7–13]	-8.224E-07	-5.293E-03	7.822	[6]
α-pinene	8.645	1305.402	-74.866	[14–20]	-2.001E-06	-4.866E-03	7.905	[6]
β-pinene	9.216	1627.341	-52.110	[14,15,20]	-1.446E-06	-5.050E-03	7.996	[6]
γ-terpinene	6.782	1514.772	205.190	[16,e]	2.788E-01	2.682E-01	661.0	[1,f]
myrcene	7.930	927.238	-134.859	[21–23]	-3.768E-05	-6.876E-03	8.358	[1,f]
(1*R*)-(−)-fenchone	9.075	1738.336	-53.341	[7,9,12,24]	-5.096E-07	5.228E-03	7.784	[6]
(−)-menthone	19.740	3299.840	-93.310	[4,d]	-4.033E-07	4.810E-03	7.240	[6]
α-pinene oxide	7.758	975.321	-127.321	[25]	-9.571E-07	-4.906E-03	7.861	[6]
eucalyptol	10.473	2436.986	1.234	[9,12,26]	-9.128E-07	-5.033E-03	7.550	[6]
(1*R*)-(+)-camphor	18.990	2962.560	-103.930	[4,d]	3.015E-01	2.960E-01	709.0	[1,f]
S-(+)-carvone	20.000	3543.190	-94.020	[4,d]	-4.877E-07	-5.046E-03	7.922	[6]
cironellal	9.151	1593.743	-96.274	[27,28]	2.502E-01	2.421E-01	740.1	[1,f]
(−)-borneol	10.062	201.721	-88.396	[29,30]	1.171E-06	-1.308E-03	6.566	- [g]
(−)-isopulegol	9.313	1739.916	-79.371	[24,31]	-9.100E-07	-4.831E-03	7.393	[6]
L-(−)-menthol	8.562	1259.270	-139.635	[9,17,32]	-5.486E-06	-1.239E-03	6.578	[6]
β-citronellol	9.900	1947.591	-93.817	[27,29,33]	-3.210E-06	-2.545E-03	6.512	[6]
geraniol	9.934	2008.731	-90.052	[27,29,33]	-3.161E-06	-2.790E-03	6.796	[6]
linalool	9.247	1582.231	-97.507	[18,34–36]	-3.680E-06	-3.230E-03	6.852	[6]

[a]The vapor pressures were calculated using the Antoine equation: $p = 10^{\left(A-\frac{B}{(T+C)}\right)}$, p/Pa, T/K.
[b]The constants of the Antoine equation were obtained by multilinear regression (Origin 8.5) of vapor pressure data available in the literature.
[c]The literature density data were fitted using the following second order polynomial equation: $\rho = AT^2 + BT + C$, ρ/kmol·m^{-3}, T/K.
[d]The vapor pressures were calculated using the following modified form of the Antoine equation: $p = exp^{\left(A-\frac{B}{(T-C)}\right)}$, p/Pa, T/K.
[e]The vapor pressures of γ-terpinene were calculated using the following modified form of Antoine equation: $p = 10^{\left(A-\frac{B}{(T-C)}\right)}$, p/mmHg, T/°C.
[f] The density data were calculated by the following equation: $\rho = AB^{-\left(1-\frac{T}{C}\right)^n}$, ρ/g· cm^{-3}, T/K (n = 0.286).
[g]The density data were predicted using COSMO-RS with BP_TZVP_C30_1701 parametrization in the temperature range between (378.15-478.15) K. The input COSMO file was generated using the TmoleX 3.3 program package with the COSMO-BP-TZVP template.

Table S4. Summary of the critical properties, acentric factor, and dipole moments of the pure terpenes.

Solute	Critical properties[a]			Acentric factor[a]	Dipole moment[c]
	T_c (K)	p_c (MPa)	V_c ($cm^{-3}\ mol^{-1}$)	ω	μ ($C\ m^{-1}$)
p-cymene	652.0[b]	2.80[b]	497.0[b]	0.374[b]	2.64E-31[d]
R-(+)-limonene	658.9	2.76	496.5	0.318	2.23E-30
α-pinene	630.8	2.89	484.5	0.326	1.16E-30
β-pinene	646.0	2.88	482.5	0.320	4.02E-30
γ-terpinene	661.0[b]	2.84[b]	448.6[b]	0.399[b]	6.50E-31[d]
myrcene	630.6[e]	2.45[e]	539.5[e]	0.381[e]	1.22E-29[e]
(1*R*)-(−)-fenchone	679.2	3.08	503.5	0.388	1.47E-29
(−)-menthone	689.7	2.60	528.5	0.412	1.45E-29
α-pinene oxide	716.4	3.09	489.5	0.369	9.76E-30
eucalyptol	661.1	2.45	509.5	0.339	8.03E-30
(1*R*)-(+)-camphor	700.2	3.08	503.5	0.388	1.53E-29
S-(+)-carvone	724.8	2.86	503.5	0.419	1.78E-29
citronellal	740.1[b]	2.38[b]	616.5[b]	0.786[b]	9.07E-30[d]
(−)-borneol	670.2	3.17	514.5	0.698	7.21E-30
(−)-isopulegol	656.8	2.77	527.5	0.698	9.70E-30
L-(−)-menthol	661.6	2.66	539.5	0.716	7.84E-30
β-citronellol	657.9	2.45	589.5	0.848	7.86E-30
geraniol	671.7	2.57	576.5	0.820	1.18E-29
linalool	633.3	2.58	565.4	0.755	9.67E-30

[a]Unless otherwise stated, the critical properties and the acentric factors were reported by Martins and co-authors,[37] where they were calculated using the Joback group contribution approach.[38]

[b]The acentric factors and the critical properties of *p*-cymene, γ-terpinene, and citronellal used in this work were reported by Yaws.[1]

[c]For most of the terpenes, the dipole moments were estimated using TURBOMOLE 6.1 program in our previous work.[39]

[d]The dipole moments of γ-terpinene and citronellal were also collected from Yaws,[1] and μ of *p*-cymene was collected from the work of Martins and co-authors.[37]

[e]For myrcene, the critical properties and the acentric factor were estimated by Kolicheski et al.[40] using the Joback group contribution approach,[38] while the dipole moment was retrieved from Riechert et al.[22]

Section SM.4 – Results and discussion

Activity coefficients at infinite dilution

Table S5. Activity coefficients at infinite dilution of the monoterpenes investigated in $[C_8mim]Cl$, $[C_4mim]Cl/[C_{12}mim]Cl$ equimolar mixture, and $[C_{12}mim]Cl$.[a]

Solute	$[C_8mim]Cl$						$[C_4mim]Cl/[C_{12}mim]Cl$ equimolar mixture						$[C_{12}mim]Cl$					
***T*/K**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**
p-cymene	8.50	8.54	8.57	8.61	8.73	8.82	7.42	7.43	7.46	7.47	7.50		3.84	3.92	3.95	4.00	4.03	4.08
R-(+)-limonene	12.10		11.68	11.51	11.49	11.19	9.35	9.30	9.25	9.14	9.05	9.12	4.13	4.17	4.24	4.25	4.21	4.25
α-pinene	18.27	18.13	17.36	16.92	16.68		13.41	13.25	13.14	13.15	13.11	13.30	4.88	4.97	5.09	5.21	5.24	5.36
β-pinene	13.17	12.89	12.62	12.36	12.28	12.19	9.91	9.79	9.66	9.53	9.39	9.30	4.12	4.15	4.18	4.20	4.21	4.23
γ-terpinene	9.66	9.84	9.94	10.07	10.17	10.24	7.67	7.82	7.99	8.14	8.28	8.67	3.38	3.59	3.75	3.91	4.01	4.04
myrcene	12.26	12.81	12.96	13.31	13.64	14.16	10.20	10.41	10.62	10.93	11.18	11.41	4.56	4.77	5.01	5.14	5.40	5.50
(1*R*)-(−)-fenchone	6.94	6.99	7.01	7.04	7.06	7.09	6.66	6.68	6.64	6.60	6.57	6.73	4.06	4.06	4.06	4.02	3.97	3.93
(−)-menthone	6.38	6.46	6.51	6.61	6.76	6.83	5.98	5.98	5.97	5.99	6.03		3.50	3.52	3.54	3.55	3.56	3.58
α-pinene oxide	2.76	2.96	3.13	3.30	3.54	3.32	2.29	2.40	2.61	2.59	2.95	3.39	2.73	2.86	3.04	3.18	3.39	3.92
eucalyptol	11.14	10.71	10.40	10.16	9.92	9.74	9.19	8.92	8.57	8.29	8.01	7.78	4.21	4.14	4.07	3.89	3.79	3.73
***T*/K**	**413.2**	**423.2**	**433.2**	**443.2**	**453.2**		**413.2**	**423.2**	**433.2**	**443.2**	**453.2**		**413.2**	**423.2**	**433.2**	**443.2**	**453.2**	
(*R*)-(+)-camphor	5.53	5.63	5.73	6.19	6.79		5.64	5.72	5.83	5.93	6.85		3.13	3.15	3.17	3.20	3.21	
S-(+)-carvone	3.56	3.64	3.87	4.04	4.23		3.43	3.55	3.78	4.30	4.90		2.37	2.38	2.41	2.43	2.44	
citronellal	6.61	6.49	6.42	6.29				6.06	6.48	7.08	7.76		3.48	3.43	3.36	3.27	3.20	
(−)-borneol			0.52	0.60	0.71				0.51	0.60	0.70				0.31	0.36	0.36	
(−)-isopulegol	0.79	0.88	0.99	1.18	1.46		0.75	0.82	0.94	1.12	1.32		0.50	0.54	0.59	0.64	0.71	
L-(−)-menthol		0.75	0.86	1.05	1.32				0.83	1.02	1.23		0.41	0.45	0.50	0.56		
β-citronellol			0.53	0.62	0.73				0.54	0.61	0.72				0.31	0.35	0.46	
geraniol			0.50	0.55	0.69				0.50	0.58	0.70				0.28	0.35	0.44	
linalool	0.71	0.78	0.87	0.98			0.65	0.73	0.84		1.20		0.42	0.47	0.52	0.59	0.66	

[a]The estimated uncertainties in the pressure, temperature and γ_{13}^{∞} are $u(T)$ = 0.1 K , $u(p) = 0.05\cdot p$, and $u(\gamma_{13}^{\infty}) = 0.04\cdot\gamma_{13}^{\infty}$.

Gas-liquid partition coefficients

Table S6. Gas-liquid partition coefficients of the monoterpenes studied in [C$_8$mim]Cl, [C$_4$mim]Cl/[C$_{12}$mim]Cl equimolar mixture, and [C$_{12}$mim]Cl.[a]

Solute		**[C$_8$mim]Cl**						**[C$_4$mim]Cl /[C$_{12}$mim]Cl equimolar mixture**						**[C$_{12}$mim]Cl**					
	***T*/K**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**	**373.2**	**383.2**	**393.2**	**403.2**	**413.2**	**423.2**
p-cymene		200.6	140.4	100.9	74.1	55.0	41.8	230.0	161.6	116.0	85.4	64.1		340.8	235.1	168.3	122.3	91.4	69.3
R-(+)-limonene		120.8		62.8	46.7	34.9	27.2	156.4	110.2	79.4	58.8	44.3	33.4	271.7	188.6	132.9	96.9	72.9	55.0
α-pinene		38.9	29.1	22.8	18.0	14.3		53.0	39.7	30.2	23.2	18.2	14.2	111.9	81.2	59.8	44.9	34.9	27.0
β-pinene		71.9	53.0	39.8	30.6	23.5	18.4	95.5	69.8	52.1	39.7	30.8	24.1	176.6	126.3	92.5	69.0	52.6	40.6
γ-terpinene		154.8	108.2	78.1	57.3	42.9	32.9	195.0	136.2	97.2	70.9	52.9	38.8	339.4	228.1	158.8	113.2	83.5	63.8
myrcene		98.1	67.0	48.6	35.7	26.8	20.2	118.0	82.5	59.4	43.4	32.7	25.1	202.5	138.2	96.6	70.9	51.8	39.9
(1*R*)-(−)-fenchone		432.7	300.9	214.5	155.9	115.6	87.2	450.0	316.0	226.6	166.5	124.4	91.9	568.1	397.3	284.7	209.4	157.7	120.5
(−)-menthone		724.5	487.0	337.8	238.4	170.7	126.3	773.2	526.3	368.7	263.4	191.5		1014.2	685.7	477.2	340.4	248.4	184.5
α-pinene oxide		781.1	521.5	361.8	258.3	185.0	138.9	941.5	643.5	434.9	329.4	222.6	155.0	606.6	414.4	285.9	205.8	148.5	
eucalyptol		128.1	92.5	67.3	49.7	37.3	28.3	155.3	111.1	81.8	61.0	46.3	35.5	260.9	183.5	132.0	99.8	74.8	56.7
	***T*/K**	**413.2**	**423.2**	**433.2**	**443.2**	**453.2**		**413.2**	**423.2**	**433.2**	**443.2**	**453.2**		**413.2**	**423.2**	**433.2**	**443.2**	**453.2**	
(*R*)-(+)-camphor		211.4	157.2	118.9	86.1	60.7		207.5	154.8	117.0	90.1	62.0		286.5	215.4	164.6	127.6	100.9	
S-(+)-carvone		546.9	389.0	272.2	197.7	145.0		568.4	400.3	279.1	185.9	125.5		630.4	456.1	335.5	251.9	192.3	
citronellal		165.7	121.5	90.3	69.2				130.3	89.6	61.6	43.0		241.5	176.0	132.1	101.9	79.7	
(−)-borneol				1564.7	955.1	579.0				1602.4	958.4	590.6				2008.2	1270.6	869.5	
(−)-isopulegol			929.1	602.9	379.9	233.8		1506.5	1000.0	637.0	401.3	258.6		1736.6	1149.0	775.1	535.5	369.5	
L-(−)-menthol			1457.5	916.4	553.6	334.2				960.7	573.1	357.3		2940.5	1890.0	1224.9	803.3		
β-citronellol				1920.1	1149.7	699.2				1904.9	1174.1	715.7				2507.2	1399.3	844.3	
geraniol				2460.9	1556.0	878.0				2451.8	1482.7	876.9				3363.6	1865.9	1050.3	
linalool		1178.0	770.9	515.3	333.8			1286.9	823.8	522.3		208.9		1503.5	972.7	643.5	426.7	357.5	

[a]The estimated uncertainties in the pressure, temperature and K_L are $u(T)$ = 0.1 K, $u(p) = 0.05 \cdot p$, and $u(K_L) = 0.04 \cdot K_L$.

Separation factors

Table S7. Experimental selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) of the terpene mixtures in [C_8mim]Cl, at 373.15 K.

Solute	k_j^{∞}	α-pinene	myrcene	β-pinene	*R*-(+)-limonene	eucalyptol	γ- terpinene	*p*- cymene	(1*R*)-(-)-fenchone	(−)-menthone	(*R*)-(+)-camphor	citronellal	α-pinene oxide	*S*-(+)-carvone	(−)-isopulegol	linalool	L-(−)-menthol	β-citronellol	(−)-borneol
α-pinene[a]	0.05																		
myrcene[a]	0.08	1.39																	
β-pinene[a]	0.08	1.49	1.07																
R-(+)-limonene[a]	0.08	1.51	1.09	1.01															
eucalyptol[a]	0.09	1.64	1.18	1.10	1.09														
γ-terpinene[a]	0.10	1.89	1.36	1.27	1.25	1.15													
p-cymene[a]	0.12	2.15	1.55	1.44	1.42	1.31	1.14												
(1*R*)-(−)-fenchone[a]	0.14	2.63	1.90	1.77	1.74	1.61	1.39	1.22											
(−)-menthone[a]	0.15	2.65	1.91	1.78	1.76	1.62	1.40	1.23	1.01										
(*R*)-(+)-camphor[b]	0.16	2.86	2.06	1.92	1.90	1.75	1.51	1.33	1.09	1.08									
citronellal[b]	0.24	4.33	3.12	2.91	2.87	2.64	2.29	2.02	1.65	1.63	1.51								
α-pinene oxide[a]	0.36	6.50	4.68	4.36	4.30	3.96	3.44	3.02	2.47	2.45	2.27	1.50							
S-(+)-carvone[b]	0.36	6.62	4.77	4.44	4.38	4.04	3.50	3.08	2.51	2.50	2.31	1.53	1.02						
(−)-isopulegol[b]	2.35	42.84	30.88	28.75	28.37	26.12	22.65	19.93	16.27	16.16	14.96	9.89	6.59	6.47					
linalool[b]	2.76	50.48	36.39	33.87	33.43	30.78	26.69	23.48	19.17	19.04	17.63	11.65	7.77	7.63	1.18				
L-(−)-menthol[b]	4.32	78.99	56.94	53.00	52.31	48.16	41.76	36.75	30.00	29.80	27.58	18.23	12.16	11.93	1.84	1.56			
β-citronellol[b]	5.33	97.43	70.23	65.38	64.53	59.41	51.51	45.33	37.01	36.75	34.02	22.48	14.99	14.72	2.27	1.93	1.23		
(−)-borneol[b]	6.01	109.77	79.13	73.66	72.70	66.93	58.04	51.07	41.70	41.41	38.33	25.33	16.89	16.58	2.56	2.17	1.39	1.13	
geraniol[b]	6.64	121.31	87.45	81.40	80.34	73.97	64.14	56.44	46.08	45.76	42.36	28.00	18.67	18.33	2.83	2.40	1.54	1.25	1.11

[a]The estimated uncertainty in the capacity and selectivity are $u(k_j^{\infty}) = 0.04 \cdot k_j^{\infty}$ and $u(S_{ij}^{\infty}) = 0.08 \cdot S_{ij}^{\infty}$, respectively.

[b]The selectivity and capacity values were calculated using the extrapolated infinite dilution activity coefficients (at 373.15 K) using data obtained in the temperature interval between (413.15 – 453.15) K; The estimated uncertainty in the capacity and selectivity are $u(k_j^{\infty}) = 0.1 \cdot k_j^{\infty}$ and $u(S_{ij}^{\infty}) = 0.2 \cdot S_{ij}^{\infty}$, respectively.

Table S8. Experimental selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) of the terpene mixtures in [C$_4$mim]Cl/[C$_{12}$mim]Cl equimolar mixture, at 373.15 K.

Solute	$\boldsymbol{k_j^{\infty}}$	α-pinene	myrcene	β-pinene	*R*-(+)-limonene	eucalyptol	γ- terpinene	*p*- cymene	(1*R*)-(-)-fenchone	(−)-menthone	(*R*)-(+)-camphor	citronellal	α-pinene oxide	*S*-(+)-carvone	(−)-isopulegol	linalool	L-(−)-menthol	β-citronellol	(−)-borneol
α-pinene[a]	0.07																		
Myrcene[a]	0.10	1.31																	
β-pinene[a]	0.10	1.35	1.03																
R-(+)-limonene[a]	0.11	1.43	1.09	1.06															
eucalyptol[a]	0.11	1.46	1.11	1.08	1.02														
γ-terpinene[a]	0.13	1.75	1.33	1.29	1.22	1.20													
p-cymene[a]	0.13	1.81	1.37	1.34	1.26	1.24	1.03												
(1*R*)-(−)-fenchone[a]	0.15	2.01	1.53	1.49	1.40	1.38	1.15	1.11											
(−)-menthone[a]	0.17	2.24	1.71	1.66	1.56	1.54	1.28	1.24	1.11										
(*R*)-(+)-camphor[b]	0.22	2.99	2.28	2.21	2.09	2.05	1.71	1.66	1.49	1.34									
citronellal[b]	0.28	3.69	2.81	2.73	2.57	2.53	2.11	2.04	1.83	1.65	1.23								
α-pinene oxide[a]	0.44	5.86	4.45	4.33	4.08	4.01	3.35	3.24	2.91	2.61	1.96	1.59							
S-(+)-carvone[b]	0.47	6.30	4.79	4.66	4.39	4.32	3.60	3.49	3.13	2.81	2.10	1.71	1.08						
(−)-isopulegol[b]	2.48	33.22	25.27	24.55	23.16	22.76	19.00	18.38	16.50	14.81	11.09	8.99	5.67	5.27					
linalool[b]	2.78	37.33	28.39	27.59	26.03	25.58	21.35	20.65	18.54	16.65	12.46	10.11	6.37	5.92	1.12				
L-(−)-menthol[b]	3.56	47.69	36.27	35.24	33.25	32.68	27.28	26.39	23.68	21.27	15.92	12.91	8.14	7.57	1.44	1.28			
β-citronellol[b]	5.32	71.31	54.24	52.70	49.72	48.87	40.79	39.46	35.42	31.80	23.81	19.31	12.18	11.31	2.15	1.91	1.50		
(−)-borneol[b]	6.21	83.33	63.39	61.58	58.10	57.11	47.66	46.11	41.39	37.16	27.83	22.57	14.23	13.22	2.51	2.23	1.75	1.17	
geraniol[b]	6.86	91.96	69.95	67.96	64.12	63.02	52.60	50.88	45.67	41.01	30.71	24.90	15.70	14.59	2.77	2.46	1.93	1.29	1.10

[a]The estimated uncertainty in the capacity and selectivity are $u(k_j^{\infty}) = 0.04 \cdot k_j^{\infty}$ and $u(S_{ij}^{\infty}) = 0.08 \cdot S_{ij}^{\infty}$, respectively.

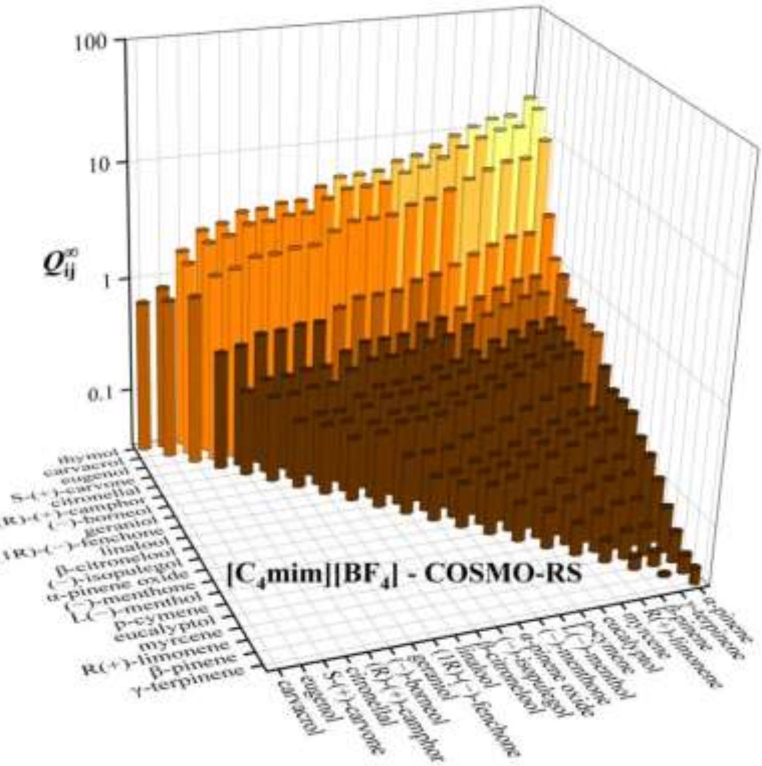
[b]The selectivity and capacity values were calculated using the extrapolated infinite dilution activity coefficients (at 373.15 K) using data obtained in the temperature interval between (413.15 – 453.15) K; The estimated uncertainty in the capacity and selectivity are $u(k_j^{\infty}) = 0.1 \cdot k_j^{\infty}$ and $u(S_{ij}^{\infty}) = 0.2 \cdot S_{ij}^{\infty}$, respectively.

Table S9. Experimental selectivities (S_{ij}^{∞}) and capacities (k_j^{∞}) of the terpene mixtures in [C$_{12}$mim]Cl, at 373.15 K.

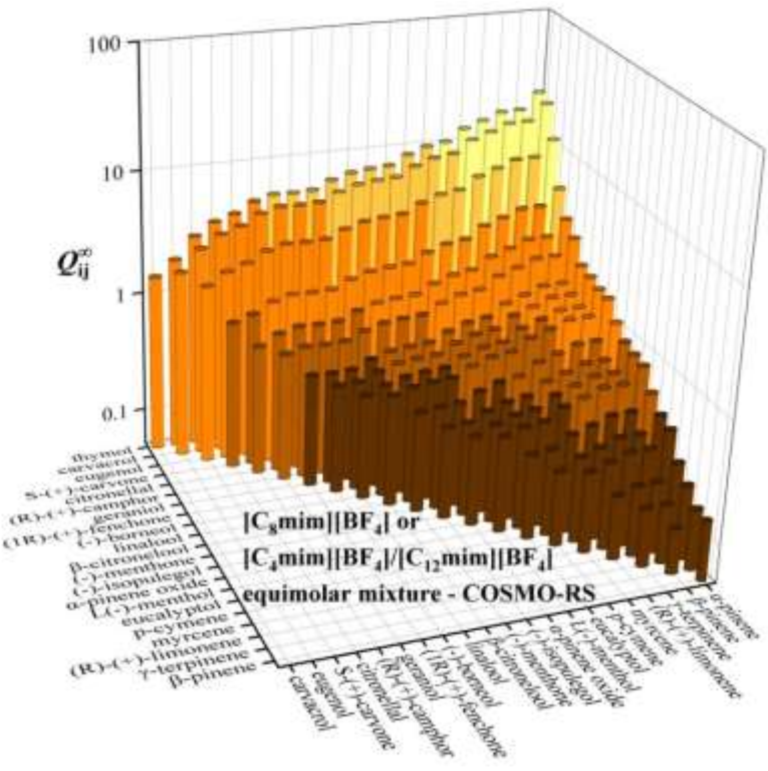
Solute	k_j^{∞}	α-pinene	myrcene	eucalyptol	*R*-(+)-limonene	β-pinene	(1*R*)-(-)-fenchone	citronellal	*p*- cymene	(−)-menthone	γ- terpinene	(*R*)-(+)-camphor	α-pinene oxide	*S*-(+)-carvone	(−)-isopulegol	L-(−)-menthol	linalool	(−)-borneol	β-citronellol
α-pinene[a]	0.20																		
myrcene[a]	0.22	1.07																	
eucalyptol[a]	0.24	1.16	1.08																
R-(+)-limonene[a]	0.24	1.18	1.10	1.02															
β-pinene[a]	0.24	1.18	1.11	1.02	1.00														
(1*R*)-(−)-fenchone[a]	0.25	1.20	1.12	1.04	1.02	1.01													
citronellal[b]	0.26	1.26	1.17	1.08	1.06	1.06	1.05												
p-cymene[a]	0.26	1.27	1.19	1.10	1.08	1.07	1.06	1.01											
(−)-menthone[a]	0.29	1.39	1.30	1.20	1.18	1.18	1.16	1.11	1.10										
γ-terpinene[a]	0.30	1.44	1.35	1.25	1.22	1.22	1.20	1.15	1.14	1.04									
(*R*)-(+)-camphor[b]	0.33	1.61	1.50	1.39	1.36	1.36	1.34	1.28	1.27	1.16	1.12								
α-pinene oxide[a]	0.37	1.79	1.67	1.54	1.51	1.51	1.49	1.42	1.41	1.28	1.24	1.11							
S-(+)-carvone[b]	0.44	2.14	2.00	1.85	1.81	1.81	1.78	1.70	1.69	1.54	1.48	1.33	1.20						
(−)-isopulegol[b]	2.85	14.19	13.26	12.24	12.01	11.98	11.81	11.29	11.17	10.18	9.83	8.81	7.94	6.62					
L-(−)-menthol[b]	3.06	15.04	14.05	12.98	12.73	12.70	12.51	11.96	11.84	10.79	10.42	9.34	8.41	7.02	1.06				
linalool[b]	3.06	15.46	14.44	13.34	13.08	13.05	12.86	12.30	12.16	11.09	10.71	9.60	8.65	7.22	1.09	1.03			
(−)-borneol[b]	5.35	26.61	24.87	22.96	22.52	22.47	22.14	21.17	20.94	19.09	18.43	16.52	14.89	12.42	1.88	1.77	1.72		
β-citronellol[b]	13.44	65.57	61.27	56.57	55.49	55.36	54.55	52.16	51.60	47.03	45.42	40.71	36.68	30.61	4.62	4.36	4.24	2.46	
geraniol[b]	19.34	90.64	84.70	78.20	76.71	76.53	75.41	72.10	71.33	65.01	62.78	56.28	50.71	42.31	6.39	6.03	5.86	3.41	1.38

[a]The estimated uncertainty in the capacity and selectivity are $u(k_j^{\infty}) = 0.04 \cdot k_j^{\infty}$ and $u(S_{ij}^{\infty}) = 0.08 \cdot S_{ij}^{\infty}$, respectively.

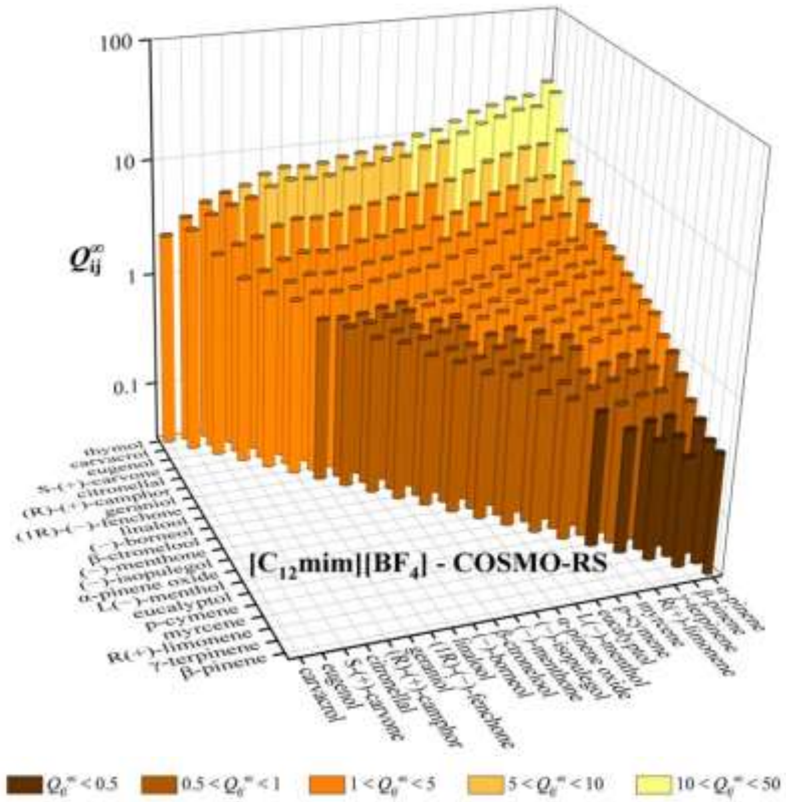
[b]The selectivity and capacity values were calculated using the extrapolated infinite dilution activity coefficients (at 373.15 K) using data obtained in the temperature interval between (413.15 – 453.15) K; The estimated uncertainty in the capacity and selectivity are $u(k_j^{\infty}) = 0.1 \cdot k_j^{\infty}$ and $u(S_{ij}^{\infty}) = 0.2 \cdot S_{ij}^{\infty}$, respectively.



100
10
1
0.1
Q^{∞}_{ij}
thymol
carvacrol
eugenol
S-(+)-carvone
citronellal
(R)-(+)-camphor
(-)-borneol
geraniol
(1R)-(-)-fenchone
linalool
β-citronelool
(-)-isopulegol
α-pinene oxide
(-)-menthone
L-(-)-menthol
p-cymene
eucalyptol
myrcene
R(+)-limonene
β-pinene
γ-terpinene
[C_4mim][BF_4] - COSMO-RS
α-pinene



100
10
1
0.1
Q^{∞}_{ij}
thymol
carvacrol
eugenol
S-(+)-carvone
citronellal
(R)-(+)-camphor
geraniol
(1R)-(+)-fenchone
(-)-borneol
linalool
β-citronelool
(-)-menthone
(-)-isopulegol
α-pinene oxide
L-(-)-menthol
eucalyptol
p-cymene
myrcene
(R)-(+)-limonene
γ-terpinene
β-pinene
[C_8mim][BF_4] or
[C_4mim][BF_4]/[C_{12}mim][BF_4]
equimolar mixture - COSMO-RS
α-pinene



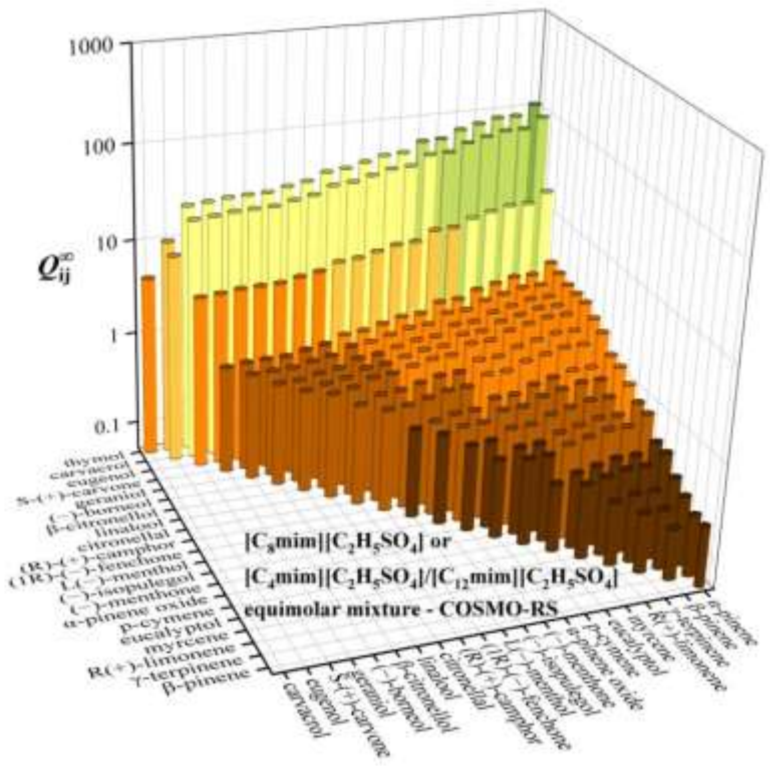


Figure S1. Predicted Q_{ij}^{∞} values, at 373.2 K, for the binary mixtures of terpenes in [C_4mim][BF_4], [C_8mim][BF_4], and [C_{12}mim][BF_4] or [C_4mim][BF_4]/[C_{12}mim][BF_4] equimolar mixture.

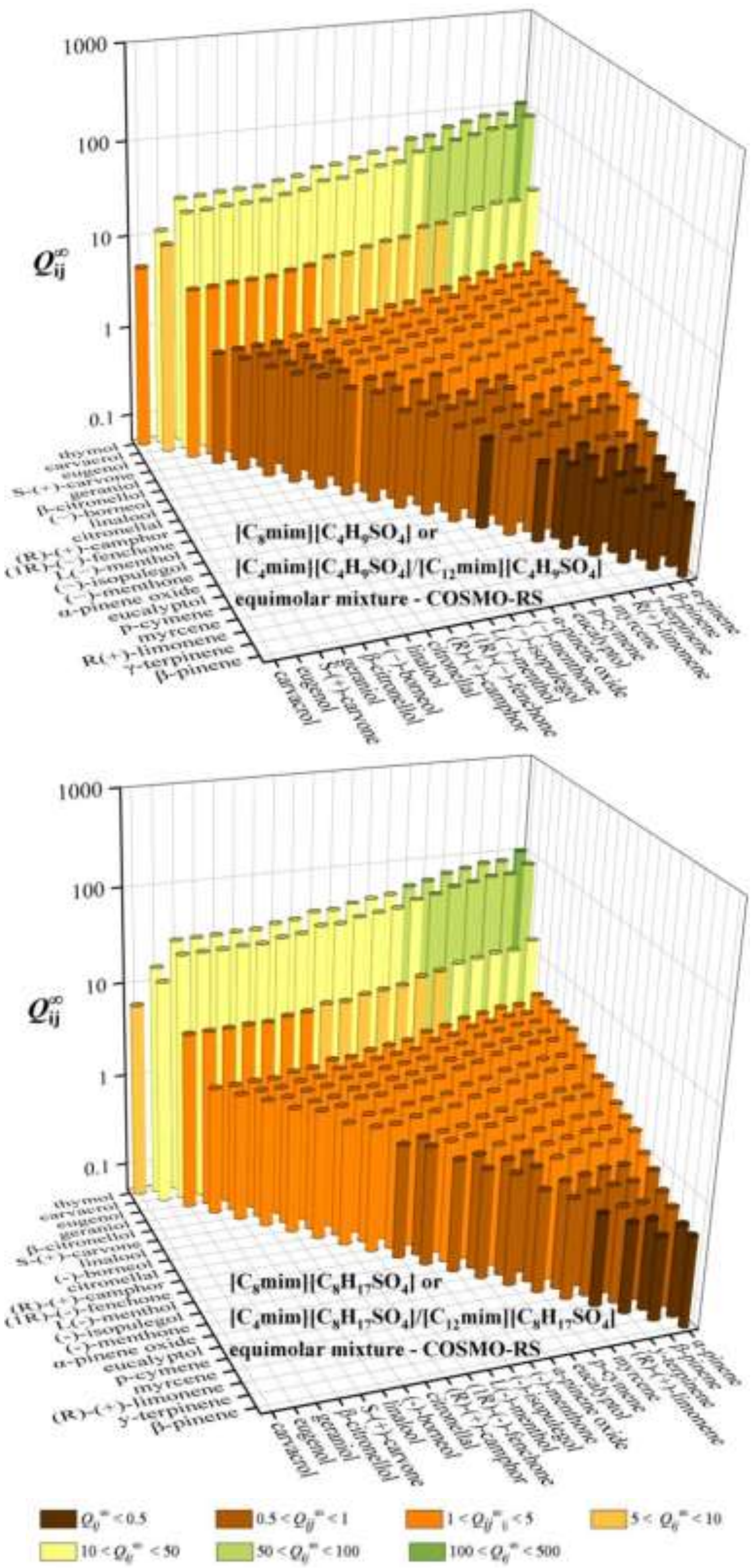


Figure S2. Predicted Q_{ij}^{∞} values for the terpene mixtures in pure [C$_8$mim][C$_2$H$_5$SO$_4$], [C$_8$mim][C$_4$H$_9$SO$_4$], [C$_8$mim][C$_8$H$_{17}$SO$_4$], and equimolar mixtures of [C$_4$mim][C$_2$H$_5$SO$_4$]/[C$_{12}$mim][C$_2$H$_5$SO$_4$], [C$_4$mim][C$_4$H$_9$SO$_4$]/[C$_{12}$mim][C$_4$H$_9$SO$_4$], and [C$_4$mim][C$_8$H$_{17}$SO$_4$]/[C$_{12}$mim][C$_8$H$_{17}$SO$_4$], at 373.15 K.

Table S10. Overview of the terpene mixture distribution through the different Q_{ij}^{∞} interval scales, for the ILs studied in this work.

			Percentage of mixtures in each Q_{ij}^{∞} interval scale									
			Scale	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Ionic liquid	**Data source**	**N_T[a]**	**Q_{ij}^{∞} interval**	**<0.5**	**0.5-1**	**1-5**	**5-10**	**10-50**	**50-100**	**100-500**	**500-1000**	**>1000**
[C_4mim]Cl	Experimental[b]	91		50.5	7.7	28.6	7.7	5.5	0	0	0	0
	COSMO-RS	231		12.1	17.7	19.5	13.4	14.7	3.9	2.6	3.9	12.1
[C_8mim]Cl	Experimental	171		29.2	7.6	9.4	4.1	10.5	10.5	25.1	3.5	0
	COSMO-RS	231		17.7	16.5	27.3	13.9	6.9	0.9	5.2	5.6	6.1
[C_4mim]Cl/[C_{12}mim]Cl mixture	Experimental	171		26.3	8.2	11.7	5.3	7.6	11.1	28.7	1.2	0
	COSMO-RS	231		17.7	16.5	27.3	13.9	6.9	0.9	5.2	5.6	6.1
[C_{12}mim]Cl	Experimental	171		33.3	12.3	1.8	1.8	18.7	11.1	7.0	7.6	6.4
	COSMO-RS	231		10.4	19.0	31.2	13.4	8.7	0.4	6.9	6.9	3.0
[C_4mim][BF_4]	COSMO-RS	231		62.3	10.4	16.9	7.4	3.0	0	0	0	0
[C_8mim][BF_4] or [C_4mim][BF_4]/[C_{12}mim][BF_4] mixture	COSMO-RS	231		26.8	25.1	32.9	10.0	5.2	0	0	0	0
[C_{12}mim][BF_4]	COSMO-RS	231		4.3	23.4	53.2	12.6	6.5	0	0	0	0
[C_4mim][$C_2H_5SO_4$]	COSMO-RS	231		37.7	22.9	16.9	3.9	13.0	5.2	0.4	0	0
[C_8mim][$C_2H_5SO_4$] or [C_4mim][$C_2H_5SO_4$]/[C_{12}mim][$C_2H_5SO_4$] mixture	COSMO-RS	231		13.0	29.9	34.6	3.9	13.0	5.2	0.4	0	0
[C_{12}mim][$C_2H_5SO_4$]	COSMO-RS	231		4.3	16.0	56.7	3.5	13.9	5.2	0.4	0	0
[C_4mim][$C_4H_9SO_4$]	COSMO-RS	231		22.5	29.9	25.1	3.9	13.0	5.2	0.4	0	0
[C_8mim][$C_4H_9SO_4$] or [C_4mim][$C_4H_9SO_4$]/[C_{12}mim][$C_4H_9SO_4$] mixture	COSMO-RS	231		7.8	24.7	45.0	3.5	13.4	5.2	0.4	0	0
C_{12}mim][$C_4H_9SO_4$]	COSMO-RS	231		2.6	10.8	63.6	3.5	13.9	5.2	0.4	0	0
[C_4mim][$C_8H_{17}SO_4$]	COSMO-RS	231		7.8	24.7	45.0	3.5	13.4	5.2	0.4	0	0
[C_8mim][$C_8H_{17}SO_4$] or [C_4mim][$C_8H_{17}SO_4$]/C_{12}mim][$C_8H_{17}SO_4$] mixture	COSMO-RS	231		2.6	10.8	63.6	3.5	13.9	5.2	0.4	0	0
[C_{12}mim][$C_8H_{17}SO_4$]	COSMO-RS	231		0	6.5	70.1	4.3	13.4	5.6	0	0	0

[a]Total number of binary mixtures. [b]Q_{ij}^{∞} calculated from the γ_{13}^{∞} collected from reference.[37]

Table S11. Overview of the relevant monoterpene mixtures, their correspondent essential oil source, and experimental Q_{ij}^{∞} values obtained with different solvents, at 373.2 K.

Terpene mixture	Essential oil	Separating agent	Q_{ij}^{∞}	Reference
α-pinene/β-pinene	Pinus[5,41,42]	$[C_4mim][CH_3CO_2]$	0.06	[39]
		$[C_4mim][CH_3SO_3]$	0.03	[37]
		$[C_4mim][(CH_3)_2PO_4]$	0.05	[37]
		$[C_4mim][CF_3SO_3]$	0.07	[37]
		$[C_4mim]Cl$	0.01	[37]
		$[C_8mim]Cl$	0.11	this work
		$[C_4mim]Cl/[C_{12}mim]Cl$	0.17	this work
		$[C_{12}mim]Cl$	0.29	this work
		$[P_{6,6,6,14}]Cl$	1.10	[39]
		$[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$	1.60	[39]
		Amine 220 (A-220)	1.03	[43]
		Carbowax 1500 (C-1500	1.45	[43]
		Carbowax 6000 (C-6000)	7.00	[43]
		Dinonyl phthalate (DNP)	1.40	[43]
		Ethylene glycol phthalate (EGP)	0.58	[43]
limonene/linalool	Citrus[44,45]	$[C_4mim][CH_3CO_2]$	56.65	[39]
		$[C_8mim]Cl$	66.68	this work
		$[C_4mim]Cl/[C_{12}mim]Cl$	106.00	this work
		$[C_{12}mim]Cl$	71.11	this work
		$[P_{6,6,6,14}]Cl$	244.33	[39]
limonene/carvone	Spearmint[40,46–48]	$[C_4mim][CH_3CO_2]$	1.17	[39]
		$[C_8mim]Cl$	1.51	this work
		$[C_4mim]Cl/[C_{12}mim]Cl$	2.06	this work
		$[C_{12}mim]Cl$	1.81	this work
		$[P_{6,6,6,14}]Cl$	1.64	[39]
		$[P_{6,6,6,14}][(C_8H_{17})_2PO_2]$	1.73	[39]
eucalyptol/linalool	Basil[49,50]	$[C_4mim][CH_3CO_2]$	0.10	[39]
		$[C_4mim][CH_3SO_3]$	0.12	[37]
		$[C_4mim][(CH_3)_2PO_4]$	1.38	[37]
		$[C_4mim][CF_3SO_3]$	0.16	[37]
		$[C_4mim]Cl$	0.14	[37]
		$[C_8mim]Cl$	61.39	this work

		$[C_4mim]Cl/[C_{12}mim]Cl$	104.18	this work
		$[C_{12}mim]Cl$	72.48	this work
		$[P_{6,6,6,14}]Cl$	218.40	[39]
camphor/borneol	flowers from *Asteraceae*[50,51] and *Lamiaceae*[52–54] families	$[C_4mim][CF_3SO_3]$	0.26	[37]
		$[C_4mim]Cl$	0.01	[37]
		$[C_8mim]Cl$	146.02	this work
		$[C_4mim]Cl/[C_{12}mim]Cl$	175.00	this work
		$[C_{12}mim]Cl$	93.52	this work
		$[P_{6,6,6,14}]Cl$	320.69	[39]
menthone/menthol	Mentha[30,55]	$[C_4mim][CH_3SO_3]$	0.43	[37]
		$[C_4mim][CF_3SO_3]$	0.20	[37]
		$[C_4mim]Cl$	1.05	[37]
		$[C_8mim]Cl$	119.56	this work
		$[C_4mim]Cl/[C_{12}mim]Cl$	152.54	this work
		$[C_{12}mim]Cl$	56.91	this work
		$[P_{6,6,6,14}]Cl$	301.00	[39]
citronellal/geraniol	Citronella[13,56]	$[C_8mim]Cl$	308.60	this work
		$[C_4mim]Cl/[C_{12}mim]Cl$	167.95	this work
		$[C_{12}mim]Cl$	1434.91	this work
eugenol/linalool	Cinnamon[57–59]	$[C_4mim][CF_3SO_3]$	21.72	[37]

References

(1) Yaws, C. L. *Thermophysical Properties of Chemicals and Hydrocarbons*, 2nd ed.; Elsevier Inc., 2014.

(2) Pence, H. E.; Williams, A. Chemspider: An Online Chemical Information Resource. *J. Chem. Educ.* **2010**, *87* (11), 1123–1124.

(3) Domańska, U.; Bogel-Łukasik, E.; Bogel-Łukasik, R. 1-Octanol/Water Partition Coefficients of 1-Alkyl-3-Methylimidazolium Chloride. *Chem. - A Eur. J.* **2003**, *9* (13), 3033–3041.

(4) Fonseca, L. A. A. P.; Sartoratto, A.; Cremasco, M. A. Experimental Determination of Thermodynamic Properties of Terpene and Aromatic Ketones by Gas Chromatography. *J. Mol. Liq.* **2021**, *322*, 114531.

(5) Ilić Pajić, J.; Ivaniš, G.; Radović, I.; Grujić, A.; Stajić-Trošić, J.; Stijepović, M.; Kijevčanin, M. Experimental Densities and Derived Thermodynamic Properties of Pure P-Cymene, α-Pinene, Limonene and Citral under High Pressure Conditions. *J. Chem. Thermodyn.* **2020**, *144*, 106065.

(6) Martins, M. A. R.; Carvalho, P. J.; Palma, A. M.; Domańska, U.; Coutinho, J. A. P.; Pinho, S. P. Selecting Critical Properties of Terpenes and Terpenoids through Group-Contribution Methods and Equations of State. *Ind. Eng. Chem. Res.* **2017**, *56* (35), 9895–9905.

(7) Batiu, I. Vapor-Liquid Equilibria in the Binary Systems n-Decane + (-)-Menthone and n-Decane + (+)-Fenchone at Temperatures between 344.45 and 390.75 K. *Fluid Phase Equilib.* **2002**, *198* (1), 111–121.

(8) Espinosa Díaz, M. A.; Guetachew, T.; Landy, P.; Jose, J.; Voilley, A. Experimental and Estimated Saturated Vapour Pressures of Aroma Compounds. *Fluid Phase Equilib.* **1999**, *157* (2), 257–270.

(9) Guetachew, T.; Mokbel, I.; Batiu, I.; Cisse, Z.; Jose, J. Vapor Pressures and Sublimation Pressures of Eight Constituets of Essential Oils at Pressures in the Range from 0.3 to 83,000 Pa. *ELDATA Int. Eletronic J. Physico-Chemical Data* **1999**, *5* (1), 43–53.

(10) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Knipmeyer, S. E.; Nguyen, A. Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Methyl Benzoate, Ethyl Benzoate, (R)-(+)-Limonene, Tert-Amyl Methyl Ether, Trans-Crotonaldehyde, and Diethylene Glycol. *J. Chem. Eng. Data* **2002**, *47* (4), 667–688.

(11) Ngema, P. T.; Matkowska, D.; Naidoo, P.; Hofman, T.; Ramjugernath, D. Vapor-Liquid Equilibrium Data for Binary Systems of 1-Methyl-4-(1- Methylethenyl)-Cyclohexene + {ethanol, Propan-1-Ol, Propan-2-Ol, Butan-1-Ol, Pentan-1-Ol, or Hexan-1-Ol} at 40 KPa. *J. Chem. Eng. Data* **2012**, *57* (7), 2053–2058.

(12) Štejfa, V.; Fulem, M.; Růžička, K.; Červinka, C. Thermodynamic Study of Selected Monoterpenes II. *J. Chem. Thermodyn.* **2014**, *79*, 272–279.

(13) Verma, R. S.; Verma, S. K.; Tandon, S.; Padalia, R. C.; Darokar, M. P. Chemical Composition and Antimicrobial Activity of Java Citronella (Cymbopogon Winterianus Jowitt Ex Bor) Essential Oil Extracted by Different Methods. *J. Essent. Oil Res.* **2020**, *32* (5), 449–455.

(14) Hawkins, J. E.; Armstrong, G. T. Physical and Thermodynamic Properties of Terpenes. III. The Vapor Pressures of α-Pinene and β-Pinene. *J. Am. Chem. Soc.* **1954**, *76* (14), 3756–3758.

(15) Reich, R.; Sanhueza, V. Vapor-Liquid Equilibria for α-Pinene and β-Pinene with 1-Butanol and 1-Pentanol. *Fluid Phase Equilib.* **1992**, *78* (C), 239–248.

(16) Wang, C.; Li, H.; Ma, L.; Han, S. (Vapour + Liquid) Equilibria for the Binary Mixtures (Cis-Pinane + α-Pinene) and (Cis-Pinane + 1-Butanol). *J. Chem. Thermodyn.* **2003**, *35* (1), 131–136.

(17) Wagner, Z.; Bendová, M.; Rotrekl, J.; Parmar, N.; Kočí, S.; Vrbka, P. Thermochemical Properties of Menthol and Terpineol. *J. Solution Chem.* **2020**, *49*, 1267–1278.

(18) Clará, R. A.; Marigliano, A. C. G.; Sólimo, H. N. Density, Viscosity, and Refractive Index in the Range (283.15 to 353.15) K and Vapor Pressure of α-Pinene, d-Limonene, (±)-Linalool, and Citral over the Pressure Range 1.0 KPa Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *54* (3), 1087–1090.

(19) Sun, L.; Liao, D.; Yang, Z.; Chen, X.; Tong, Z. Measurement and Correlation of (Vapor + Liquid) Equilibrium Data for {α-Pinene + p-Cymene + (S)-(-)-Limonene} Ternary System at Atmospheric Pressure. *J. Chem. Thermodyn.* **2013**, *58*, 416–421.

(20) Štejfa, V.; Fulem, M.; Růžička, K.; Červinka, C.; Rocha, M. A. A.; Santos, L. M. N. B. F.; Schröder, B. Thermodynamic Study of Selected Monoterpenes. *J. Chem. Thermodyn.* **2013**, *60*, 117–125.

(21) Chapman, A. C. LVII.—Essential Oil of Hops. *J. Chem. Soc. Trans.* **1903**, *83*, 505–513.

(22) Riechert, O.; Zeiner, T.; Sadowski, G. Measurement and Modeling of Phase

Equilibria in Systems of Acetonitrile, n-Alkanes and Β-myrcene. *Ind. Eng. Chem. Res.* **2015**, *54*, 1153–1160.

(23) Umnahanant, P.; Zafar, A.; Kankala, V.; Chickos, J. Vapor Pressure and Vaporization Enthalpy Studies of (+)-Longifolene, (−)-Isolongifolene and Β-Myrcene by Correlation Gas Chromatography. *J. Chem. Thermodyn.* **2019**, *131*, 583–591.

(24) Kobe, K. A.; Okabe, T. S.; Ramstad, M. T.; Huemmer, P. M. P-Cymene Studies. VI. Vapor Pressure of p-Cymene, Some of Its Derivatives and Related Compounds. *J. Am. Chem. Soc.* **1941**, *63* (12), 3251–3252.

(25) Roon, A. van; Parsons, J. R.; Govers, H. A. J. Gas Chromatographic Determination of Vapour Pressure and Related Thermodynamic Properties of Monoterpenes and Biogenically Related Compounds. *J. Chromatogr. A* **2002**, *955*, 105–115.

(26) Torcal, M.; García-Abarrio, S.; Pardo, J. I.; Mainar, A. M.; Urieta, J. S. P, p, T Measurements and Isobaric Vapor - Liquid - Equilibria of the 1,3,3-Trimethyl-2-Oxabicycle[2,2,2]Octane + Propan-1-Ol Mixture: Cubic and Statistical Associating Fluid Theory-Based Equation of State Analysis. *J. Chem. Eng. Data* **2010**, *55* (12), 5932–5940.

(27) Lecat, M. Nouveaux Azeotropes Binaires: Cinquième Liste. *Recl. des Trav. Chim. des Pays-Bas* **1927**, *46* (4), 240–247.

(28) Povh, F. P.; Rodrigues, V. M.; Meireles, M. A. A.; Pinheiro, N. Determinação Da Pressão de Vapor de Compostos Orgânicos Por Cromatografia Gasosa. *Cienc. e Tecnol. Aliment.* **2006**, *26* (2), 465–474.

(29) Štejfa, V.; Dergal, F.; Mokbel, I.; Fulem, M.; Jose, J.; Růžička, K. Vapor Pressures and Thermophysical Properties of Selected Monoterpenoids. *Fluid Phase Equilib.* **2015**, *406*, 124–133.

(30) Vanstone, E. E. XLVII. - The Vapour Pressures of Two Perfectly Miscible Solids and Their Solid Solutions. *J. Chem. Soc. Trans.* **1910**, *97* (1), 429–443.

(31) Štejfa, V.; Fulem, M.; Růžička, K. Thermodynamic Study of Selected Monoterpenes IV. *J. Chem. Thermodyn.* **2020**, *144*, 106013.

(32) Keating, L.; Harris, H. H.; Chickos, J. S. Vapor Pressures and Vaporization Enthalpy of (−) α-Bisabolol and (Dl) Menthol by Correlation Gas Chromatography. *J. Chem. Thermodyn.* **2017**, *107*, 18–25.

(33) Murata, A.; Oba, S.; Ishikawa, T.; Hirata, M. Vapor-Liquid Equilibria and Distillation of Mixtures of Geraniol, Nerol and Citronellol. *Kagaku Kogaku*

Ronbunshu **1982**, *8* (6), 655–658.

(34) Lecat, M. Nouveaux Azeotropes Binaires: Huitième Liste. *Recl. des Trav. Chim. des Pays-Bas* **1928**, *47* (1), 13–18.

(35) Deng, D.; Li, H.; Han, S. Isobaric (Vapour + Liquid) Equilibria of (Linalool + 1propanol) and (Linalool + 1butanol). *J. Chem. Thermodyn.* **2002**, *34* (9), 1431–1437.

(36) Zaitsau, D. H.; Verevkin, S. P.; Sazonova, A. Y. Vapor Pressures and Vaporization Enthalpies of 5-Nonanone, Linalool and 6-Methyl-5-Hepten-2-One. Data Evaluation. *Fluid Phase Equilib.* **2015**, *386*, 140–148.

(37) Martins, M. A. R.; Domańska, U.; Schröder, B.; Coutinho, J. A. P.; Pinho, S. P. Selection of Ionic Liquids to Be Used as Separation Agents for Terpenes and Terpenoids. *ACS Sustain. Chem. Eng.* **2016**, *4* (2), 548–556.

(38) Joback, K. G.; Reid, R. C. Estimation of Pure-Component Properties from Group-Contributions. *Chem. Eng. Commun.* **1987**, *57* (1–6), 233–243.

(39) Vilas-Boas, S. M.; Teixeira, G.; Rosini, S.; Martins, M. A. R.; Gaschi, P. S.; Coutinho, J. A. P.; Ferreira, O.; Pinho, S. P. Ionic Liquids as Entrainers for Terpenes Fractionation and Other Relevant Separation Problems. *J. Mol. Liq.* **2021**, *323*, 114647.

(40) Kokkini, S.; Karousou, R.; Lanaras, T. Essential Oils of Spearmint (Carvone-Rich) Plants from the Island of Crete (Greece). *Biochem. Syst. Ecol.* **1995**, *23* (4), 425–430.

(41) Kumar, S.; Srivastava, V. C.; Nanoti, S. M.; Kumar, A. Solvent Evaluation for Desulfurization and Denitrification of Gas Oil Using Performance and Industrial Usability Indices. *AIChE J.* **2015**, *61* (7), 2257–2267.

(42) Aligiannis, N.; Kalpoutzakis, E.; Mitaku, S.; Chinou, I. B. Composition and Antimicrobial Activity of the Essential Oils of Two Origanum Species. *J. Agric. Food Chem.* **2001**, *49* (9), 4168–4170.

(43) Díaz, E.; Cortiñas, J.; Ordóñez, S.; Vega, A.; Coca, J. Selectivity of Several Liquid Phases for the Separation of Pine Terpenes by Gas Chromatography. *Chromatographia* **2004**, *60* (9–10), 573–578.

(44) Arce, A.; Soto, A. Citrus Essential Oils: Extraction and Deterpenation. *Tree For. Sci. Biotechnol.* **2008**, *2* (Special Issue 1), 1–9.

(45) Ozturk, B.; Esteban, J.; Gonzalez-Miquel, M. Deterpenation of Citrus Essential Oils Using Glycerol-Based Deep Eutectic Solvents. *J. Chem. Eng. Data* **2018**, *63* (7),

2384–2393.

(46) Younis, Y. M. H.; Beshir, S. M. Carvone-Rich Essential Oils from Mentha Longifolia (l.) Huds. Ssp. Schimperi Briq. and Mentha Spicata L. Grown in Sudan. *J. Essent. Oil Res.* **2004**, *16* (6), 539–541.

(47) Hussain, A. I.; Anwar, F.; Shahid, M.; Ashraf, M.; Przybylski, R. Chemical Composition, and Antioxidant and Antimicrobial Activities of Essential Oil of Spearmint (Mentha Spicata L.) from Pakistan. *J. Essent. Oil Res.* **2010**, *22* (1), 78–84.

(48) Monfared, A.; Nabid, M. R.; Rustaiyan, A. Composition of a Carvone Chemotype of Mentha Longifolia (l.) Huds. from Iran. *J. Essent. Oil Res.* **2002**, *14* (1), 51–52.

(49) Mahboubi, M.; Heidarytabar, R.; Mahdizadeh, E.; Hosseini, H. Antimicrobial Activity and Chemical Composition of Thymus Species and Zataria Multiflora Essential Oils. *Agric. Nat. Resour.* **2017**, *51* (5), 395–401.

(50) Morteza-Semnani, K. Composition of the Essential Oil of Tanacetum Polycephalum Schultz Bip. *J. Essent. Oil Res.* **2006**, *18* (2), 129–130.

(51) Avato, P.; Raffo, F.; Aldouri, N. A.; Vartanian, S. T. Essential Oils of Varthemia Iphionoides from Jordan. *Flavour Fragr. J.* **2004**, *19* (6), 559–561.

(52) Salgueiro, L.; Vila, R.; Tomas, X.; Tomi, F.; Cañigueral, S.; Casanova, J.; Proença da Cunha, A.; Adzet, T. Chemical Polymorphism of the Essential Oil of Thymus Carnosus from Portugal. *Phytochemistry* **1995**, *38* (2), 391–396.

(53) Tabanca, N.; Kirimer, N.; Demirci, B.; Demirci, F.; Can Başer, K. H. Composition and Antimicrobial Activity of the Essential Oils of Micromeria Cristata Subsp. Phrygia and the Enantiomeric Distribution of Borneol. *J. Agric. Food Chem.* **2001**, *49* (9), 4300–4303.

(54) Tomaino, A.; Cimino, F.; Zimbalatti, V.; Venuti, V.; Sulfaro, V.; De Pasquale, A.; Saija, A. Influence of Heating on Antioxidant Activity and the Chemical Composition of Some Spice Essential Oils. *Food Chem.* **2005**, *89* (4), 549–554.

(55) Pedro, S. N.; Freire, M. G.; Freire, C. S. R.; Silvestre, A. J. D. Deep Eutectic Solvents Comprising Active Pharmaceutical Ingredients in the Development of Drug Delivery Systems. *Expert Opin. Drug Deliv.* **2019**, *16* (5), 497–506.

(56) Kaur, H.; Bhardwaj, U.; Kaur, R. Cymbopogon Nardus Essential Oil: A Comprehensive Review on Its Chemistry and Bioactivity. *J. Essent. Oil Res.* **2021**, *33* (3), 205–220.

(57) Raina, V. K.; Srivastava, S. K.; Aggarwal, K. K.; Ramesh, S.; Kumar, S. Essential

Oil Composition of Cinnamomum Zeylanicum Blume Leaves from Little Andaman, India. *Flavour Fragr. J.* **2001**, *16* (5), 374–376.

(58) Schmidt, E.; Jirovetz, L.; Buchbauer, G.; Eller, G. A.; Stoilova, I.; Krastanov, A.; Stoyanova, A.; Geissler, M. Composition and Antioxidant Activities of the Essential Oil of Cinnamon (Cinnamomum Zeylanicum Blume) Leaves from Sri Lanka. *J. Essent. Oil-Bearing Plants* **2006**, *9* (2), 170–182.

(59) Chericoni, S.; Prieto, J. M.; Iacopini, P.; Cioni, P.; Morelli, I. In Vitro Activity of the Essential Oil of Cinnamomum Zeylanicum and Eugenol in Peroxynitrite-Induced Oxidative Processes. *J. Agric. Food Chem.* **2005**, *53* (12), 4762–4765.