Supercritical CO_2 as a green solvent for eucalyptus and citrus essential oils processing: role of thermal effects upon mixing

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ELECTRONIC SUPPLEMENTARY INFORMATION

Excess enthalpies for CO_2 + citral mixtures

Table S. 1. Excess molar enthalpy, H_m^E, for the binary system [CO_2 (x) + citral (1–x)]

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
313.15 K and 7.64 MPa					
0.111	–866	0.485	–3278	0.817	–5419
0.160	–1055	0.584	–3837	0.847	–5047
0.249	–1753	0.616	–4080	0.874	–4178
0.327	–2143	0.665	–4389	0.923	–2666
0.362	–2415	0.749	–5025	0.972	–1065
0.427	–2845				
313.15 K and 10.00 MPa					
0.117	–346	0.501	–1281	0.891	–1603
0.193	–522	0.599	–1484	0.927	–1463
0.302	–795	0.679	–1577	0.984	–699
0.377	–989	0.679	–1581	0.987	–599
0.443	–1149	0.722	–1632		
313.15 K and 12.00 MPa					
0.066	–122	0.397	–727	0.698	–1183
0.126	–217	0.464	–855	0.776	–1222
0.154	–294	0.522	–960	0.838	–1205
0.231	–437	0.574	–1033	0.908	–1045
0.278	–500	0.619	–1106	0.933	–936
0.321	–604	0.661	–1142	0.969	–602

Table S.1 (continued)

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
323.15 K and 7.64 MPa					
0.135	–906	0.427	–3073	0.792	–3559
0.136	–979	0.537	–3823	0.841	–2704
0.183	–1302	0.584	–4144	0.885	–2032
0.249	–1767	0.627	–4499	0.923	–1270
0.289	–2023	0.665	–4694	0.923	–1269
0.327	–2404	0.680	–4779	0.972	–575
0.362	–2617	0.734	–4587		
323.15 K and 10.00 MPa					
0.117	–565	0.501	–2270	0.827	–3650
0.193	–834	0.553	–2449	0.881	–3508
0.217	–943	0.577	–2581	0.891	–3268
0.302	–1360	0.649	–2915	0.927	–2657
0.341	–1498	0.714	–3189	0.959	–1913
0.377	–1724	0.746	–3283	0.966	–1776
0.443	–1977	0.802	–3543		
323.15 K and 12.00 MPa					
0.126	–338	0.522	–1391	0.815	–1901
0.181	–510	0.574	–1498	0.860	–1834
0.207	–537	0.619	–1603	0.908	–1707
0.321	–893	0.661	–1670	0.933	–1547
0.360	–986	0.698	–1776	0.969	–1049
0.386	–1047	0.762	–1823		
0.464	–1211	0.776	–1872		

Intermolecular interactions in CO_2 + terpene systems

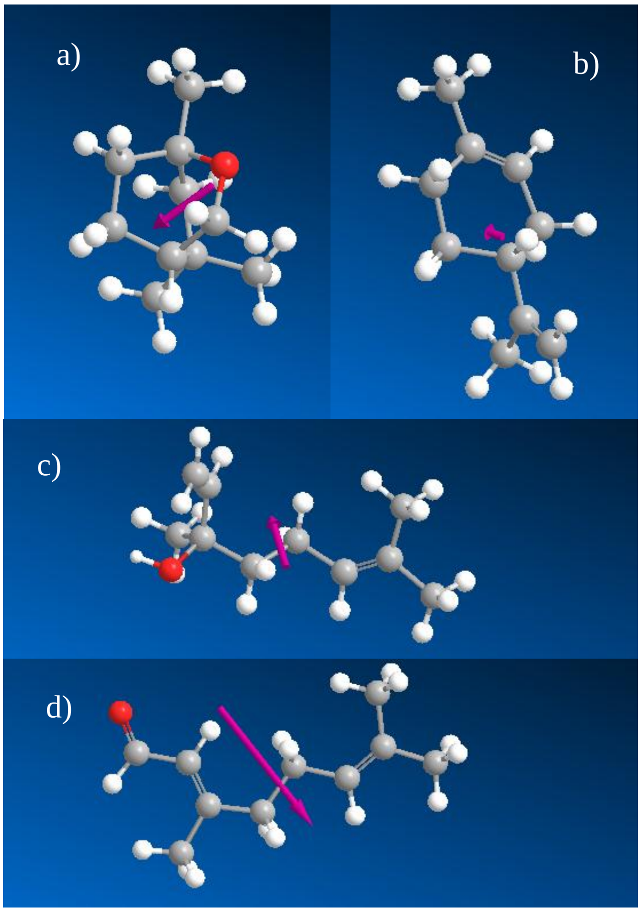

Figure S. 1 Optimised molecular structures of the different terpenes calculated using GAMESS (method HF, wave function: R-closed-Shell and Basis Set: 3-21G). a) 1,8-cineole, b) limonene, c) linalool and d) citral. The pink arrows show the calculated dipole moment.

Excess enthalpies for CO_2 + 1,8-cineole + limonene

Table S.2. Pseudobinary excess molar enthalpy, $H_m^{E,\,pseu}$ and ternary excess molar enthalpy, $H_m^{E,ter}$, of [{CO_2 (x_1) + [1,8-cineol(x_2)+limonene(x_3)]} at x_2/x_3=0.78/0.22, 313.15 K, and 7.64 and 10.00 MPa.

x_1	x_2	$H_m^{E,pseu}$ (J mol^{-1})	$H_m^{E,ter}$ (J mol^{-1})	x_1	x_2	$H_m^{E,pseu}$ (J mol^{-1})	$H_m^{E,ter}$ (J mol^{-1})
7.64 MPa							
0.107	0.696	–624	–588	0.576	0.331	–3340	–3323
0.201	0.624	–1187	–1154	0.658	0.267	–3834	–3820
0.243	0.591	–1378	–1347	0.743	0.201	–4233	–4222
0.355	0.503	–2075	–2049	0.871	0.101	–4627	–4622
0.319	0.531	–1792	–1764	0.920	0.062	–3550	–3547
0.419	0.453	–2464	–2440	0.963	0.029	–1473	–1471
0.477	0.408	–2781	–2760	0.982	0.014	–664	–663
10.00 MPa							
0.088	0.712	–168	–131	0.528	0.368	–747	–728
0.143	0.669	–247	–212	0.575	0.331	–840	–823
0.242	0.591	–384	–353	0.657	0.267	–944	–930
0.282	0.560	–433	–404	0.727	0.213	–1037	–1026
0.354	0.504	–509	–483	0.812	0.147	–1132	–1124
0.418	0.454	–599	–575	0.920	0.062	–1028	–1025
0.503	0.388	–727	–707	0.963	0.029	–762	–760

Correlation of binary H_m^E data involved in the ternary mixture CO_2 + 1,8-cineole + limonene using the Peng-Robinson equation state

The ternary excess enthalpy data for the CO_2 + 1,8-cineole + limonene ternary system were predicted using the Peng-Robinson equation state and binary excess enthalpy data for the three related binary systems. The method used for the binary mixtures in the main manuscript (equations 2 – 5) was applied to the ternary mixtures using the values for the pure component parameters shown in Table 2. Values for the binary interaction parameters required to extend the classical mixing rule to ternary mixtures were determined as follows. The binary H_m^E data previously obtained for the CO_2 + 1,8–cineole[2] and CO_2 + limonene[3] systems at the same conditions of temperature and pressure of ternary data (313.15 K and 7.64 and 10.00 MPa) were correlated using one or two binary interaction parameters. Values for k_{ij} or k_{ij} and δ_{ij} thus obtained are shown in Table S.3. In the case of CO_2 + 1,8–cineole, data were not available at 313.15 K and 10.00 MPa, the parameter values reported in Table S.3 were obtained from data taken at 308.15 and 323.15 K and 10.00 MPa[2]. Table S.3 also shows values for the standard deviation between experimental and calculated excess enthalpies, σ (J mol^{-1}) and the percentage ratio between σ and maximum absolute value of H_m^E, σ%, obtained in these correlations. On the other hand, H_m^E data for the 1,8-cineole + limonene system at 313.15 K and high pressure were not available and the H_m^E values at atmospheric pressure reported by Comelli et al.[4] were used. The Peng-Robinson equation state provided a poor description of H_m^E for these liquid mixtures. Therefore, it was decided that this contribution should be evaluated setting to zero the binary interaction parameters.

Table S.3 Correlation of binary H_m^E data (J mol^{-1}) related to {CO$_2$ (x_1) + [1,8-cineol (x_2)+limonene(x_3)]} system using the Peng–Robinson EOS [Eqs. (2)–(5)] of the main manuscript: values for the binary parameters k_{ij} and δ_{ij}, standard deviation between experimental and calculated excess enthalpies, σ , and the percentage ratio between σ and maximum absolute value of H_m^E , σ% = 100 σ / H_m^E .

System	T (K)	P (MPa)	Binary Parameters	σ (J mol^{-1})	σ %
CO$_2$ + 1,8-cineole	313.15	7.64	$k_{12} = 0.07525$	52	1.1
			$k_{12} = 0.08127$ $\delta_{12} = 0.00438$	51	1.0
	308.15, 323.15	10.00	$k_{12} = 0.10168$	110	4.0
			$k_{12} = 0.06914$ $\delta_{12} = -0.02546$	83	3.0
CO$_2$ + limonene	313.15	7.64	$k_{13} = 0.11044$	140	3.1
			$k_{13} = 0.04361$ $\delta_{13} = -0.04895$	35	0.78
		10.00	$k_{13} = 0.14570$	43	5.1
			$k_{13} = 0.12756$ $\delta_{13} = -0.01375$	18	2.2

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