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ORIGINAL ARTICLE

Retention of a plethora of essential oils and aromas in deep eutectic solvent:water:cyclodextrin mixtures

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Abstract

Essential oils (EOs) and aromas have long been used in the perfume, cosmetic, pharmaceutical and food industries. Yet, aside their poor solubility and instability, their high volatility limits their application. Their encapsulation in cyclodextrins (CDs) or their solvation in deep eutectic solvents (DESs) are two efficient strategies to resolve such problems. Thus, the present study aims to investigate the retention ability of the combination of DESs and CDs towards a wide variety of EOs and aromas. Thus, the capacity of formulations combining choline chloride:urea (ChCl:U) DES, CDs and water to retain and decrease the volatility of twenty EOs and twenty-one aromas was examined. Also, the formation constants (K_f) of CD/aroma inclusion complexes in this new non-conventional medium were determined. Results showed that ChCl:U DES:water 70:30 wt% mixed with 10 wt% CD had an efficient ability to retain all the studied EOs and aromas. Also, the addition of CDs in this mixture was shown to be advantageous in improving the efficiency of the formulation even if lower complexation ability towards the aromas was observed compared to water. Altogether, the obtained results will encourage the use of DES:water:CD mixtures for the incorporation of EOs and aromas in different preparations.

Keywords Aromas · Cyclodextrins · Deep eutectic solvents · Essential oils · Retention

Introduction

Essential oils (EOs) are complex mixtures of volatile aromas naturally produced by aromatic plants. They constitute a large group of agro-based industrial products and have applications in various fields such as food and beverages, perfumes, cosmetics, aromatherapy and pharmaceuticals. This is mainly because of their aromatic properties but also for their large spectrum of biological properties (antiviral, antibacterial, antimycotic, antiparasitic and insecticidal) [1–4]. However, EOs have some drawbacks in term of practical applications because of their low solubility and high volatility [4]. Thus, a considerable attention should be given for maximizing the retention of EOs and aromas, and consequently their effectiveness. Encapsulation in cyclodextrins (CDs) was shown to be effective in overcoming the main concerns related to volatile compounds manipulation [5]. CDs are cyclic oligosaccharides that possess the capacity to form inclusion complexes with poorly soluble compounds, such as EOs components [6]. This is because of their tridimensional structure that appears as a hollow truncated cone possessing an inner hydrophobic cavity and an outer hydrophilic surface [7]. Native CDs, known as α-CD, β-CD and γ-CD, are composed of six, seven and eight glucose units, respectively. CD derivatives, such as 2-hydroxypropyl-β-CD (HP-β-CD), with higher aqueous solubility and improved safety profile were also synthesized. The interest of the use of CD encapsulation for EOs and aromas solubilization and retention was already proved in pure water and in mixtures of water and organic solvents [3, 4, 8–11].

Owing to the urgent need for safer environmental impact, the use of eco-friendly solvents like deep eutectic solvents (DESs) has recently experienced important growth in the scientific field [12]. DESs, discovered in 2003, are defined as binary or ternary mixtures of compounds that are able to associate mainly via hydrogen bonds [13]. At a certain molar

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ratio, an eutectic mixture could be obtained at which the melting temperature of the solvent is lower than its starting compounds or their ideal mixture [14, 15]. The first discovered and most studied DES is reline, composed of choline chloride and urea (ChCl:U) in 1:2 molar ratio. The latter is liquid at room temperature and displays a melting point of 12 °C [13]. Recently, DESs are being extensively used for the solubilization and extraction of natural molecules owing to the advantages they provide because of their low vapor pressure, non-flammability, high thermal stability and low thermal conductivity [16]. Lately, they have been used to retain EOs and aromas [17, 18].

Recently, CDs were combined to DESs in order to increase the solvation and retention of volatile organic compounds [19–22]. Only few studies promptly examined the retention ability of CDs and DESs combination towards a single aroma compound or a specific EO [18, 23]. However, to the best of our knowledge, no systematic study was conducted to prove the retention efficiency of this combination towards a wide variety of EOs and aromas. This constitutes the main objective of this study with the use of ChCl:U DES. Also, it was proved that the addition of water was of utmost necessity to improve the retention efficiency of formulations based on DESs and CDs [18]. Thus, the influence of water addition is also explored herein.

Results and discussion

This study was performed in order to evaluate the effects of ChCl:U DES, CDs, water and their combination on the retention of twenty EOs and twenty-one aromas. The chosen aromas belong to various chemical classes including hydrocarbons, oxygenated terpenoids (alcohols, aldehydes, ketones, oxides, esters, phenols) and phenylpropanoids. The chemical structures of the studied aromas, their octanol/water partition coefficients (logP values), their aqueous solubilities (S_0 values) as well as their relative percentages in the investigated EOs are listed in Table 1. It is worthy to note that some of the EOs were composed of only one aroma as example, *Cinnamomum camphora var. linaloolifera Y.Fujita* containing 99.25% of (l)-linalool; and some of them have a high percentage of a certain compound as example, *Artemisia dracunculus L.* contains more than 79% of estragole; *Cymbopogon martinii* is mainly composed of geraniol; *Foeniculum vulgare* and *Ocimum basilicum L.* have more than 75% of *trans*-anethol and estragole, respectively.

Volatility studies were carried out using static headspace-gas chromatography (SH-GC). A decrease in the chromatographic peak areas corresponds to a decrease in the volatility of the EOs or aromas, meaning an increase in their solubility in the studied formulations.

Influence of water content in DES:water:CD mixtures on the retention of EOs

Firstly, the influence of water addition on the retention ability of ChCl:U DES towards *Rosmarinus officinalis L.* EO in the absence or presence of 10 wt% HP-β-CD was studied. The obtained results are presented in Fig. 1. The total areas in Fig. 1a and b are normalized to those obtained in water in the absence or presence of 10 wt% HP-β-CD, respectively.

In the absence of HP-β-CD (Fig. 1a), a decrease in the total area was observed when increasing the wt% of ChCl:U DES, which indicated a decrease in the volatility of *R. officinalis L.* EO. A 1.6-fold decrease in the volatility was observed in the presence of 100 wt% DES compared to water. The same tendency was observed in the literature with *Eucalyptus citriodora EO*. The decrease in the EO volatility could be correlated to the lower polarity of the pure DES compared to water [18]. Therefore, this proved that the polarity is the dominant factor governing the solubilization mechanism in DES.

In water, the EO volatility was found to be 20-times lower in the presence of HP-β-CD than in its absence. Thus, the effect of CDs alone (20-times) (Fig. 1b) was higher than the effect of DESs alone (1.6-times) (Fig. 1a). In addition, from Fig. 1b, we can see that a relatively linear decrease in the volatility of *R. officinalis L.* EO was observed when increasing the wt% of ChCl:U DES between 0 and 70 wt%. An increase in the EO volatility was obtained above DES:water 80:20 wt%, but without reaching the level observed in water containing CDs. Thus, results (Fig. 1b) showed that ChCl:U DES:water 70:30 wt% containing 10 wt% HP-β-CD seems to be close to the optimal ratio for the retention of EOs in accordance with previous findings obtained with *E. citriodora* EO [18].

The existence of an optimal DES:water:CD mixture for the retention of EO could be due to the fact that increasing DES wt% decreases the polarity of the medium which is advantageous for the solvation of EO in the bulk medium but harmful for the complexation phenomenon.

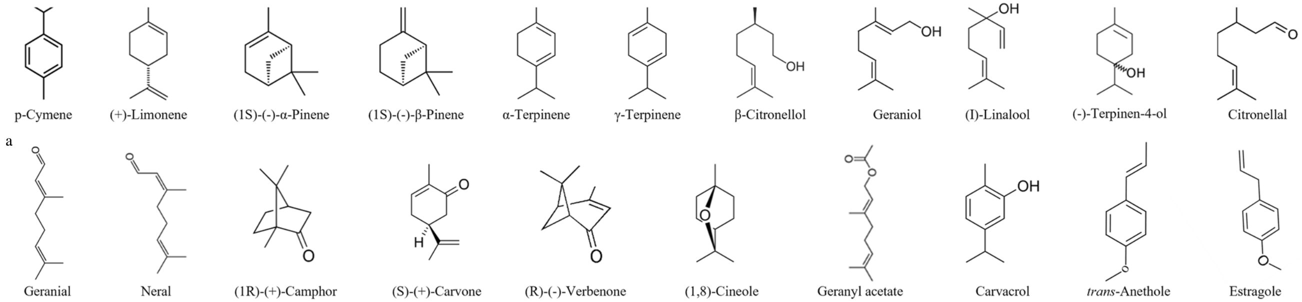
This observation is in total agreement with literature data where authors showed a decrease in the K_f values of CD inclusion complexes when increasing the DES wt% in the medium [18] or other organic solvents (ethanol, dimethylsulfoxide) [10, 11]. Indeed the addition of water to the ChCl:U DES is essential to allow CDs to experience an aqueous-like environment capable of maintaining their encapsulation capacities [30] and tuning the DES:water mixture for highest solubilization of target molecules [31]. Also, it was proved that the addition of certain amount of water was advantageous to ensure enhanced performances and lower cost [32] with maintaining DES nanostructure

Table 1 Chemical structures, octanol/water partition coefficients (logP), aqueous solubility (S_0) values and the relative percentages of the studied aromas in the selected essential oils

Aromas^{a}	Hydrocarbons						Alcohols				Aldehydes			Ketones			Oxide	Ester	Phenol	Phenylpropanoids	
	p-Cymene	(+)-Limonene	(1S)-(-)-α-Pinene	(1S)-(-)-β-Pinene	α-Terpinene	γ-Terpinene	β-Citronellol	Geraniol	(I)-Linalool	(−)-Terpinen-4-ol	Citronellal	Geranial	Neral	(1R)-(+)-Camphor	(S)-(+)-Carvone	(R)-(−)-Verbenone	(1,8)-Cineole	Geranyl acetate	Carvacrol	*trans*-Anethole	Estragole
LogP^{b}	4.10	4.57	4.42	4.49	4.25	4.50	3.91	3.56	2.97	3.26	3.53	2.76	2.76	2.38	1.27	2.23	2.74	4.04	3.49	3.11	3.47
S_0 (mM)	0.38^{c}	0.09^{d}	0.02^{e}	0.23^{d}	0.10^{d}	0.06^{e}	10.41^{c}	7.72^{c}	18.45^{c}	8.82^{d}	0.90^{f}	3.80^{f}	3.80^{f}	3.61^{d}	10.20^{f}	46.53^{d}	2.15^{d}	0.09^{d}	5.26^{g}	0.22^{h}	0.32^{i}
Artemisia dracunculus L.	–	4.12	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	79.22
Carum carvi	–	19.71	0.01	–	–	–	–	–	–	–	–	–	–	–	79.72	–	–	–	–	–	–
Cinnamomum camphora var. linaloolifera Y.Fujita	–	–	–	–	–	–	–	–	99.25	–	–	–	–	–	–	–	–	–	–	–	–
Citrus limon	–	66.44	1.87	12.16	–	8.93	–	–	–	–	–	1.49	–	–	–	–	–	–	–	–	–
Citrus reticulata	–	68.85	2.20	1.60	–	19.42	–	–	0.15	–	–	–	–	–	–	–	–	–	–	–	–
Cymbopogon flexuosus	–	0.29	–	–	–	–	–	5.88	1.21	–	–	41.42	32.06	–	–	–	–	–	–	–	–
Cymbopogon martinii	–	0.18	–	–	–	–	–	80.85	1.88	–	–	0.46	0.23	–	–	–	–	11.22	–	–	–
Cymbopogon winterianus	–	3.24	–	–	–	–	10.59	21.81	–	–	–	–	–	–	–	–	–	2.82	–	–	–
Eucalyptus citriodora	0.83	0.45	1.32	1.04	–	–	4.84	0.09	0.29	–	74.77	–	–	–	–	–	0.38	–	–	–	–
Foeniculum vulgare	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	75.30	3.10
Melaleuca alternifolia	2.02	1.15	2.42	–	10.53	21.49	–	–	–	41.51	–	–	–	–	–	–	3.99	–	–	–	–
Melaleuca viridiflora Solander ex Gaërtner	–	7.69	8.65	2.33	–	1.86	–	–	–	–	–	–	–	–	–	–	57.22	–	–	–	–
Mentha viridis/spicata	–	19.95	–	–	–	–	–	–	–	–	–	–	–	–	61.82	–	–	–	–	–	–
Ocimum basilicum L.	–	0.05	–	–	–	–	–	0.05	18.12	–	–	0.50	0.50	–	–	–	0.14	–	–	–	75.90
Origanum compactum	5.19	–	–	–	1.72	14.60	–	–	1.08	–	–	–	–	–	–	–	–	–	61.40	–	–
Origanum majorana L.	2.71	1.09	–	–	5.97	11.76	–	–	2.11	13.15	–	–	–	–	–	–	–	–	13.72	–	–

Table 1 (continued)

Aromas[a]	Hydrocarbons						Alcohols				Aldehydes			Ketones			Oxide	Ester	Phenol	Phenylpropanoids	
	p-Cymene	(+)-Limonene	(1S)-(−)-α-Pinene	(1S)-(-)-β-Pinene	α-Terpinene	γ-Terpinene	β-Citronellol	Geraniol	(I)-Linalool	(−)-Terpinen-4-ol	Citronellal	Geranial	Neral	(1R)-(+)-Camphor	(S)-(+)-Carvone	(R)-(−)-Verbenone	(1,8)-Cineole	Geranyl acetate	Carvacrol	*trans*-Anethole	Estragole
Pelargonium graveolens L.'Hér	–	–	–	–	–	–	34.19	13.11	4.63	–	–	–	–	–	–	–	–	–	–	–	–
Rosmarinus officinalis	0.74	2.19	10.37	9.01	–	1.28	–	–	0.72	–	–	–	–	8.83	–	–	47.05	–	–	–	–
Rosmarinus officinalis L.	1.06	4.08	20.09	1.84	–	1.31	–	–	1.52	–	–	–	–	14.48	–	10.47	8.16	–	–	–	–
Satureja montana L.	11.28	–	–	–	1.74	11.58	–	–	–	–	–	–	–	–	–	–	–	–	52.05	–	–



[b] LogP values are provided by PubChem Compound' database from 'National Center for Biotechnology Information' (NCBI)

[c] [24]

[d] [25]

[e] [26]

[f] [27]

[g] [28]

[h] [11]

[i] [29]

up to 42 wt% water as demonstrated by neutron total scattering and empirical potential structure refinement experiments [33].

Retention of a plethora of EOs in DES:water:CD mixtures

Since positive influence of adding 30 wt% of water to DES on the retention of *Rosmarinus officinalis L.* EO in DES:water:CD mixtures was proved (Fig. 1), the retention of twenty EOs was studied in pure ChCl:U DES and in ChCl:U DES:water 70:30 wt%, both containing 10 wt% HP-β-CD, in order to confirm tendency for all the other EOs. The areas are normalized to those obtained in water in the absence of CDs for each EOs. Results obtained for eight EOs are illustrated in Fig. 2. The other results are regrouped in Fig. S1 in SI. It can be clearly noticed that all the EOs exhibited a weaker volatility in both mixtures compared to water. Additionally, the volatility of all EOs was lower in ChCl:U DES:water 70:30 wt% compared to pure DES, both containing CDs. Altogether, these results proved the efficiency of the combined formulation, containing DES and CDs, in retaining EOs and confirmed the beneficial impact of the presence of 30 wt% water when CD is employed.

Then, the retention ability of different CDs (β-CD and HP-β-CD) in water and in DES:water 70:30 wt% was evaluated towards the twenty selected EOs (Error! Reference source not found.). The total areas are normalized to the areas obtained in water alone. Due to its low aqueous solubility, a β-CD aqueous solution of 1 wt% was used [34], leading to weaker retention ability for all EOs than HP-β-CD (10 wt%), as could be expected from the greater amount of CDs cavities available in such more concentrated solution (Fig. 3; Fig. S2 in SI).

ChCl:U DES:water 70:30 wt% also showed a significant retention ability for all EOs. This could be due to the moderate decrease in the polarity of the medium compared to water upon DES addition leading to the retention of EOs components [18]. However, this formulation was less efficient than that of both CDs aqueous solutions. This suggests that the influence of the inclusion phenomena on the retention of EOs was more pronounced than the polarity of the mixture. Thus, ChCl:U DES:water 70:30 wt% could be used in preparations where a reduced amount of water is required.

Similar EOs retention abilities were observed when high CD concentration were used (HP-β-CD = 10 wt%) both in water or in ChCl:U DES:water 70:30 wt%. This indicated that at high CD content, the type of the solvent didn't significantly affect the complexation ability. In addition, since a higher amount of native β-CD could be dissolved in ChCl:U DES:water 70:30 wt% compared to water [35], 10 wt% of β-CD were dissolved in this mixture. The same efficiency of both 10 wt% β-CD or HP-β-CD was detected in ChCl:U DES:water 70:30 wt%. This showed that the CD type did not significantly affect the retention ability of the mixture.

Retention of aromas in DES:water:CD mixtures

Since EOs components present a great variety of structures and chemical functions, the CD/aromas complexation was checked in the optimized non-conventional media: ChCl:U DES:water 70:30 wt%. Therefore, the retention of twenty-one aromas was studied in ChCl:U DES:water 70:30 wt% in the absence and presence of CDs and compared to water in the absence and presence of CDs (Error! Reference source not found.). The area is normalized to the area obtained in water alone for each aroma.

As observed with EOs, the obtained results showed that the use of a high CD content led to a very important decrease in the volatility of all aromas, whatever the type of CD (β-CD or HP-β-CD) or that of the medium (water or DES:water 70:30 wt%) are.

Also, no discrimination in aromas retention was observed in the new mixture whatever the type of the CDs. This could be due to the high concentration of CD used and to the high ability of DES to solubilize aromas, thus retaining them. It is stated that the higher the ability of compounds to form hydrogen bonds with DES, the higher is their solubility, which was obtained for example with glucose solubilized in ChCl:ethylene glycol DES [36]. In addition, it should be noted that the encapsulation of guests in the CD cavity influences more on the aromas retention. This phenomenon depends not only on the hydrophobicity of the molecules (LogP values), but also on their molecular volume that should fit the CD cavity [4] (Fig. 4; Fig. S3).

Then, the complexation curves of all the CD/aroma complexes in DES:water 70:30 wt% mixture were constructed. Figure 5 shows, as example, the complexation curves of β-CD/β-citronellol and HP-β-CD/β-citronellol.

The obtained complexation curves confirmed the formation of inclusion complexes with a 1/1 (CD/aroma) stoichiometry between all studied CDs and aromas in this non-conventional medium [28, 37]. Then, the formation constants (K_f) values of all CD/aroma inclusion complexes were calculated and listed in Table 2 in comparison to those found from literature in water. Lower K_f values were obtained in the DES:water 70:30 wt% mixture as compared to water. This decrease could be mostly due to the lower polarity of the DES:water mixture in comparison to water, which induced the solubilization of the aromas in the solvent rather than their encapsulation in the CDs cavities. Similar tendencies were observed in literature for other aromas and volatile organic compounds (VOCs) [18–23]. The K_f value of β-CD/toluene, for example, decreased from 287 M^{-1} in water to 79 M^{-1} in hydrated

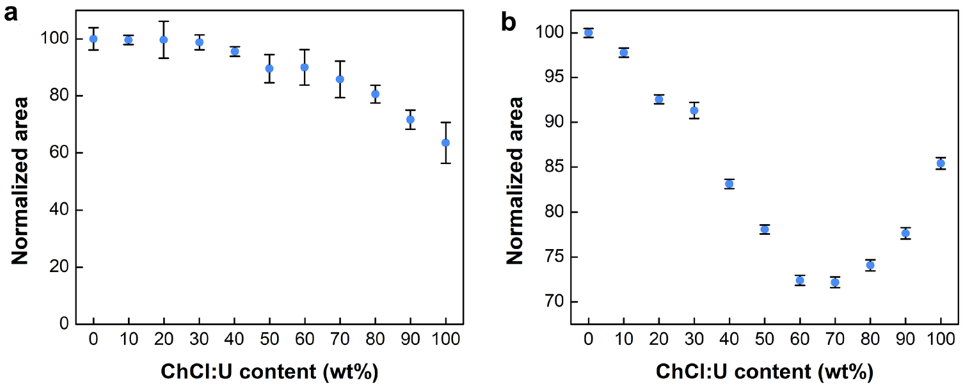


Fig. 1 Normalized areas of *Rosmarinus officinalis L.* EO, obtained from SH-GC analysis at 30 °C as a function of the ChCl:U DES content (wt%), **a** in the absence of CD where the reference mixture is water and **b** in the presence of 10 wt% of HP-β-CD where the reference mixture is water containing 10 wt% HP-β-CD

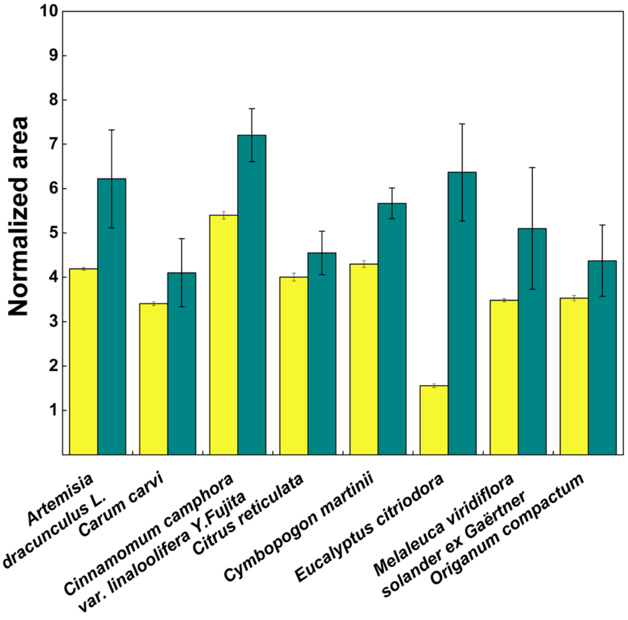


Fig. 2 Normalized area of EOs, obtained from SH-GC analysis, in ChCl:U DES:water 70:30 wt% with 10 wt% HP-β-CD (yellow histograms) and in pure ChCl:U DES with 10 wt% HP-β-CD (green histograms), at 30 °C. Water is used as reference

reline [20]. Also, the observed solvent effect was similar to that detected with other solvents such as ethanol and DMSO [11]. The K_f value of β-CD/*trans*-anethole decreased to 36 and 73 M^{-1} in DMSO:water 35:65 wt% and ethanol:water 35:65 wt%, respectively (K_f of β-CD/*trans*-anethole in DES:water 70:30 wt% equal to 39 M^{-1}).

Conclusion

This study aimed to examine the retention of twenty EOs and twenty-one aromas in non-conventional medium composed of DES, water and CDs. The results showed that the combination of CDs and ChCl:U DES:water 70:30 wt% enhanced the retention of all EOs and aromas compared to water alone. The formation of inclusion complexes with a 1:1 (CD:aroma) stoichiometry between all studied CDs and aromas in ChCl:U DES:water 70:30 wt% was proved to be the main mechanism responsible of such efficient volatility reduction. However, lower formation constants (K_f) values were obtained in ChCl:U DES:water 70:30 wt% as compared to water. The obtained results showed that DES:water:CD mixtures could constitute new solvents for the retention and solubilization of EOs and aromas and could be used in different domains.

Experimental section

Materials

Choline chloride (ChCl, 98%) was purchased from Sigma-Aldrich, China. Urea (U, 99%) was purchased from Sigma-Aldrich, USA. β-CD was provided by Wacker-Chemie, Lyon, France. Hydroxypropyl-β-CD (HP-β-CD, MS = 0.65) was provided by Roquette Frères, Lestrem, France. Citronellal was provided by Merck group, Germany. (−)-Terpinen-4-ol, *trans*-anethole, *p*-cymene and (R)-(−)-verbenone were purchased from Acros Organics, France. Geraniol, (+)-limonene, (I)-linalool, (1,8)-cineole, (1S)-(−)-α-pinene and (1S)-(−)-β-pinene were provided by Aldrich-Chemie, France. β-Citronellol, γ-terpinene, carvacrol, estragole, α-terpinene, citral (mixture of geranial and neral) and (1R)-(+)-camphor were purchased from Sigma-Aldrich, France. (S)-(+)-Carvone and geranyl acetate were provided by Alfa Aesar, France. All EOs were provided by Herbes et Traditions, Comines, France. The composition of the various EOs is provided in Table 1 (data provided by Herbes et Traditions). ChCl was dried at 60 °C for at least 2 weeks before use. All other compounds were used as received. Distilled water was used throughout this work.

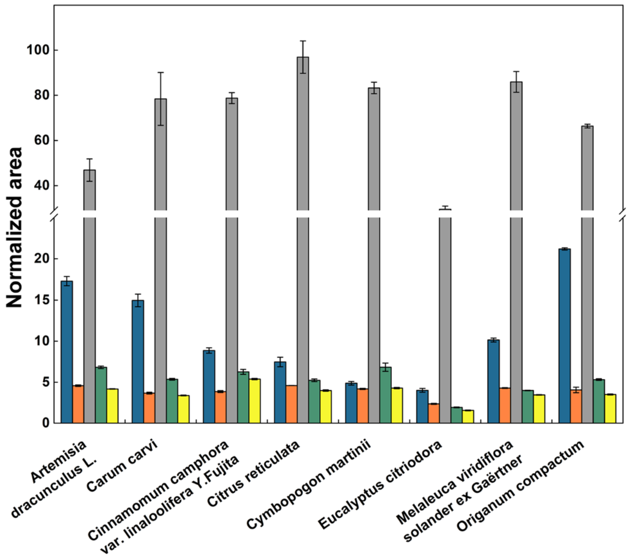


Fig. 3 Normalized areas of EOs, obtained from SH-GC analysis, in five different formulations, water with 1 wt% β-CD (blue histograms), water with 10 wt% HP-β-CD (orange histograms), ChCl:U DES:water 70:30 wt% (grey histograms), ChCl:U DES:water 70:30 wt% with 10 wt% β-CD (green histograms) and ChCl:U DES:water 70:30 wt% with 10 wt% HP-β-CD (yellow histograms), at 30 °C. Water is used as reference

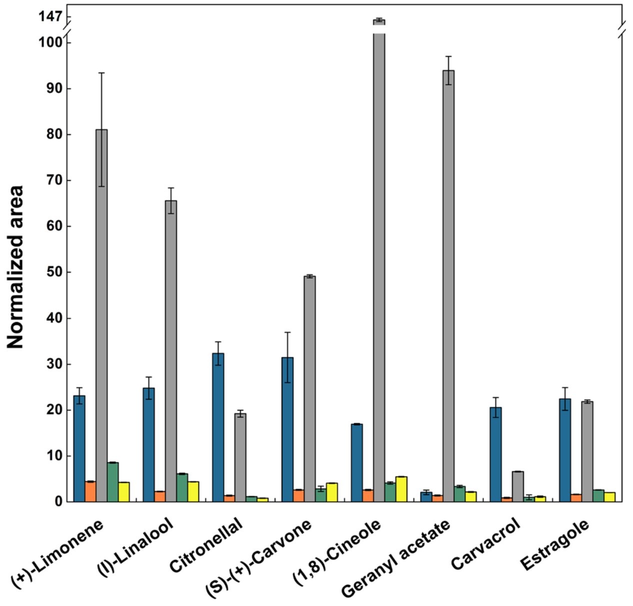


Fig. 4 Normalized areas of the major aromas, obtained from SH-GC analysis, in five different formulations, water with 1 wt% β-CD (blue histograms), water with 10 wt% HP-β-CD (orange histograms), ChCl:U DES:water 70:30 wt% (grey histograms), ChCl:U DES:water 70:30 wt% with 10 wt% β-CD (green histograms) and ChCl:U DES:water 70:30 wt% with 10 wt% HP-β-CD (yellow histograms), at 30 °C. Water is used as reference

Preparation of deep eutectic solvent

ChCl:U DES was prepared using the heating method by mixing ChCl and U in a 1:2 molar ratio under stirring at 60 °C until the formation of a clear and homogenous liquid. The water content of DES was determined using the Karl Fisher titration method (Mettler Toledo DL31) and was equal to 0.049%.

Retention studies

The retention ability of water, aqueous solutions of CDs, ChCl:U DES, and their combination towards twenty EOs and twenty-one aromas was evaluated using SH-GC.

Influence of water content in DES:water:CD mixtures on the retention of EOs

ChCl:U DES:water mixtures were prepared using various DES wt% ranging from 0 to 100 wt% and introduced to vials containing or not HP-β-CD (10 wt%). *Rosmarinus officinalis L.* EO (99 ppm) was then added to all vials. After equilibrium at 30 °C, the vials were subjected to SH-GC analysis. For the other nineteen EOs, experiments were only carried out in water as well as in pure ChCl:U DES and ChCl:U DES:water 70:30 wt%, both in the presence of 10 wt% of HP-β-CD.

Retention of various EOs and aromas in DES:water:CD mixtures

3 ml water or ChCl:U DES:water 70:30 wt% were introduced to vials containing or not β-CD or HP-β-CD. The final CD wt% was equal to 10 wt% except for β-CD in water (1 wt%) because of its limited aqueous solubility. Then, an appropriate amount of EO (99 ppm) or aroma (49.5 ppm) was added to all mixtures. Vials were then equilibrated at 30 °C and subjected to SH-GC analysis.

Results for EOs were expressed as:

$$Normalized\ area\ (\%) = \frac{\sum A_m}{\sum A_0} \times 100 \quad (1)$$

where ΣA_m and ΣA_0 stand for the sum of peak areas of the EOs components in the studied mixtures and in water, respectively.

And results for aromas were expressed as:

$$Normalized\ area\ (\%) = \frac{A_m}{A_0} \times 100 \quad (2)$$

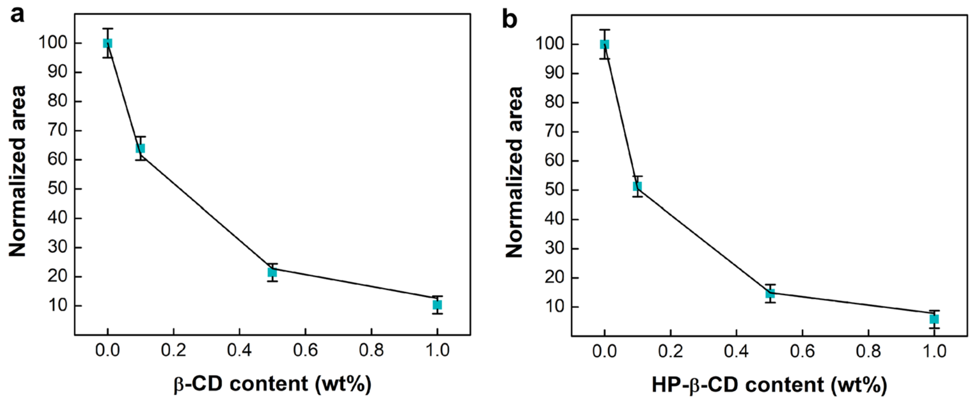


Fig. 5 Complexation curves of a) β-CD/β-citronellol and b) HP-β-CD/β-citronellol in ChCl:U DES:water 70:30 wt% along with the theoretical fitted curves (full line), at 30 °C. ChCl:U DES:water 70:30 wt% in the absence of CDs was the reference mixture

Table 2 Formation constant (M^{-1}) values of β-CD/aroma and HP-β-CD/aroma inclusion complexes obtained in ChCl:U DES:water 70:30 wt% and in water at 30 °C

Aromas	ChCl:U DES:water 70:30 wt%		Water	
	β-CD	HP-β-CD	β-CD	HP-β-CD
Hydrocarbons				
p-Cymene	116	167	2525[a]	2230[a]
(+)-Limonene	244	478	2605[a]	3076[a]
(1S)-(−)-α-Pinene	257	267	2540[a]	1361[a]
(1S)-(−)-β-Pinene	394	551	4646[a]	1742[a]
α-Terpinene	102	218	–	–
γ-Terpinene	155	360	1640[a]	1554[a]
Alcohols				
β-Citronellol	716	1497	3141[b]	2578[b]
Geraniol	313	635	528[b]	712[b]
(l)-Linalool	176	196	1058[a]	675[a]
(−)-Terpinen-4-ol	314	385	–	–
Aldehydes				
Citronellal	177	303	1523[a]	815[a]
Geranial	61	50	–	1560[b]
Neral	75	86	–	1560[b]
Ketones				
(1R)-(+)-Camphor	1120	837	2058[c]	1280[c]
(S)-(+)-Carvone	110	148	180[b]	–
(R)-(−)-Verbenone	177	229	–	–
Oxide				
(1,8)-Cineole	361	329	615[b]	334[b]
Ester				
Geranyl acetate	689	794	–	–
Phenol				
Carvacrol	63	165	2620[b]	2154[b]
Phenylpropanoids				
trans-Anethole	39	67	630[c]	1042[c]
Estragole	46	120	987[d]	1508[d]

[a] [4]

[b] [6]

[c] [8]

[d] [38]

where A_m and A_0 stand for the peak area of each aroma in the studied mixtures and in water, respectively.

Determination of the formation constants (K_f)

The formation constants (K_f) of the CD/aroma inclusion complexes were determined using a SH-GC titration method developed in our laboratory for volatile organic compounds and using an algorithmic calculation [39, 40]. Aromas (49.5 ppm) were added to 3 mL of ChCl:U DES:water 70:30 wt% containing increasing wt% of CDs (β-CD or HP-β-CD) (0, 0.1, 0.5 and 1 wt%). Vials were then equilibrated at 30 °C and subjected to SH-GC analysis. The complexation curves, representing the normalized area as a function of CD content, were plotted. K_f values were calculated using an algorithmic treatment.

Chromatographic conditions

All measurements were carried out with a Thermo Scientific™ TriPlus™ 500 Headspace Sampler coupled to TRACE™ 1300 Series GC equipped with a flame ionization detector and P/N 260E113P column (TR-5; 7 m long; 0.32 mm ID; 0.25 mm film thickness) using nitrogen as carrier gas. The GC column temperature conditions were set as follows: initial temperature of 50 °C for 2 min, increased to 200 °C at 5 °C.min^{-1}, then hold for 2 min, giving a total runtime of 34 min. Each experiment was repeated 3 times.

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Author contributions L.N. prepared all figures and tables.L.N and M.K. wrote the main manuscript.All authors reviewed the main manuscript.

Declarations

Competing interests The authors declare no competing interests.

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