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Deep eutectic solvents as absorbents for VOC and VOC mixtures in static and dynamic processes

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Abstract

Volatile organic compounds (VOCs) are primary air pollutants emitted directly from industries with adverse health effects and environmental impacts. Absorption is an attractive method to treat industrial exhaust loaded with VOCs, but most actual absorbents are often toxic and non-biodegradable. This work aims to evaluate deep eutectic solvents (DESs) as absorbents for VOCs using static and dynamic processes. The determination of vapour-liquid partition coefficient was performed for nine VOCs, from different chemical families, in eight hydrophilic and hydrophobic DESs, at different temperatures. The influence of VOC mixtures on DESs absorption capacities was determined for two different mixtures. DESs showed high absorption capacities for a variety of VOCs, without saturation even at high VOC concentration. The absorption capacities of DESs were also evaluated using a dynamic set-up which simulated an industrial absorption column. This set-up allows the modulation of the VOC flow rate, water content and column temperature. Both static and dynamic results are in good agreement. The DES based on tetrabutylammonium bromide and decanoic acid displayed high absorption capacities and versatility for the different tested VOCs, with a maximum enhancement of absorption reaching 60000-folds for 1-decene at 303 K, compared to water. The regeneration of the absorbent was carried out by several absorption/desorption cycles or after water removal, without loss of absorption capacity. The overall results show that DESs have characteristics that allow them to be considered as promising solvents for VOCs absorption.

Keywords: Deep eutectic solvents, volatile organic compounds, absorption, regeneration

Abbreviations: CDs: cyclodextrins; ChCl: choline chloride; Dec: decanoic acid; DCM: dichloromethane; DESs: deep eutectic solvents; EG: ethylene glycol; G: glycerol; HBD: hydrogen bond donor; ILs: ionic liquids; Lev: levulinic acid; MEK: methylethylketone; PRV: phase ratio variation; SH-GC: static headspace-gas chromatography; TBABr: tetrabutylammonium bromide; TBPBr: tetrabutylphosphonium bromide; U: urea; VOCs: volatile organic compounds; VPC: vapour phase calibration.

1. Introduction

Because of their relatively high vapour pressures at room temperature, volatile organic compounds (VOCs) are among the most common indoor air pollutants [1,2]. VOCs are emitted from a wide array of products including solvents, paints and lacquers, cleaning supplies, building materials, furnishings, office equipment, glues and adhesives [3] and so they can easily be concentrated in domestic or industrial environments. Upstream treatments are foreseeable in industrial settings but elsewhere VOC concentration can only be reduced through air treatment using adsorption, condensation, absorption, membrane permeation, oxidation (thermal or catalytic) or biological processes [4–10]. The choice of the most appropriate treatment depends on the nature of the VOCs, their concentration and other factors such as safety or economic considerations. Absorption technologies are commonly used with the advantage of easy coupling with biological or photocatalytic processes to enhance the overall performance [2,11–13]. The design or optimisation of a VOC absorption process always requires the appropriate choice of the absorbent and of the scrubber.

The absorbent is primarily chosen on the basis of the vapour-liquid partition coefficient that describes the distribution of the volatile compound between the liquid and the vapour phase [14,15]. Other relevant properties are its volatility, fluidity, chemical stability, compatibility with the equipment, price and toxicity. Tested absorbents for VOCs include aqueous solutions, heavy organic solvents (silicone oils, adipates, phthalates...), and, more recently, ionic liquids (ILs) [16–19].

ILs show appealing physical properties as absorbents. They have good absorption capacities for VOCs, negligible vapor pressure and good thermal and chemical stabilities, which enable easy regeneration [17,20,21]. ILs can be designed for the capture of the more common hydrophobic VOCs (including toluene) for which aqueous solutions are less efficient and furthermore some have showed promising performances for persistent fluorinated VOCs [22,23]. Bedia and co-workers studied *in silico* more than 200 ILs and found that alkyimidazolium bis(trifluoromethylsulfonyl)imide ILs, $[C_nC_1Im][NTf_2]$ with $n > 6$ are the most suitable absorbents for toluene [24]. Rodriguez Castillo and co-workers evaluated the absorption of toluene and dichloromethane by measuring their partition coefficients in 23 hydrophobic ILs and their diffusion coefficients in four selected ILs. ILs appear in general as more performant than silicone oil for toluene but less for dichloromethane [17]. Recent studies have shown that performances similar to silicone oil are observed using different bio-based

ILs [25], vegetable or industrial oils for the absorption of hydrophobic and hydrophilic VOCs [26–28]. However, the cost and possible toxicity of ILs make their large-scale use still rare.

Deep eutectic solvents (DESs) are presented as promising complying to the challenges of VOCs air treatment [29,30]. DESs are liquid mixtures of two or more environmentally friendly, easily available compounds with tuneable properties [31–33]. In fact, DES can be prepared from non-toxic, non-volatile components and the mixtures can be designed to selectively absorb specific VOCs from gas mixtures. DESs are already proposed for large scale use in metal processing, catalysis, electrochemistry, extraction and separation processes [34–38] and, although they are not the only possible absorbents for VOCs capture, they surely need to be considered as promising in more sustainable air treatment processes for VOCs capture.

Moura and co-workers recently reviewed the literature on the solubility of gases in DESs and found that more than 85 different eutectic mixtures have been used as absorbents for 10 gases with solubilities spanning for one order of magnitude (when expressed as Henry's law constants), a behaviour explained by the different interactions between the gases and the eutectic mixtures [39]. Comparatively, studies evaluating DESs as VOCs' absorbents are still relatively rare. We have highlighted since 2017 the potential of DESs as absorbents of toluene, acetaldehyde and dichloromethane by studying the VOCs vapour/liquid partition in mixtures based on choline chloride, tetrabutylphosphonium and tetrabutylammonium salts mixed with urea, ethylene glycol, glycerol, levulinic acid and decanoic acid [9]. Toluene, considered as model VOC, has been thoroughly studied since 2019 with hydrophilic DESs based on choline chloride and glycols efficiently absorbing it from biogas [40]. COSMO modelling and experiments using a dynamic scrubber and model biogas mixtures showed that also hydrophobic DESs including long alkyl chain fatty acids (*i.e.* tetraethylammonium chloride:oleic acid (1:3) [41], lauric acid:decanoic acid [42], syringol:levulinic acid (1:1) [43]) lead to efficient physical absorptions of toluene with facile recovery and recyclability. The behaviour of the mixtures has been explained by favourable interactions of toluene with the components of the DES [41], in particular by the balance of H-bonding and van der Waals interactions between the DES components and the different volatile organics [43]. For siloxanes, which are efficiently removed from biogas by DESs composed of carvone and carboxylic acids, H-bonding was evidenced by NMR and FT-IR in a number of eutectics screened using COSMO-RS [44]. Mixtures of modified cyclodextrins (CDs) with levulinic acid form DESs analogues [45,46] that have been tested

for the capture of acetaldehyde, methylethylketone, dichloromethane and thiophene. The vapour-liquid partition coefficients were reduced by 250-fold compared to water while retaining absorption capacities after several absorption/desorption cycles. Chen and co-workers have found that thymol:decanoic acid 1:1 efficiently and reversibly capture acetone [47] proving that hydrophilic VOCs can also be absorbed by appropriately designed DES. The high absorption capacity is explained by the favourable interaction of the oxygen atom of acetone with the hydrogen atom of thymol.

We present an original study of the absorption of nine VOCs and their mixtures (that mimic real industrial effluents) by eight DESs, both hydrophilic and hydrophobic. In each case, the performances of the DES are compared with those of water at different temperatures. This original approach is accompanied by the evaluation of the different DESs in a laboratory-scale dynamic scrubber to treat air streams with different VOC concentrations, at different temperatures and distinct water contents. We went further to study the regeneration of the DESs by evaluating their performance in successive absorption/desorption cycles.

2. Materials and methods

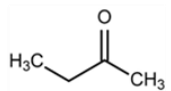
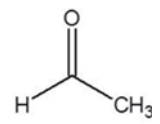
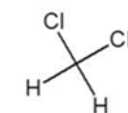
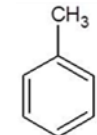


2.1. Chemicals

Choline chloride (ChCl) (98.0%), tetrabutylammonium bromide (TBABr) (98.0%), tetrabutylphosphonium bromide (TBPBr) (98.0%), levulinic acid (Lev) (98.0%), decanoic acid (Dec) (98%), glycerol (G) (99.5%), ethylene glycol (EG) (99.8%), urea (99%), methylethylketone (99.5%), toluene ($\geq 99.5\%$), benzene ($\geq 99.0\%$), ethylbenzene (99.0%) and *n*-heptane (99.0%) were purchased from Sigma-Aldrich, France. Acetaldehyde (99.5%), *o*-xylene (99.0%), dichloromethane (99.8%) and 1-decene ($\geq 99.0\%$) from Across Organics, France. ChCl was dried by placing it in an oven at 333 K for 2 weeks prior to use, the other compounds were used as received. Table 1 gathers the structures and the water solubility of the studied VOCs.

Table 1

Structure, vapour pressure at 303.15 K and water solubility at 293.15 K of the studied VOCs.

Methyl-ethylketone	Acetaldehyde	Dichloromethane	Toluene	<i>n</i> -Heptane	1-decene
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Vapour pressure (kPa), 303.15 K	15.46	144.1	70.52	4.88	7.77	0.30
Water solubility (mol.L ⁻¹) 293.15 K	3x10 ²	1x10 ²	2x10 ¹	5x10 ⁻¹	3x10 ⁻³	1x10 ⁻⁴

2.2. Preparation of the eutectic mixtures

DESs were prepared by stirring the two compounds, at the desired molar ratio at 333 K until a homogeneous colourless liquid was obtained. The eight DESs prepared in this study are listed in Table 2.

Table 2

Composition and acronyms of the DESs prepared during this work.

DES	Component 1 (Salt)	Component 2 (hydrogen bond donor, HBD)	Molar ratio
ChCl:U	Choline chloride	Urea	1:2
ChCl:EG		Ethylene glycol	1:2
ChCl:G		Glycerol	1:2
ChCl:Lev		Levulinic acid	1:2
TBPBr:EG	Tetrabutylphosphonium bromide	Ethylene glycol	1:2
TBPBr:G		Glycerol	1:1
TBPBr:Lev		Levulinic acid	1:6
TBABr:Dec	Tetrabutylammonium bromide	Decanoic acid	1:2

2.3. Partition coefficient measurement

The tendency of a species to distribute between two phases in equilibrium can be expressed as the ratio of the mole fractions of the component in each phase. For a liquid mixture in equilibrium with its vapour, this constant is normally called *K*, the vapour-liquid equilibrium ratio or the vapour-liquid partition coefficient:

$$K \equiv \frac{y_i}{x_i} \quad (1)$$

Where y_i is the mole fraction in the vapour in equilibrium with a liquid solution with a mole fraction concentration of x_i . At the conditions of equilibrium, each species has the same fugacity in each phase and so

$$f_i^V = f_i^L \leftrightarrow \phi_i y_i P = \gamma_i x_i f_i^0 \quad (2)$$

Where f_i^V , f_i^L and f_i^0 are the fugacities of component i in the vapour phase, in the liquid phase and in an appropriate standard state, respectively; ϕ_i is the fugacity coefficient and γ_i the activity coefficient [48].

The vapour-liquid partition coefficient, defined in equation (1) can also be expressed in volumetric concentrations as: [49]

$$K = \frac{C_G}{C_L} \quad (3)$$

where C_G is the concentration of the solute in the vapour phase in equilibrium with a liquid solution of concentration C_L in the solute.

The value of K at different temperatures for the VOCs in the studied DESs was determined experimentally by static headspace-gas chromatography (SH-GC) using a combination of the phase ratio variation method (PRV) for the VOCs in water and the vapour phase calibration method (VPC) for the VOCs in the DESs [9,50]. All measurements were carried out with an Agilent G1888 headspace sampler coupled with a Perkin Elmer Autosystem XL gas chromatography equipped with a flame ionization detector and a DB624 column using nitrogen as carrier vector. The static headspace settings were as follows: an oven temperature of 303 K with an equilibrium time of 120 min, 333 or 353 K with an equilibrium time of 240 min. The transfer line temperature was set at 523 K.

For the determination of the vapour-liquid partition coefficients of the VOCs in water, several vials were prepared containing different amounts of water to which the same amount of VOC was added.

Using essentially the PRV method as described by Kolb and Etre [50], the values of K were

determined at 303, 333 and 353 K, by the relationship between the reciprocal chromatographic peak areas and the vapour-liquid volumetric ratio (V_G/V_L , with V_G and V_L being the vapour volume and the liquid volume, respectively):

$$\frac{1}{AV_L} = \frac{1}{\alpha V_L} + \frac{1}{\alpha K} \quad (4)$$

Where A is the peak area, α is a constant incorporating several parameters and K is the vapour-liquid partition coefficient, directly calculated from the ratio of the slope and intercept of the fit of the experimental data obtained after allowing a vapour-liquid equilibrium time of 30 min in the static headspace oven.

For the study of the VOCs in the DES solutions, the VPC method was used. First, several vials with a same water volume and different amounts of VOCs were prepared in order to draw a calibration curve relating the concentration of VOC in the vapour phase, C_G , with the area under the chromatographic peak, A , using the previously determined vapour-liquid partition coefficients of the VOCs in water.

$$C_G = \frac{n_{VOC}K}{V_L + KV_G} \quad (5)$$

where n_{VOC} is the total amount of VOCs added to each vial. Since this concentration C_G is proportional to the area under the chromatographic peak, we can draw the calibration curve between the area and the gaseous concentration.

In a second series of experiments, different amounts of VOCs were added to vials containing the same amount of DES. These vials were then sealed and incubated at 303, 333, 353 K, under stirring for 24 hours, to obtain well equilibrated solutions, before their analysis by SH-GC. The experimental chromatographic peak areas allowed the determination of C_G and the concentration of the VOC in DES, C_{DES} , is calculated from the mass balance. The vapour-liquid partition coefficients of the VOCs in the different DESs were calculated using these two concentrations. Then the absorption capacities of the DESs were determined. All the experiments were performed in triplicate and the partition coefficients did not vary more than 5 %.

After analysis, vials were uncapped and stirred at 333 K during 48 hours. The absence of detectable VOC was checked by SH-GC.

FTIR spectra of fresh DESs, VOCs and VOCs loaded DESs were recorded using a BRUKER Vertex 70 FT-IR instrument. 64 spectra were averaged from scans ranging between 3500 and 400 cm^{-1} with a 2 cm^{-1} resolution.

2.4. Dynamic absorption

A lab-scale set-up was developed in order to mimic the industrial absorption process generally based on a scrubber (Fig. 1) [51]. The contaminated air was generated by injecting liquid VOC into a nitrogen stream. The injection was performed by mean of a Hamilton syringe mounted on a syringe dispenser. Flow rate of the stream to the mixing chamber was controlled by a mass flow meter and set to 35 $\text{L}\cdot\text{hr}^{-1}$. The loaded stream then flowed to the absorption bubbling system filled with water or DES. Inlet and outlet gases were analysed by a total hydrocarbon analyser (COSMA Graphite 655). The impinger was filled with around 30 g of absorbent and thermostated using a controlled heating cable coupled to a temperature probe.

Each experiment consists of two steps: (i) absorption, the loaded gas flows by the by-pass, and is analysed by the total hydrocarbon analyser. Once the concentration is stable, valves are switched and air flows through the bubbling vessel. Outlet gas concentration is followed until absorbent saturation, which corresponds to a gas concentration equal to the inlet gas concentration measured before and stable in time; (ii) desorption, the VOC source is removed from the system and nitrogen gas is used to strip and regenerate the DES. The integration of the obtained curves allows the determination of the amount of VOC trapped in the absorbent. The curves representing the absorption and desorption processes are shown in Fig.S1 in the supplementary information (SI).

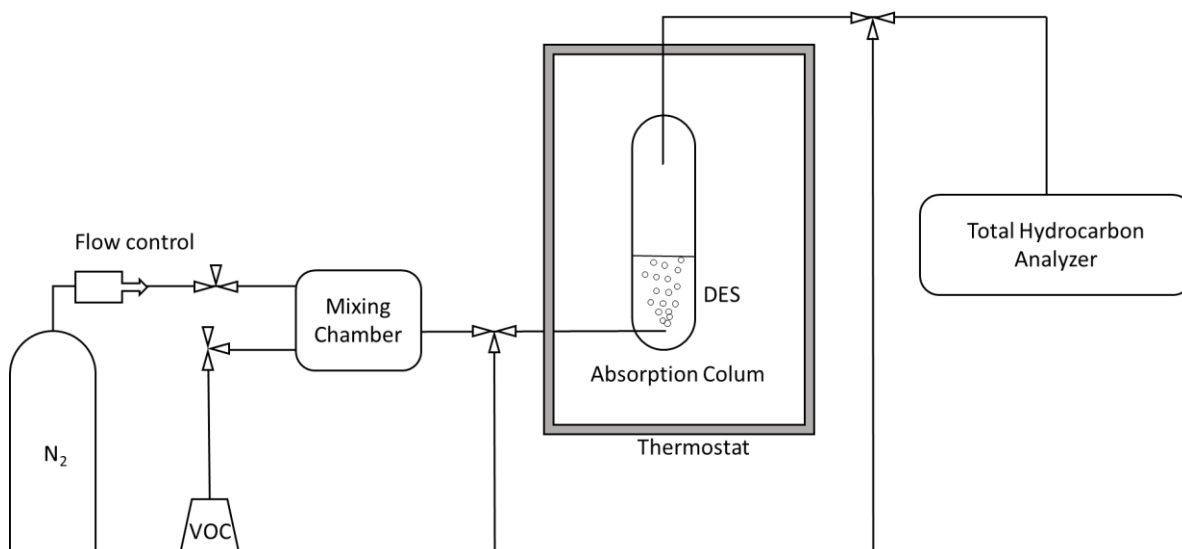


Fig. 1 Laboratory scale dynamic absorption set-up

The effect of initial VOC concentration (obtained with a syringe dispenser rate of 36, 73 and 146 $\mu\text{L}\cdot\text{hr}^{-1}$), temperature (303, 313, 323 and 333 K) and water addition (10, 15, 20, 30 and 50 % *wt*) on the absorption of the VOCs were investigated. The absorption capacities of the DESs after water removal were also evaluated.

3. Results and discussion

3.1. Partition coefficients

The vapour-liquid partition coefficients (K) determined at 303 K for the different VOCs in water and in eight DESs, along with the $K_{\text{H}_2\text{O}}/K_{\text{DES}}$ ratio, are listed in Table 3. A lower value of K is linked to a better absorption of the VOC by the liquid phase. The $K_{\text{H}_2\text{O}}/K_{\text{DES}}$ ratio allows a comparison of the performance of the DES absorbents with that of water, values higher than 1 meaning that the VOC is better absorbed by the DES, the higher the ratio the more performant the DES when compared with water.

All the VOCs are better absorbed by the studied DESs than by water, except for methylethylketone in the case of ChCl-based eutectics and TBPBr:EG. This is a surprising result when compared with acetaldehyde as both VOCs show a similar K in water, but different behaviour in the studied DESs. For methylethylketone, only three DESs perform better than water as absorbents (TBPBr:G, TBPBr:Lev and TBABr:Dec) whereas all DESs are better absorbents than water for acetaldehyde.

When compared to water, the DESs with the best absorption capacities for dichloromethane are those based on alkylphosphonium or alkylammonium salts with K_{H_2O}/K_{DES} ratios as high as 35 for TBPBr:EG. It has been previously shown that dichloromethane is better absorbed in hydrophobic ILs based in ions with long alkyl chains than in water [17] or in silicone oils [26]. This trend is also identified in our study.

Toluene is often considered as a model for hydrophobic and aromatic VOCs and so it has been frequently studied. In this work, we clearly identified two groups of DESs as absorbents: those based in ChCl and those based in tetrabutylphosphonium or ammonium salts, the latter showing partition coefficients one order of magnitude lower than the former. Song and co-workers have shown, using COSMO-SAC calculations, that DESs containing long alkyl chain salts exhibit higher toluene absorption capacities [41]. More recently, Chen and co-workers have demonstrated experimentally that longer alkyl chains in both components of the DES, especially when they include carboxylic acids, contribute to increase toluene absorption capacities [42]. This is in good agreement with our study where we have measured particularly low partition coefficients for toluene in the DESs containing long chain carboxylic acids (TBPBr:Lev and TBABr:Dec) with considerable improvement when compared with water – K_{H_2O}/K_{DES} of 200 and 280, respectively (Table 3).

Table 3

Vapour-liquid partition coefficients (K) for different VOCs in water and in DESs at 303 K, and corresponding K_{H_2O}/K_{DES} ratios.

	Methylethylketone		Acetaldehyde		Dichloromethane		Toluene		<i>n</i> -Heptane		1-decene	
	$\frac{K}{10^{-4}}$	$\frac{K_{H_2O}}{K_{DES}}$	$\frac{K}{10^{-4}}$	$\frac{K_{H_2O}}{K_{DES}}$	$\frac{K}{10^{-4}}$	$\frac{K_{H_2O}}{K_{DES}}$	$\frac{K}{10^{-4}}$	$\frac{K_{H_2O}}{K_{DES}}$	$\frac{K}{10^{-4}}$	$\frac{K_{H_2O}}{K_{DES}}$	$\frac{K}{10^{-4}}$	$\frac{K_{H_2O}}{K_{DES}}$
H ₂ O	55	1	51	1	1400	1	2500	1	270000	1	250000	1
ChCl:U	460	0.1	0.1	500	550	2.5	960	3	110000	2.5	12000	20
ChCl:EG	840	0.06	1.0	50	340	4	220	10	180	1500	6400	40
ChCl:G	230	0.2	0.5	130	370	4	540	5	180	1500	11000	25
ChCl:Lev	65	0.9	4.0	15	80	17	50	70	2700	100	290	860
TBPBr:EG	130	0.4	1.3	40	40	35	18	140	470	600	11	23000
TBPBr:G	23	2.4	0.4	130	53	26	40	65	1100	250	120	2000
TBPBr:Lev	40	1.3	1.7	30	60	23	13	200	340	800	15	17000
TBABr:Dec	40	1.3	4.0	15	50	30	9.0	280	33	8000	4.0	60000

Figure 2 presents $K_{H_2O}/K_{solvent}$ ratios reported for toluene in different families of solvents, including those studied herein. When compared with water, two ILs show the best performances explained by favourable interactions (van der Waals, π - π) between toluene, the aromatic ring and the long alkyl-side chains of the cations [17]. The performance of these two absorbents is closely followed by the lauric acid:decanoic acid DES reported by Chen and co-workers [42]. Other DESs, including those tested in this work, perform as well as organic solvents and silicone oils [26,52]. Remarkably, an enhancement of the capacity of DESs including CDs has been reported and explained by the formation of a complex CD/toluene [45,46].

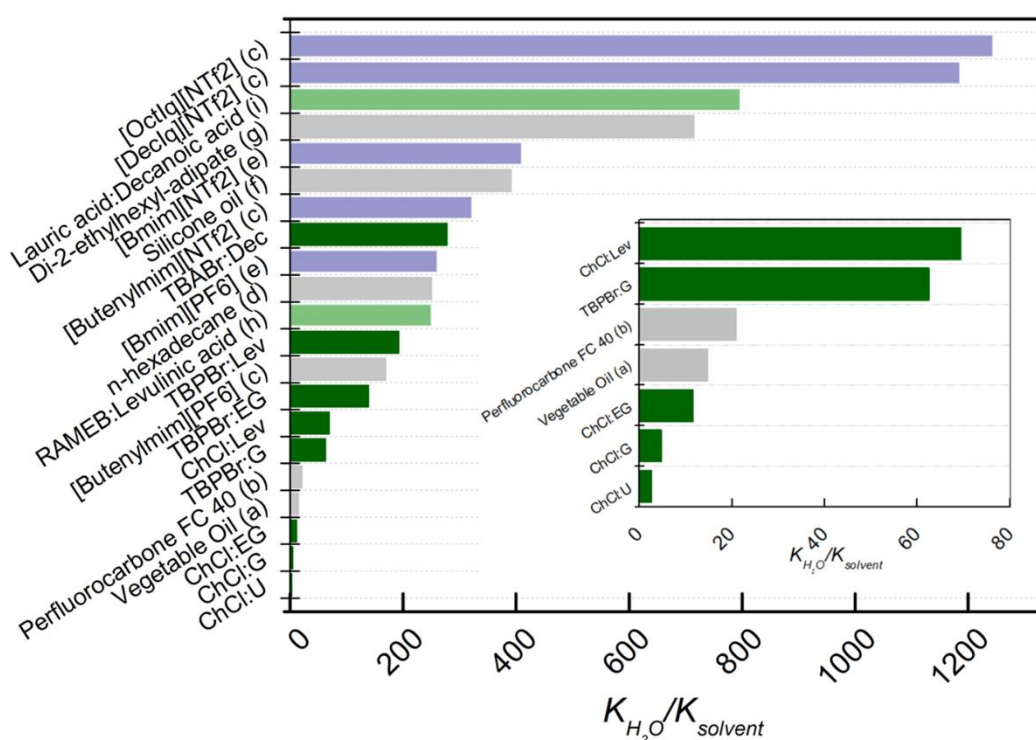


Fig. 2 Comparison of the ratio of the partition coefficient in water and in various solvents for toluene, with grey bars for organic solvents, blue bars for ionic liquids, light green bars for DESs from the literature and green bars for the DESs in the study. All the measurements from the literature are done at 298 K except for Panda and co-workers; Chen and co-workers and this study which are done at 303 K. [Octlq]:1-n-octylisoquinolinium; [Dectlq]:1-n-detylisoquinolinium; [NTf2]:bis(trifluoromethylsulfonyl)imide; [Bmim] : 1-n-butyl-3-methylimidazolium; [Butenylmim] :1-n-butenyl-3-methylimidazolium; [PF6]: hexafluorophosphate. (a) Hariz and co-workers [28], (b) Cesári and co-workers [52], (c) Rodriguez Castillo and co-workers [17], (d) Vuong and co-workers [53], (e) Quijano and co-workers [54], (f) Darracq and co-workers [16], (g) Quijano and co-workers [10], (h) Panda and co-workers [46] and (i) Chen and co-workers [42].

The linear hydrocarbons, *n*-heptane and 1-decene, show similar affinity profile as toluene for the tested DESs. However, higher K_{H_2O}/K_{DES} ratios are obtained for both compounds compare to toluene. The effectiveness of the DESs to absorb these hydrophobic VOCs seems to decrease when the number of hydroxyl groups present in the HBD increases as seen by comparing the *K* values in TBPBr:G and TBPBr:EG.

3.1.1. Effect of initial VOC concentration

We studied the absorption capacity of the DESs as a function of the initial concentration of VOC. Figure 3 represents the absorption capacities of three DESs in the case of toluene. The absorption capacities of the ChCl:Lev, TBPBr:Lev and TBABr:Dec DESs reached 5.7, 13.3 and 24.9 mg of toluene/g of DES for initial concentrations of toluene of 1200, 2700 and 5150 $g.m^{-3}$, respectively (Figure 3). The linear variation with the initial VOC concentration suggests a physical absorption that will facilitate the desorption and the reuse of the absorbent.

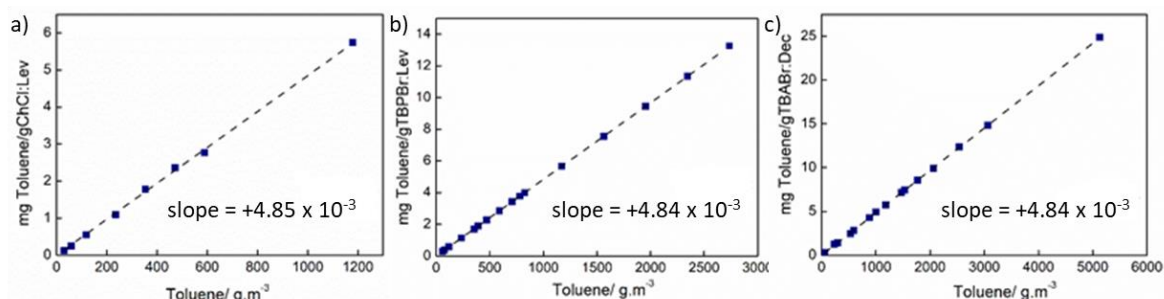


Fig. 3 Absorption capacity at 303 K of ChCl:Lev (a), TBPBr:Lev (b) and TBABr:Dec (c) for toluene at various initial concentrations.

The TBABr:Dec DES shows the highest absorption capacity for all studied VOCs. Table 4 gathers the VOCs absorption capacities of TBABr:Dec expressed in mg of VOC per g of the DES and in percentage.

The initial VOC concentration represents the highest possible amount of VOC added to the vial to allow the treatment of the chromatographical pic. Therefore, and under these conditions, all the studied DESs did not reached saturation. At least 97% of the total amount of VOCs could be absorbed. In the case of dichloromethane, the TBABr:Dec DES absorbed up to 37.26 mg per g of DES for an initial concentration of 5900 $g.m^{-3}$ of VOC.

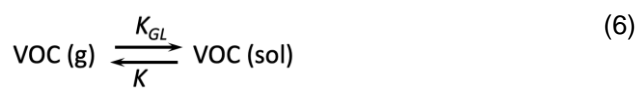
Table 4

Absorption capacity of TBABr:Dec for the tested VOCs at 303 K.

	VOC initial concentration / g.m ⁻³	Absorption capacity / mg VOC . g ⁻¹ TBABr:Dec	VOC Absorption / %
Methylethylketone	3540	13.69	98
Acetaldehyde	1180	4.492	99
Dichloromethane	5900	37.26	97
Toluene	5150	24.90	99
<i>n</i> -Heptane	885	4.202	98
1-Decene	4720	16.91	99

3.1.2. Effect of absorption temperature

The gas–liquid partition coefficients as defined by equation (3) can be regarded as an equilibrium constant between the VOC in the gas phase and dissolved in the liquid DES:



where VOC(g) is the VOC in the vapour phase with concentration C_G and VOC(sol) is the VOC dissolved in the liquid DES with concentration C_L . The variation of K_{GL} (or reciprocally K) with temperature can be interpreted in light of a van't Hoff type equation.

The partition coefficients, K , for acetaldehyde and toluene at three temperatures from 303 to 353 K are listed in Table 5 and represented in Fig. 4 for the studied DES. The highest VOC absorption by the DES is always observed at the lowest studied temperature, indicating an exothermic absorption. This corresponds to a negative enthalpy of the VOC transfer from the gas phase into the liquid solution, a tendency already observed in different absorbents [28,55–57]. The variation of enthalpy is related to the interactions between the solute and the solvent in the liquid solution whereas the variation of entropy reveals the changes in the solvent structure linked with the solute dissolution, both determining the partition of the VOC between the vapour phase and the solution:

$$\Delta G = -RT \ln K_{GL} = \Delta H - T\Delta S \quad (7)$$

where ΔG is the Gibbs energy involved in the transfer of the VOC from the gas phase to the solution, K_{GL} in the inverse of the partition coefficient defined in equation (3) and ΔH the variation of enthalpy associated with the transfer of the VOC from the gas phase into the liquid solution. R is the universal gas constant and T the temperature. When representing the $\ln K_{GL}$ as a function of the inverse temperature, a straight line should be obtained with a slope equal to $-\Delta H/R$ and an intercept equal to $\Delta S/R$, ΔS being the variation of entropy associated with the transfer of the VOC from the gas phase into the liquid solution.

The variations of enthalpy and entropy associated with the transfer of the VOCs to the different DES were thus calculated for the temperature range studied and are listed in Table 5. The values of ΔH and $T\Delta S$ are quite different for the different DESs, pointing towards different mechanisms of dissolution. The negative values of ΔH are a sign of favourable interactions of the VOC with the liquid DES but the enthalpic contribution to the absorption of the VOC is significantly different for the different DES.

In the case for acetaldehyde in ChCl:U, for example, the high VOC absorption is explained by favourable entropy and enthalpy of solvation, the latter being less negative than those observed for other DES. Acetaldehyde interacts more favourably with all the other DES when compared with ChCl:U with average values of ΔH in the 303–353 K temperature range varying from -41 to -15 kJmol^{-1} (compared to -9.8 kJmol^{-1} for ChCl:U) and following the order: TBPBr:Lev < ChCl:EG < TBPBr:G < TBABr:Dec < ChCl:Lev < ChCl:G. The partition of acetaldehyde between the gaseous phase and the DES (the average value in the 303–353 K temperature range) follows a different order: ChCl:G > TBPBr:G > ChCl:U > ChCl:EG > TBPBr:Lev > ChCl:Lev > TBABr:Dec, showing the VOC–DES interactions are not the only important point to consider when designing the best DES to absorb a given VOC. The case of ChCl:G is interesting as, although it is the most performant DES to absorb acetaldehyde, it does not show the most favourable enthalpic contribution, the entropy of absorption playing an important role as in the case of ChCl:U. The most favourable enthalpy of absorption is found for TBPBr:Lev but this DES is not the most performant to absorb the acetaldehyde as the entropic contribution in this case counteracts the favourable VOC–DES interactions.

A similar situation is observed for toluene in the DES studied. In this case, the interactions of the VOC with the DES, as expressed by the negative enthalpy of absorption, follow the order: ChCl:Lev < TBPBr \approx ChCl:EG < TBABr:Dec < ChCl:U \approx ChCl:G < TBPBr:G. The partition of toluene between the

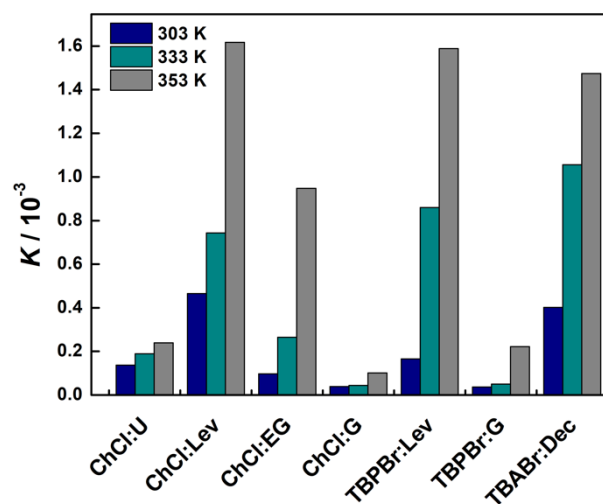
gaseous phase and the DES varies differently as: TBABr:Dec > TBPBr:Lev > TBPBr:G > ChCl:Lev > ChCl:EG > ChCl:G > ChCl:U showing that both the enthalpic and entropic terms need to be considered in the design of most effective DES to absorb toluene. The case of TBPBr:Lev is particularly interesting as the absorption of toluene is important but the enthalpy is not particularly favourable (when compared, for example, with ChCl:Lev), the absorption being explained in this case by the favourable entropic contribution.

Table 5

Partition coefficients for acetaldehyde and toluene in the DES at three different temperatures. Variation of enthalpy and entropy for the transfer of the VOCs from the vapour to the liquid DES phase, calculated at the average temperature of 330 K from the experimental data.

DES	$K/10^{-4}$			$\Delta H / \text{kJmol}^{-1}$	$-T\Delta S / \text{kJmol}^{-1}$	
	303 K	333 K	353 K			
	Acetaldehyde					
ChCl:U	0.14	1.89	2.39	-9.8	-14	
ChCl:Lev	4.66	7.43	16.2	-21	+1.8	
ChCl:EG	0.97	2.65	9.48	-39	+17	
ChCl:G	0.39	0.44	1.01	-15	+11	
TBPBr:Lev	1.65	8.60	15.9	-41	+21	
TBPBr:G	0.37	0.51	2.22	-30	+3.5	
TBABr:Dec	4.02	10.60	14.7	-24	+4.3	
	Toluene					
ChCl:U	960	$180 \times 10^{+1}$	$460 \times 10^{+1}$	-27	+22	
ChCl:Lev	50.0	250	369	-43	+31	
ChCl:EG	220	932	$132 \times 10^{+1}$	-33	+26	
ChCl:G	540	$185 \times 10^{+1}$	$230 \times 10^{+1}$	-27	+21	
TBPBr:Lev	13.0	50.0	138	-33	+19	
TBPBr:G	40.0	48.0	147	-21	+7.4	
TBABr:Dec	9.00	10.0	73.4	-29	+12	

a)



b)

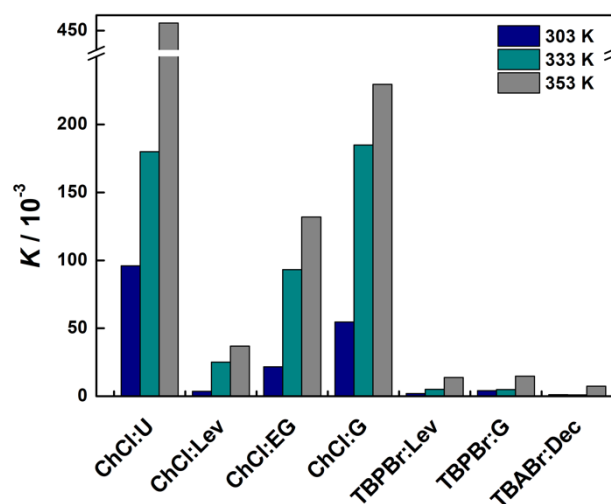


Fig. 4 Partition coefficient of acetaldehyde (a) and toluene (b) in the tested DESs at different temperature.

3.1.3. Absorption mechanism

To further explore the absorption mechanism, the DESs were examined by FTIR prior to and after VOC absorption. Spectra of the fresh and toluene-absorbed TBPBr:Lev and TBABr:Dec DESs are shown in Figure S2. Negligible changes were observed in peaks associated with -OH (3000 cm^{-1}), -C=O (1700 cm^{-1}) or -CH₃ (2900 cm^{-1}) stretching from the DES components after toluene absorption (Figure S4). Same observations could be done in the case of C=C stretching (1500 cm^{-1}), aromatic and alkyl C-H stretching ($3000\text{-}2900\text{ cm}^{-1}$) and C-H bending (700 cm^{-1}) for toluene. These results suggest that toluene undergoes a physical absorption, without formation of new chemical bonds with the DESs. The easy regeneration of the absorbent, as observed in Figure 10, also supports the

physical absorption of VOC in DESs. The analysis of the thermodynamic properties of absorption of the different VOCs by the DESs also shows a typical behaviour of a physical absorption with a balance between enthalpic effects, related with the interactions of the VOC with the DES components, and entropic effects that are connected with the structure of the solution. The data reported in Table 5 for toluene and acetaldehyde clearly show that the mechanisms of physical absorption differ from one DES to another as revealed by distinct balances between entropy and entropy of absorption.

These observations are in good agreement with previously results that underlined that only van der Waals or both hydrogen bonds and van der Waals interactions are the main driving forces for the removal of VOCs from gas streams [43,47].

3.1.4. Effect of VOC mixtures

Real gaseous effluent contains generally a wide variety of VOCs, however, literature lacks this kind of studies as they only focused on the absorption of one VOC. Therefore, we assessed the effect of mixture of VOCs on the partition coefficient of the individual VOCs. Two mixtures were studied: (i) BTEX (benzene, toluene, ethylbenzene and *o*-xylene) and (ii) DMTHDc (dichloromethane, methylethylketone, toluene, *n*-heptane and 1-decene). The first mixture is a usual industrial effluent that gathers four structurally similar aromatic hydrocarbons and the later gathers hydrophilic and hydrophobic VOCs from different chemical families with different physicochemical properties. Four DESs were evaluated for their absorption capacities of the mixtures: ChCl:U, ChCl:Lev, TBPBr:Lev and TBABr:Dec.

Fig. 5 represents the K values of the VOC individually or in the mixture at 303 K. In the case of BTEX mixture, it is clear that the K values are not affected by the presence of other VOCs (Fig. 5 a). This could be due to the structural analogy between the VOCs. Furthermore, the DESs maintain their high absorption capacity towards VOCs with the TBABr:Dec DES showing the highest absorption capacity leading to an decrease of ethylbenzene K values up to 30000 times compared to water.

In the case of the DMTHDc mixture, most of the K values are identical to the one obtained for the individual VOCs. Nonetheless, a significant variation of K values is observed in the case of 1-decene in the ChCl:U DES, with a K value decreasing from 1.2 for the pure VOC to 7.4×10^{-2} in the mixture (20-fold factor). The same tendency is observed for 1-decene in the DES TBABr:Dec, with an enhancement of the absorption of this VOC in the mixture versus the pure VOC. This increase of 1-

decene absorption could be due to the overall increase in the hydrophobicity of the DES+VOCs solution. Indeed, this behaviour was already observed during liquid-liquid extraction of toluene from toluene + linear alkanes systems by DESs or ILs. It was observed that in these ternary systems (toluene + linear alkanes + DESs or ILs), increasing of toluene content in DESs or ILs leads to the growth of amount of linear alkanes transferred from organic-rich phase to the DESs or ILs [58–60].

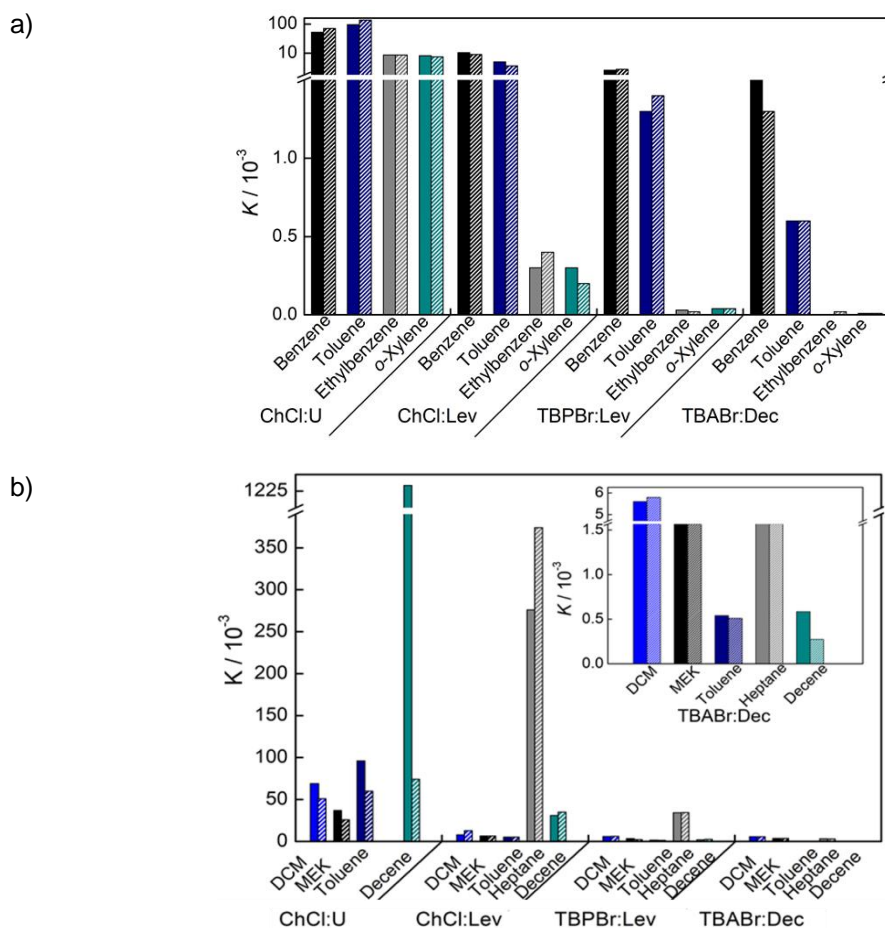


Fig. 5 Partition coefficients of the pure VOCs (solid column) and the VOCs in the mixture (hatch column) with a total VOCs concentration of 59 g.m^{-3} , at 303 K. a) BTEX mixture; b) DMTHDc mixture (DCM: dichloromethane, MEK: methylethylketone). The insert represents the K values in TBABr:Dec.

3.2. Dynamic absorption

The efficiency of an absorbent to trap a VOC is related to the partition coefficient of the VOC in this absorbent. Therefore, to evaluate the capacity of the DESs in conditions mimicking an absorption column, we chose three solvents that show high absorption capacity and versatility towards the

different VOCs (ChCl:Lev, TBPBr:Lev and TBABr:Dec). Therefore, we used a lab scale bubbling set-up (Fig. 1) developed in a previous study [51]. We selected three VOCs (methylethylketone, toluene and heptane) as these VOCs represents a wide range of aqueous solubility and structural heterogenicity.

The absorption capacities of the three DESs for the three VOCs at 303 K and at a VOC flow rate of $73 \mu\text{L}\cdot\text{hr}^{-1}$ are represented in Fig. 6. In the case of methylethylketone, the ChCl:Lev DES is the least effective DES with a capacity around 0.48 mg of VOC per g of DES at 303 K. Water showed higher capacities reaching 0.60 mg methylethylketone per g of water. By comparing the K values of methylethylketone, the one in water is smaller than that in ChCl:Lev, indicating a higher affinity between water and methylethylketone (Table 3). TBPBr:Lev and TBABr:Dec DESs show higher absorption capacity reaching 1.05 and 0.91 mg of methylethylketone per g of DES respectively. The K values for methylethylketone in these DESs (Table 3) are identical, which is in agreement with the obtained values in the dynamic mode.

In the case of toluene, the absorption capacities of ChCl:Lev, TBPBr:Lev and TBABr:Dec DESs (0.55, 1.42 and 2.37 mg of toluene per g of DES at 303 K, respectively) are higher than water (0.04 mg/g at 303 K). The highest absorption capacity for toluene is obtained in TBABr:Dec, having the lowest K value. The same trend is observed for heptane, with a 50-fold increase of the absorption capacity in TBABr:Dec.

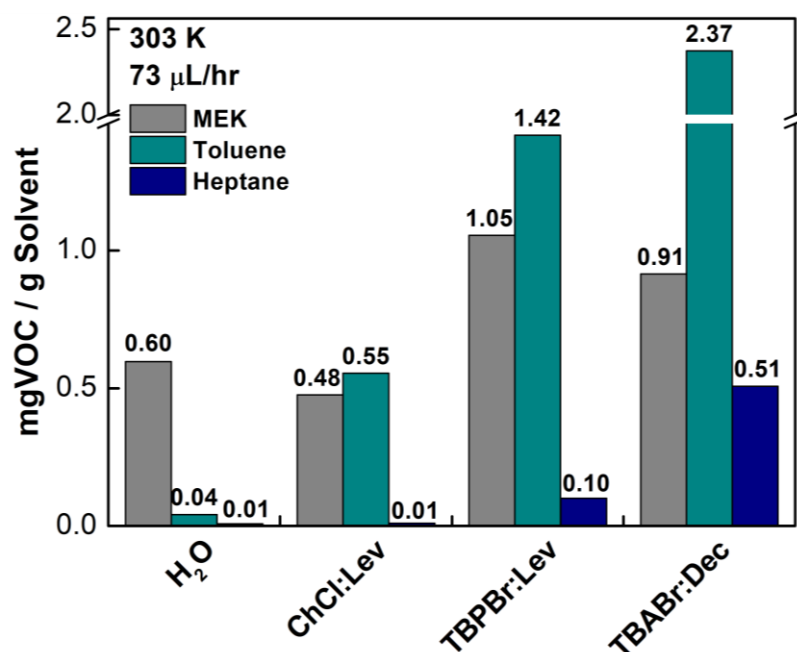


Fig. 6 Absorption capacity (mg/g) of methylethylketone (MEK), toluene and heptane in water and in DESs.

3.2.1. Effect of initial VOC concentration

The effect of initial VOC concentration was studied using three different flow rates: 36, 73 and 146 $\mu\text{L}\cdot\text{hr}^{-1}$ at 303 K as at this temperature the lowest partition coefficients are found. The amount of trapped VOC increased linearly with the VOC flow rate for all the tested DESs except for TBPBr:Lev/heptane (Fig. 7). This observation could be linked to the saturation of the DES, meaning that we reached the solubility limit of heptane in this DES.

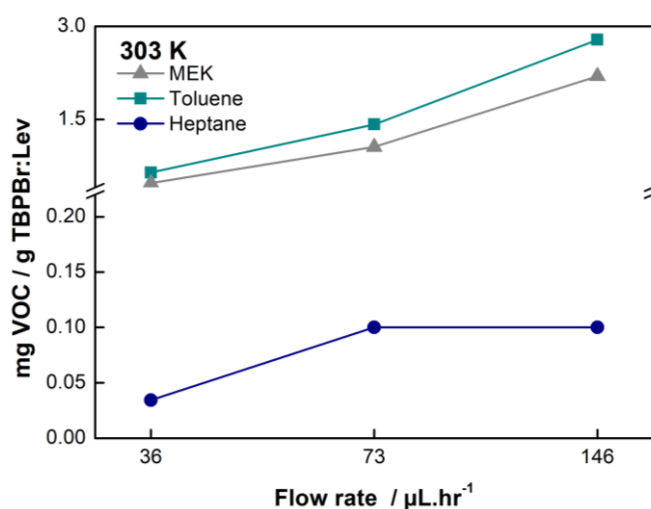


Fig. 7 Absorption capacity (mg/g) of methylethylketone (MEK), toluene and heptane in the DES TBPBr:Lev at

different VOC concentrations.

3.2.2. Effect of absorption temperature

The effect of temperature on absorption capacity has been studied from 303 K to 333 K. Fig. 8 represents the evolution of the absorption capacity of TBABr:Dec for heptane at a VOC flow rate of $73 \mu\text{L}\cdot\text{hr}^{-1}$. Absorption capacity falls from 0.51 mg to 0.26 mg of heptane per g of TBABr:Dec. The absorption capacity gradually decreases with the increase of the temperature for all the tested DES/VOC systems. The lowering of the absorption capacity is linked to the increase of K values with the temperature (Fig. 4).

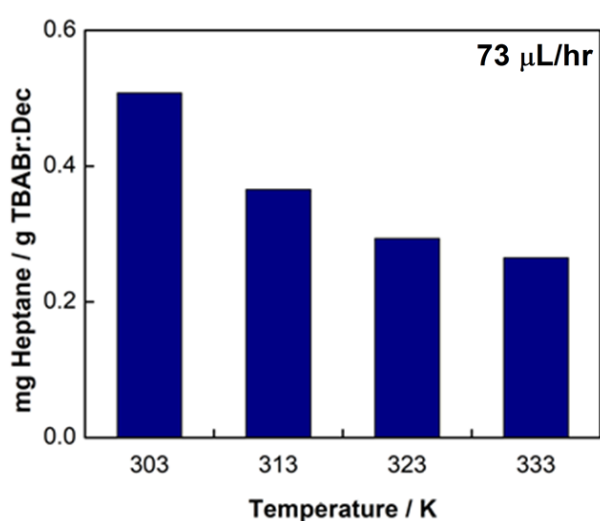


Fig. 8 Effect of the temperature on the absorption capacity of TBABr:Dec for heptane.

Similar behaviour was observed with ILs based on [Bmim][NTf₂] where the absorption capacity of toluene decreases by increasing the temperature from 293 K to 353 K [61]. Likewise, the absorption capacity of the DES based on thymol:decanoic acid for acetone decreased sharply with temperature [47]. It is noteworthy to mention, that the decrease in the viscosity of the DESs with temperature reported by Moura and co-workers [9], although benefits the mass transfer between the phases of the system is not sufficient to counterbalance the decrease in the affinity between DES and VOC.

3.2.1. Effect of water content

It is interesting to study the effect of water content on the absorption capacity of the DES, for both fundamental and practical point of view as industrial effluents contains humidity. Therefore, different

DESs solutions with increasing amount of water (10, 15, 20, 30 and 50% wt) were prepared and their absorption capacities were followed for the three VOCs (Fig.9). The absorbents capacities present various behaviour with respect to the aqueous solubility of each VOC and the DES properties.

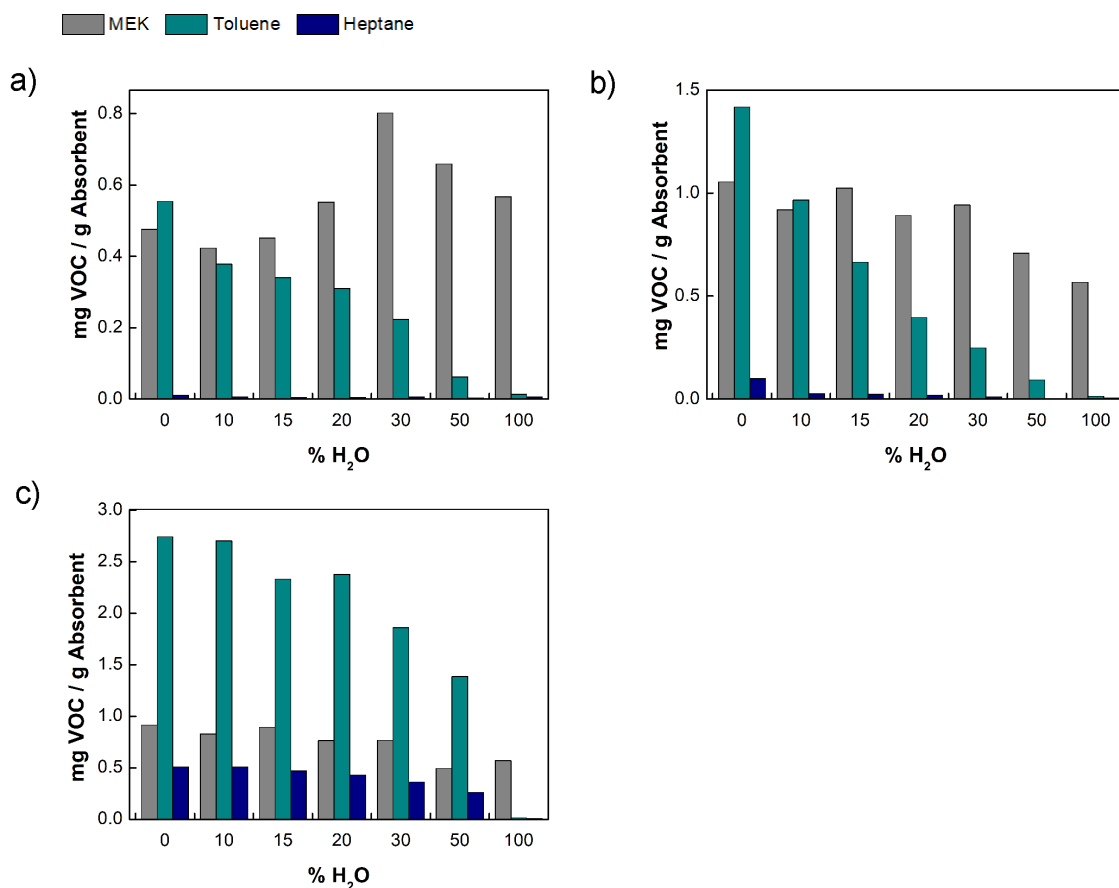


Fig. 9 Effect of water content on the absorption capacity (mg VOC/g Absorbent) of a) ChCl:Lev, b) TBPBr:Lev and c) TBABr:Dec for methylethylketone (MEK), toluene and heptane at 303 K with a VOC flow rate of 73 $\mu\text{L}\cdot\text{hr}^{-1}$

In the case of ChCl:Lev (Fig. 9 a), an inverted U-shape curve is obtained for methylethylketone with a maximum of 0.80 mg of methylethylketone per g of absorbent for ChCl:Lev + 30% wt of water . This value is higher than the one obtained in water (0.60 mg per g of water). Regarding toluene, the addition of water leads to a decrease in the absorption capacity of DES progressively, up to 30% wt of water content. The absorption capacity decreases from 0.55 mg of toluene per g of ChCl: Lev to 0.22 mg per g of mixture with 30% wt of water. At a 50% wt of water content the absorption capacity (0.06 mg per g of mixture) is however still 5 times higher than the ones obtained in water. For heptane, even at 10% wt of water, the absorption capacity decreases from 0.01 mg per g of DES to 0.006 mg

per g of mixture. The absorption capacity continues to decrease gradually reaching values comparable to those found in water.

Regarding TBPBr:Lev, the addition of water up to 30% *wt* does not affect its affinity for methylethylketone with an average absorption of 0.97 mg of methylethylketone per g of the solvent (Fig. 9 b). However, the addition of 50% *wt* of water results in a decrease in the absorption capacity (0.71 mg per g of absorbent). Despite this decrease, the absorption capacity remains always higher than water. For toluene, we could observe a gradual decrease in the absorption capacity of the DES + water mixture. At 50% *wt* of water, the mixture retains an absorption capacity 7 times greater than water. Heptane exhibits the same behaviour in the case ChCl:Lev.

Concerning TBABr:Dec, the absorption capacities of methylethylketone and hexane are slightly affected up to 30% *wt* of water. However, if we consider the absorption capacities related to the amount of DES and not to the amount of absorbent (DES + water), addition of water has no impact as water is only partially miscible with TBABr:Dec (Fig. S3 and S4) [62].

Many studies focus on the effect on water on the structural integrity of the DES, since the hydrogen bonding is one of the interactions occurring between the components of the DES, leading its formation. Del Monte and co-workers introduced the concept of “water-in-DES” and “DES-in-water” regime and determine the transition from one regime to the other [63]. Indeed, DES/water binary mixtures with high DES contents could be visualized as a “water-in-DES” system composed of an extended DES network with isolated aqueous domains that evolved upon dilution into, first, a “DES-in-water” system and, ultimately, a simple dilution of DES components. We observed a change in the absorption capacity of the mixture for several DES-water/VOC systems at around 30% *wt* of water which may be due to the limit where we switch from the “water-in-DES” to the “DES-in-water” regime. In the ChCl:Lev /toluene system, the decrease in absorption capacity follows a greater slope beyond the addition of 30% *wt* of water. Molecular studies should be undergone to characterise the system and the interactions between all the components of the mixture: the salt, the HBD, water and the VOC.

3.3. Regeneration of the DESs

The capacity to regenerate the absorbent is vital from an economical and green chemistry point of view for future industrial applications. Therefore, the absorption performance of the

regenerated DESs were determined. The higher partition coefficient obtained at higher temperatures has been utilized as a desorption condition. The absorbed VOCs could therefore be released by heating the mixtures at 333 K during 48 hr. The regeneration could also be performed by bubbling nitrogen gas into the mixtures in the case of the dynamic studies. The removal of VOC was proven by analysing the samples after the regeneration process. As can be seen in Fig. 10, in the case of TBPBr:Lev, the absorption capacities were stable after 5 cycles. All of the studied DESs achieved similar stability after at least 5 absorption and desorption cycles demonstrating facile and feasible recycling of the proposed absorbents. Moreover, we can conclude that heating at 333K did not modify significantly the composition of the mixture as no difference in the properties of the liquid absorbent was observed.

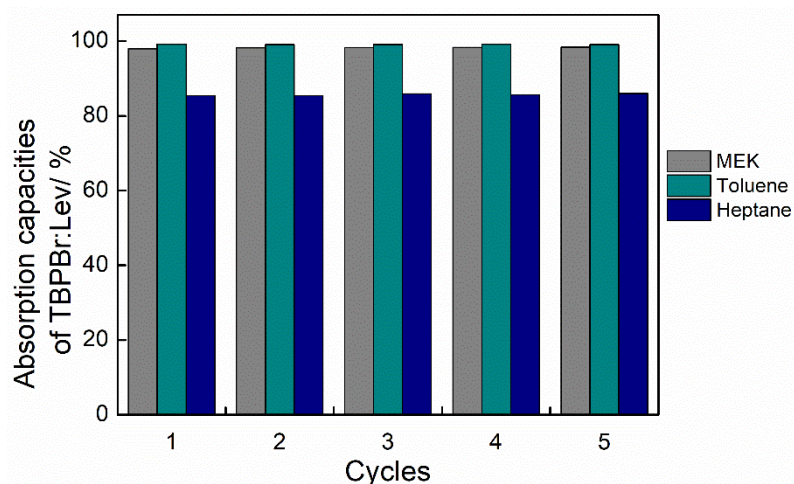


Fig. 10 Absorption capacity at 303 K of TBPBr:Lev for VOCs during five consecutive absorption/desorption cycles

We also evaluated the regeneration of DESs using the dynamic absorption set-up by following the desorption of DES at two temperatures (303 K and 333 K). During the desorption phase, nitrogen gas is put into contact with the DES loaded with VOC, at a flow rate of $35 \text{ L}\cdot\text{h}^{-1}$. The DES TBABr:Dec, which has the greatest absorption capacity for toluene, is regenerated faster when increasing the temperature from 303 K to 333 K (Fig. S5). Indeed, the time required to desorb toluene decreases by half and goes from 6 hrs for 303 K to almost 3 hrs for 333 K. Ozturk and Yilmaz tested waste vegetable and lubricant oils as VOC absorbents [64]. These authors showed the importance of preheating the desorption column which will reduce the time of this phase and therefore reduce the

overall cost of the treatment. They increased the column temperature to 423 K to be able to regenerate toluene and benzene saturated oils in 3 hrs. In our case, we observed the same time to regenerate the DES TBABr:Dec, as that observed by Ozturk and Yilmaz, but with increasing the temperature only to 333 K.

Finally, as absorption capacities of ChCl:Lev and TBPBr:Lev were effected with the addition of water, we evaluate them after water removal (Fig. 11). We can observe that the two DESs regain their initial absorption capacity after elimination of the added water.

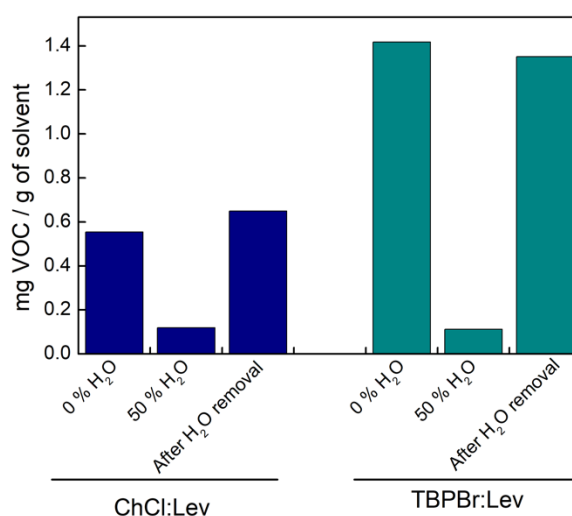


Fig. 11 Absorption capacities of DESs for different water content (*wt%*) and after their regeneration for toluene at 303 K

4. Conclusion

The absorption of a wide variety of VOCs in DESs was studied under various conditions by determining the vapour-liquid partition coefficients via static headspace-gas chromatography and the DESs' absorption capacity via a dynamic set-up. The obtained partition coefficients underlined that the eight DESs tested effectively retained both hydrophilic and hydrophobic VOCs, with up to 60000 folds increase compared to water in the case of 1-decene at 303 K. Furthermore, we demonstrated for the first time that DESs retain high absorption capacities for VOCs mixtures. The obtained results were confirmed by using a dynamic absorption set-up. Additionally, the effect of water on the DESs' absorption capacities is dependent on both the hydrophobicity of VOC studied and the nature of the DES. Finally, the absorption mechanisms probed by FTIR analyses indicated that VOCs were physically absorbed by the studied DESs, resulting in facile regeneration of the absorbent by heating.

Therefore, DESs demonstrate to be promising candidate for VOCs absorption, with the advantage to be cheap and eco-friendly solvents. Furthermore, as the physicochemical properties of DES could be easily tuned, new DESs could be designed targeting specific VOCs.

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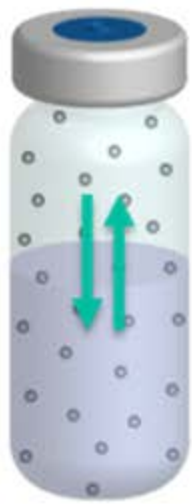
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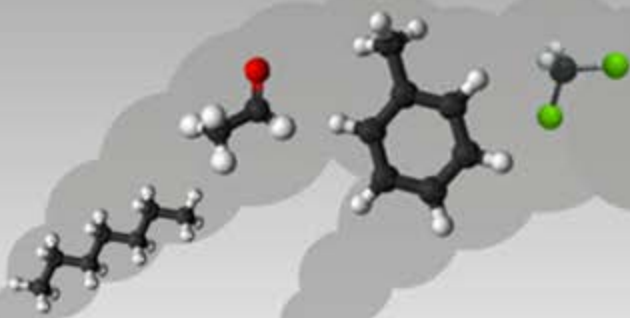
$$K = \frac{C_G}{C_L}$$

Static process



Dynamic process

DES



High volatile organic compounds absorption capacities associated with an easy recovery process