



# Air pollution: new bio-based ionic liquids absorb both hydrophobic and hydrophilic volatile organic compounds with high efficiency

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## Abstract

Emission of volatile organic compounds (VOCs) in the atmosphere is a major health concern for the World Health Organization (WHO). For instance, more than 4 million premature deaths are attributed yearly to outdoor air pollution, thus calling for advanced remediation techniques. Absorption systems using solvents are commonly used to remove air pollutants, yet efficiency is limited by a solvent property, which is either hydrophilic or hydrophobic. As a consequence, classical solvents are not able to capture both hydrophilic and hydrophobic contaminants. Therefore, we synthesized the following ionic liquids from choline chloride and fatty acids: hexylcholinium levulinate, octylcholinium levulinate, hexylcholinium lactate and octylcholinium lactate. Ionic liquids were then tested for absorption of toluene, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and methyl ethyl ketone. Ionic liquids were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, infrared spectroscopy, differential scanning calorimetry and thermal gravimetric analysis, density, viscosity and polarity. Vapor–liquid partition coefficients of VOC were determined for ionic liquids. We found that solvents were able to solubilize both hydrophobic and hydrophilic VOC. Moreover, no saturation was detected up to an initial VOC concentration of 3000 g/m<sup>3</sup>, whereas classical absorption processes usually involve gas streams containing VOC concentrations up to 1000 g/m<sup>3</sup>. Moreover, the solvent can be successfully recycled with unchanged capacity during five absorption–desorption cycles. Overall, our solvents appear promising for the treatment of industrial gaseous effluents.

**Keywords** Bio-based ionic liquids · Choline · Absorption · Partition coefficient · Volatile organic compounds · Air pollution

## Abbreviations

Chol	Choline	<i>K</i>	Vapor–liquid partition coefficient
DESs	Deep eutectic solvents	Lac	Lactic acid
DSC	Differential scanning calorimetry	Lev	Levulinic acid
FTIR	Fourier transform infrared spectroscopy)	NMR	Nuclear magnetic resonance
HBA	Hydrogen-bond acceptor	TGA	Thermogravimetric analysis
HBD	Hydrogen-bond donor	UV–Vis	UV–visible
ILs	Ionic liquids	VOCs	Volatile organic compounds

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## Introduction

Volatile organic compounds (VOCs) are a class of hazardous substances of greatest concern as they are playing an increasingly significant role in environmental pollution, health damage and economical losses (Parmar and Rao 2009; Karimi et al. 2016; Feng et al. 2019). An estimated 4.2 million premature deaths globally are linked to ambient air pollution (WHO 2020). However, despite their recognized harmfulness, it is difficult to replace them in most industrial

processes. Due to their deleterious effect, their atmospheric emissions are regulated by several international protocols and European legislations, pushing scientists to develop more efficient, less costly and greener technologies.

Currently available treatments include thermal or catalytic oxidation, adsorption, biological treatment condensation and absorption (Le Cloirec 1998). Absorption is in principle the most simple and efficient treatment for capturing VOCs from industrial gases by dissolving the pollutant into a liquid solvent (Heymes et al. 2006). Water or aqueous solutions using bases, acids or oxidizing reagents are the most common absorbent, restricting the use of this process to water-soluble VOCs. In the case of hydrophobic VOCs (e.g., aromatic and aliphatic hydrocarbons), various absorbents are available including silicone oils (Guillerm et al. 2016, 2017) or poly(ethyleneglycol) (Vuong et al. 2009). Unfortunately, many disadvantages are linked to the use of these solvents such as high cost, energy requirement for regenerating absorbents, losses, solvent degradation or equipment corrosion. Therefore, the design of more satisfactory, economic and efficient absorbent is needed to avoid or eliminate the shortcomings of the usual solvent used for capturing VOCs from industrial gases. For this purpose, waste cooking oils (Lhuisier et al. 2018; Mannu et al. 2019), ionic liquids (ILs) (Quijano et al. 2011; Rodriguez Castillo et al. 2018, 2019; Yu et al. 2018; Cichowska-Kopczyńska and Aranowski 2020), cyclodextrins (Blach et al. 2008; Landy et al. 2012) or deep eutectic solvents (DESs) (Moura et al. 2017) were evaluated as solvent for absorption process. However, if ionic liquids present high affinity for various VOCs, some of these solvents are classified as carcinogenic, like 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C4mim][NTf<sub>2</sub>]), or are still expensive.

Ionic liquids are special molten salts with melting points below 100 °C that are generally constituted of organic cations and inorganic anions (Yi et al. 2015; Hu et al. 2019). Their numerous properties make them an attractive choice of solvent in many important chemical processes (Swatloski et al. 2003; Kostić and Divac 2019; Lu et al. 2019). They have long been considered as green solvent; however, recent data have shown that the ionic nature does not necessarily infer an absolute non-toxic or low toxic character (Diallo et al. 2012). Several ionic compounds showed significant toxicity leading the scientific community to reduce the use of ionic liquids or to find other greener alternatives (Singh and Savoy 2020). The use of renewable, biodegradable and non-toxic resources, such as amino acids, amino alcohols or sugars, could improve the green character of ionic liquids (Chiappe et al. 2010; McDonald et al. 2014).

We recently developed various ionic liquids based on ammonium or phosphonium with anion from natural acids, L-proline and its derivatives as well as glycerol (Hayouni et al. 2016, 2017; Mbakidi and Bouquillon 2018). These

compounds showed in general lower toxicity toward various organisms than usual chlorinated and commercial ionic liquids. In this study, new bio-based ionic liquids obtained from choline chloride and fatty acids were synthesized, characterized and evaluated as absorbent for VOCs. As the affinity of the pollutant with the absorbent liquid phase is the key to the absorption process, partition coefficient of various representative VOCs was determined in these new ionic liquids as well as in the corresponding deep eutectic solvents obtained with choline chloride and both fatty acids.

## Experimental section

### Materials

Choline chloride (≥ 98%), levulinic acid (99%), lactic acid (85%), toluene (99.8%), methyl ethyl ketone (≥ 99%), dichloromethane (99.8%), Nile Red (≥ 98.0%), methanesulfonic acid (≥ 99%), hexanoic acid (≥ 99%), octanoic acid (≥ 98%), sodium perchlorate (≥ 98%) and potassium lactate (60% in water) were purchased from Sigma-Aldrich. Choline chloride was dried at 60 °C for 2 weeks prior to use. Other compounds were used as received. All aqueous solutions were prepared with distilled water.

### Physicochemical analysis

Elemental analyses (C, H and N) were carried out on a PerkinElmer 2400 C, H and N element analyzer. IR spectra of liquid and solid compounds were recorded on a Bruker Alpha-T FTIR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature with a Bruker AC 500 spectrometer (500 MHz for <sup>1</sup>H, 62.5 MHz for <sup>13</sup>C). Chemical shifts (in ppm) for <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual protic solvent peaks. The decomposition temperatures of the ionic liquids were measured using a Netzsch TG 209 F3 Tarsus thermogravimetric analyzer (TGA) under argon atmosphere. Samples (~ 10–20 mg) were heated from 30 to 400 °C with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) experiments were carried out using a Q1000 DSC (TA Instruments, New Castle, DE) at a temperature range from – 100 to 30 °C and at a thermal scanning rate of 5 °C/min. All the samples were encapsulated in aluminum pans (sample weight ~ 10–15 mg), sealed with hermetic lids and characterized. The instrument is a heat-flux DSC, and experiments were performed under nitrogen flow (50 mL/min). Densities and viscosities were measured with an Anton Paar Stabinger SVM 3001 in the temperature range of 25–60 °C.

## Ionic liquids synthesis

### General procedure for the synthesis of alkyl cholinium perchlorate (Chol- $C_n$ -ClO<sub>4</sub>)

To a suspension of dried choline chloride (40 g, 286 mmol, 1.0 equiv.) in methanesulfonic acid (1.5 equiv.) was added an excess of hexanoic or octanoic acid (3 equiv.). The reaction mixture was gradually heated to 90–100 °C under reduced pressure (50–100 mbar) to remove the water. After 30 min, the reaction mixture became homogeneous, and after 6 h, the brown mixture was cooled to room temperature under atmospheric pressure. Water was added (100–200 mL) to the crude material that was firstly washed with diethyl ether (5 × 100 mL) and secondly with dichloromethane (5 × 100 mL) to remove the excess of fatty carboxylic acid.

Then, an excess of sodium perchlorate (3 equiv.), previously dissolved in a minimum of water (10–20 mL), was added to a solution of crude material in water to eliminate the excess of unreacted choline chloride. The mixture was stirred at room temperature for 24 h. The product Chol- $C_n$ -ClO<sub>4</sub> was dissolved in dichloromethane for a washing with water (5 × 100 mL) to remove the excess of sodium perchlorate and the free choline sometimes still present. The solvent was distilled under reduced pressure and addition of diethyl ether precipitated the compound. After filtration, the product was obtained as a white powder.

**Hexylcholinium perchlorate (Chol- $C_6$ -ClO<sub>4</sub>)** Yield (69 g, 229 mmol, 80%). White powder, mp = 64 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 0.84 (t, 3 H, *J* = 7.5 Hz, CH<sub>3</sub>), 1.23 (m, 4 H), 1.57 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.37 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>O), 3.25 (s, 9 H, (CH<sub>3</sub>)<sub>3</sub>N), 3.70 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO), 4.49 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>COO) ppm. <sup>13</sup>C NMR: δ<sub>C</sub> (62.5 MHz, CDCl<sub>3</sub>): 14.1 (CH<sub>3</sub>), 22.5, 24.6, 29.1, 31.8 (CH<sub>2</sub>), 54.2 ((CH<sub>3</sub>)<sub>3</sub>N), 57.6 (CH<sub>2</sub>CH<sub>2</sub>COO), 65.1 (CH<sub>2</sub>CH<sub>2</sub>O), 77.4 (CH<sub>2</sub>CH<sub>2</sub>O), 171.9 (C=O) ppm. IR: ν (cm<sup>-1</sup>) 1071 (ClO<sub>4</sub>), 1746 (CO). Anal. calcd.: C<sub>11</sub>H<sub>24</sub>ClNO<sub>6</sub>: C 43.78; H 8.02, N 4.64%; found: C 41.90; H 8.13; N 4.21%.

**Octylcholinium perchlorate (Chol- $C_8$ -ClO<sub>4</sub>)** Yield (82 g, 252 mmol, 88%). Light beige powder, mp = 69 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 0.87 (t, 3 H, *J* = 7.5 Hz, CH<sub>3</sub>), 1.25 (m, 8 H), 1.59 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.35 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>O), 3.28 (s, 9 H, (CH<sub>3</sub>)<sub>3</sub>N), 3.74 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO), 4.51 (t, 2 H, *J* = 7.5 Hz, CH<sub>2</sub>COO) ppm. <sup>13</sup>C NMR: δ<sub>C</sub> (62.5 MHz, CDCl<sub>3</sub>): 14.1 (CH<sub>3</sub>), 22.7, 24.6, 29.1, 29.3, 31.9, 33.9 (CH<sub>2</sub>), 54.2 ((CH<sub>3</sub>)<sub>3</sub>N), 57.6 (CH<sub>2</sub>CH<sub>2</sub>COO), 65.2 (CH<sub>2</sub>CH<sub>2</sub>O), 77.4 (CH<sub>2</sub>CH<sub>2</sub>O), 171.9 (C=O) ppm. IR: ν (cm<sup>-1</sup>) 1071 (C-ClO<sub>4</sub>), 1746 (C=O). Anal. calcd.: C<sub>13</sub>H<sub>28</sub>ClNO<sub>6</sub>: C 47.34; H 8.56; N 4.25%; found: C 47.86; H 8.83; N 4.21%.

### General procedure for the synthesis of alkyl cholinium lactate (Chol- $C_n$ -Lac) and levulinate (Chol- $C_n$ -Lev)

A slight excess of potassium lactate or levulinate (1.2 equiv.) in ethanol (20 mL) was added to a solution of Chol- $C_n$ -ClO<sub>4</sub> (1 equiv.) in ethanol (100 mL). The reaction mixture was stirred at room temperature for 24 h. The precipitated solid KClO<sub>4</sub> was filtered, and the solvent was evaporated under reduced pressure. The product was washed with diethyl ether and dried under vacuum for 3 days to obtain pure compounds.

**Hexylcholinium levulinate (Chol- $C_6$ -Lev)** Yield (*m* = 70 g, 75%). Liquid at room temperature. TGA: *T*<sub>dec</sub> = 206 °C. NMR <sup>1</sup>H: δ<sub>H</sub> (500 MHz; DMSO-*d*<sub>6</sub>): 0.82 (3 H, t, *J* = 7.5 Hz, CH<sub>3</sub>), 1.21 (4 H, m), 1.53 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.16 (3 H, s, CH<sub>3</sub>CO (Levu.)), 2.24 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO (Levu.)), 2.36 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>O), 2.55 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO (Levu.)), 3.21 (9 H, s, (CH<sub>3</sub>)<sub>3</sub>N), 3.77 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO), 4.51 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO) ppm. <sup>13</sup>C NMR: δ<sub>C</sub> (62.5 MHz; DMSO-*d*<sub>6</sub>): 14.2 (CH<sub>3</sub>), 22.6 (CH<sub>3</sub>COCH<sub>2</sub>, Levu.), 24.6, 28.9, 29.1 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>CH<sub>2</sub>COO), 40.4 (CH<sub>3</sub>CO(CH<sub>2</sub>)<sub>2</sub>COO, Levu.), 53.6 (CH<sub>3</sub>)<sub>3</sub>, 58.2 (CH<sub>2</sub>CH<sub>2</sub>O), 64.1 (CH<sub>2</sub>CH<sub>2</sub>O), 172.83 (CO), 176.6 (CH<sub>2</sub>COO, Levu.), 210.0 (CH<sub>3</sub>COCH<sub>2</sub>, Levu.) ppm. IR: ν (cm<sup>-1</sup>) 1746 (C=O). Anal. calcd.: C<sub>16</sub>H<sub>31</sub>NO<sub>5</sub>: C 60.54; H 9.84; N 4.41%; found: C 60.19; H 9.56; N 4.22%.

**Octylcholinium levulinate (Chol- $C_8$ -Lev)** Yield (*m* = 85 g, 86%). Light beige wax, mp = 50 °C. TGA: *T*<sub>dec</sub> = 229 °C. <sup>1</sup>H NMR: δ<sub>H</sub> (500 MHz; DMSO-*d*<sub>6</sub>): 0.85 (3 H, t, *J* = 7.5 Hz, CH<sub>3</sub>), 1.24 (8 H, m), 1.53 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.06 (3 H, s, CH<sub>3</sub>CO (Levu.)), 2.21 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO (Levu.)), 2.33 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>O), 2.51 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO (Levu.)), 3.16 (9 H, s, (CH<sub>3</sub>)<sub>3</sub>N), 3.72 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO), 4.45 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO) ppm. <sup>13</sup>C NMR: δ<sub>C</sub> (62.5 MHz; DMSO-*d*<sub>6</sub>): 14.2 (CH<sub>3</sub>), 22.4 (CH<sub>3</sub>C-OCH<sub>2</sub>, Levu.), 24.2, 28.7, 29.2, 29.3, 29.3 (CH<sub>2</sub>), 32.4 (CH<sub>2</sub>CH<sub>2</sub>COO), 40.2 (CH<sub>3</sub>CO(CH<sub>2</sub>)<sub>2</sub>COO, Levu.), 53.1 (CH<sub>3</sub>)<sub>3</sub>, 58.4 (CH<sub>2</sub>CH<sub>2</sub>O), 63.1 (CH<sub>2</sub>CH<sub>2</sub>O), 172.7 (C=O), 176.6 (CH<sub>2</sub>COO, Levu.), 208.9 (CH<sub>3</sub>COCH<sub>2</sub>, Levu.) ppm. IR: ν (cm<sup>-1</sup>) 1746 (C=O). Anal. calcd.: C<sub>18</sub>H<sub>35</sub>NO<sub>5</sub>: C 62.58; H 10.21; N 4.05%; found: C 62.19; H 9.98; N 4.32%.

**Hexylcholinium lactate (Chol- $C_6$ -Lac)** Yield (*m* = 64 g, 77%). Liquid at room temperature. TGA: *T*<sub>dec</sub> = 198 °C. NMR <sup>1</sup>H: δ<sub>H</sub> (500 MHz; DMSO-*d*<sub>6</sub>): 0.86 (3 H, t, *J* = 7.5 Hz, CH<sub>3</sub>), 1.03 (3 H, d, *J* = 7.5 Hz, CH<sub>3</sub>CH (Lac.)), 1.21 (4 H, m), 1.52 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 2.31 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>O), 3.06 (9 H, s, (CH<sub>3</sub>)<sub>3</sub>N), 3.27 (1 H, q, *J* = 7.5 Hz, CH<sub>3</sub>CH (Lac.)), 3.78 (2 H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>2</sub>COO),

4.56 (2 H, t,  $J=7.5$  Hz,  $\text{CH}_2$  COO) ppm.  $^{13}\text{C}$  NMR:  $\delta_{\text{C}}$  (62.5 MHz;  $\text{DMSO}-d_6$ ): 14.3 ( $\text{CH}_3$ ), 18.9 ( $\text{CH}_3\text{CHCOO}$ , **Lact.**), 22.5, 24.6, 29.1 ( $\text{CH}_2$ ), 40.2 ( $\text{CH}_2\text{CH}_2\text{COO}$ ), 53.4 ( $\text{CH}_3$ )<sub>3</sub>, 53.6 ( $\text{CH}_3\text{CHCOO}$ , **Lac.**), 53.7 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 67.6 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 172.9 (CO), 178.0 (CO, **Lac.**) ppm. IR:  $\nu$  ( $\text{cm}^{-1}$ ) 1746 (C=O). Anal. calcd.:  $\text{C}_{14}\text{H}_{29}\text{NO}_5$ : C 57.71; H 10.03; N 4.81%; found: C 57.54; H 9.98; N 4.32%.

**Octylcholinium lactate (Chol-C<sub>8</sub>-Lac)** Yield ( $m=83$  g, 90%). Liquid at room temperature. TGA:  $T_{\text{dec}}=218$  °C. NMR  $^1\text{H}$ :  $\delta_{\text{H}}$  (500 MHz;  $\text{DMSO}-d_6$ ): 0.86 (3 H, t,  $J=7.5$  Hz,  $\text{CH}_3$ ), 1.07 (3 H, d,  $J=7.5$  Hz,  $\text{CH}_3\text{CH}$  (**Lac.**)), 1.25 (8 H, m), 1.54 (2 H, t,  $J=7.5$  Hz,  $\text{CH}_2\text{CH}_2\text{O}$ ), 2.34 (2 H, t,  $J=7.5$  Hz,  $\text{CH}_2\text{O}$ ), 3.16 (9 H, s, ( $\text{CH}_3$ )<sub>3</sub>N), 3.47 (1 H, q,  $J=7.5$  Hz,  $\text{CH}_3\text{CH}$  (**Lac.**)), 3.71 (2 H, t,  $J=7.5$  Hz,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 4.45 (2 H, t,  $J=7.5$  Hz,  $\text{CH}_2$  COO) ppm.  $^{13}\text{C}$  NMR:  $\delta_{\text{C}}$  (62.5 MHz;  $\text{DMSO}-d_6$ ): 14.1 ( $\text{CH}_3$ ), 18.2( $\text{CH}_3\text{CHCOO}$ , **Lact.**), 21.9, 22.5, 24.5, 29.2, 29.3 ( $\text{CH}_2$ ), 41.2 ( $\text{CH}_2\text{CH}_2\text{COO}$ ), 53.2 ( $\text{CH}_3$ )<sub>3</sub>, 53.4( $\text{CH}_3\text{CHCOO}$ , **Lac.**), 53.7 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 67.0 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 172.5 (CO), 177.8 (CO, **Lac.**) ppm. IR:  $\nu$  ( $\text{cm}^{-1}$ ) 1746 (C=O). Anal. calcd.:  $\text{C}_{16}\text{H}_{33}\text{NO}_5$ : C 60.16; H 10.41; N 4.38%; found: C 59.64; H 9.98; N 4.32%.

## Preparation of the deep eutectic solvents

We prepared two deep eutectic solvents (DESs) based on choline chloride as hydrogen-bond acceptor (HBA) and levulinic (ChCl/Lev, molar ratio 1:2) or lactic acid (ChCl/Lac, molar ratio 1:2) as hydrogen-bond donor (HBD), in order to compare results between ionic liquids and deep eutectic solvents. Deep eutectic solvents were obtained by stirring both the HBA and the HBD at the desired molar ratio at 60 °C until the formation of a clear homogenous liquid.

## Polarity study

A stock solution of Nile Red was prepared in ethanol, with a concentration of  $10^{-4}$  mol/L. A volume of 100  $\mu\text{L}$  of this solution was placed in vials, and ethanol was evaporated. Then, the studied solvents were added in the vials and stirred at 30 °C for 24 h, to ensure the solubilization of the probe. UV–Vis spectra were recorded with a PerkinElmer Lambda 2S spectrophotometer, between 400 and 700 nm with a quartz cell equipped with a thermostatically controlled bath which allows absorbance to be measured at a temperature of 30 °C with an accuracy of  $\pm 0.1$  °C. The wavelength at which the maximum visible-light absorption of Nile Red occurred,  $\lambda_{\text{max}}$ , was determined for each solvent, and the Nile Red polar parameter  $E_{\text{NR}}$  (in kcal/mol) was calculated using Eq. (1).

$$E_{\text{NR}}(\text{kcal/mol}) = \frac{28591}{\lambda_{\text{max}}(\text{nm})} \quad (1)$$

## Vapor–liquid partition coefficients measurements

The vapor–liquid partition coefficient ( $K$ ) could be expressed as defined by Kolb and Ettre (2006) by Eq. (2):

$$K = \frac{C_g}{C_l} \quad (2)$$

where  $C_g$  is the concentration of the solute in the vapor phase in equilibrium with a liquid solution of concentration  $C_l$  in the solute.

For the determination of  $K$ , an accurate mass of the studied solvents (about 3.4 g) was placed in headspace vials of 20 mL and a precise amount of volatile compounds (toluene, dichloromethane or methyl ethyl ketone) was added to the samples. The samples were then stirred during 24 h at 30 °C in order to reach equilibrium and left another 120 min in the headspace oven at 30 °C prior to the analysis. Measurements were carried out with an Agilent G1888 headspace sampler coupled to a PerkinElmer Autosystem XL gas chromatography equipped with a flame ionization detector and a DB624 column using nitrogen as the carrier vector. The gas chromatography column temperature was set at 40, 60 and 80 °C for dichloromethane, methyl ethyl ketone and toluene, respectively. The transfer line temperature was set at 250 °C. The determination of  $K$  in water was performed using the phase ratio variation method described by Kolb and Ettre (2006).

## Regeneration of the ionic liquids

After analysis, vials containing the different ionic liquids were uncapped and stirred at 60 °C during 48 h. Then, SH-GC was used to verify that there was no detectable VOC in the headspace of these vials after another 24 h of equilibration time. The absorption capacities of ionic liquids after regeneration were evaluated following the procedure described above. Five absorption/desorption cycles were performed.

## Results and discussion

### Ionic liquids synthesis

We synthesized four new ionic liquids, hexylcholinium levulinate, octylcholinium levulinate, hexylcholinium lactate and octylcholinium lactate, using a synthetic method that follows green chemistry principles, especially on the nature of solvent or the resources used (Bouquillon and Mbakidi

2019). The first transformation of choline chloride is an esterification with hexanoic and octanoic acids (Fig. 1a). This reaction was catalyzed by methylsulfonic acid playing also the role of the reaction solvent and performed under vacuum to remove the water generated during the reaction; thus, the equilibrium is shifted toward the formation of the desired esters.

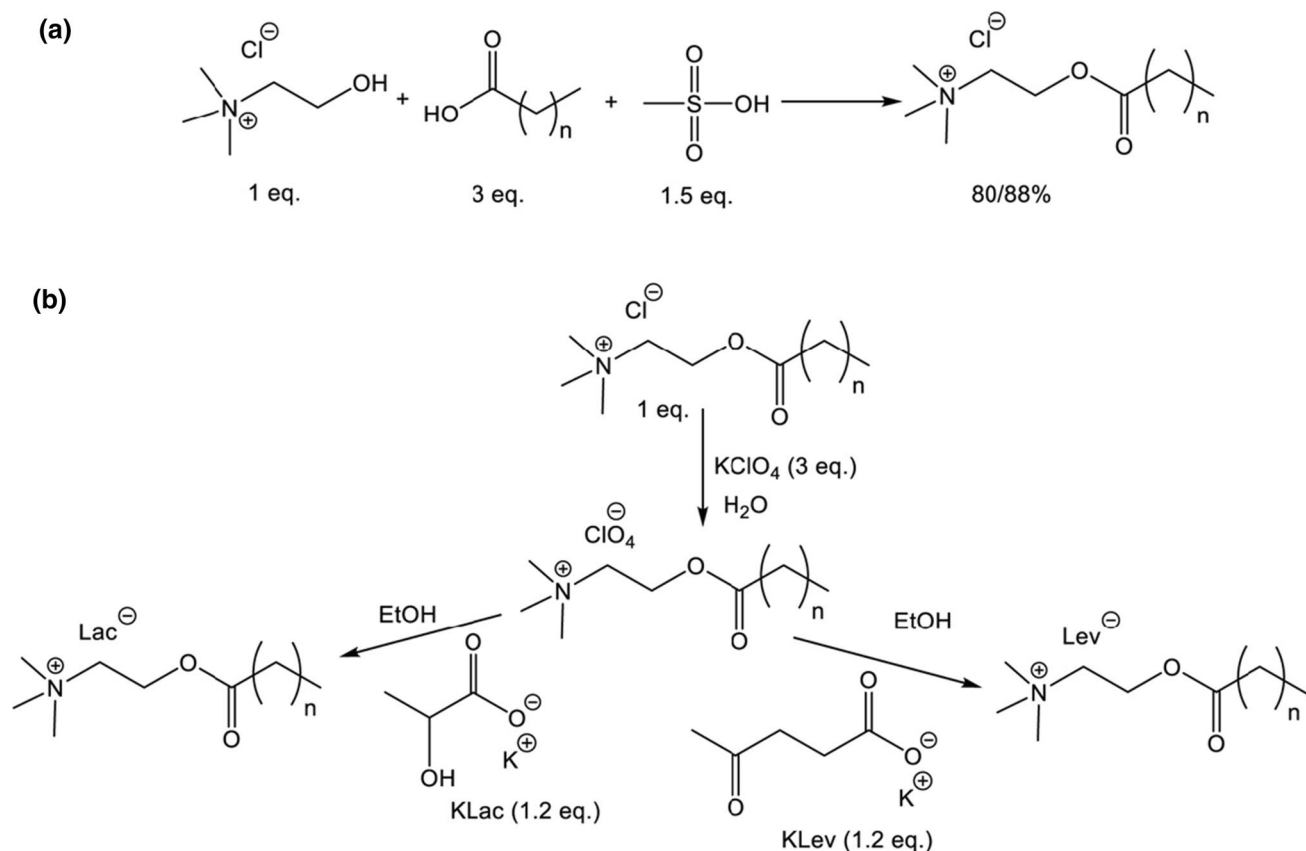
Then, a metathesis reaction has been realized with perchlorate salt in order to purify the ionic compound because residual choline chloride was always present as well as the excess of  $\text{CH}_3\text{SO}_3\text{H}$  (Fig. 1b). By exchanging the chloride anion by the perchlorate one, we modified some physical properties of our ionic liquids, in particular their solubility (De Gaetano et al. 2015). Indeed, the various perchlorate derivatives with C6 and C8 chains precipitated in the aqueous phase which facilitated the purification by simple filtration and successive washings with cold water. A second metathesis was performed with the potassium levulinate or the potassium lactate. The levulinate is a biosourced anion derived from the levulinic acid which is a very important synthetic intermediate, used in the synthesis of pharmaceutical compounds. Levulinic acid is also a precursor of

polymers or rubbers and also of chemicals in the industrial production of other chemicals.

Concerning the choice of the anion lactate derived from lactic acid, this latter is easily produced by bacterial fermentation of beet. Moreover, the lactate has good coordinating properties and is also a good hydrogen bonds acceptor. Furthermore, the choice of the ethanol as solvent for the metathesis reaction is crucial because the solubility of the potassium perchlorate is very weak in this solvent facilitating the purification of the final ionic liquid. Finally, four bio-based ionic liquids (Table 1) have been prepared with good yields through a three-step process.

**Table 1** New bio-based ionic liquids synthesized in this work, their acronym, molecular weight and yields

Ionic liquids (ILs)	Acronym	Molecular weight (g/mol)	Global yields (%)
Hexylcholinium levulinate	Chol-C <sub>6</sub> -Lev	317.2	60
Octylcholinium levulinate	Chol-C <sub>8</sub> -Lev	345.3	69
Hexylcholinium lactate	Chol-C <sub>6</sub> -Lac	291.2	68
Octylcholinium lactate	Chol-C <sub>8</sub> -Lac	319.2	80

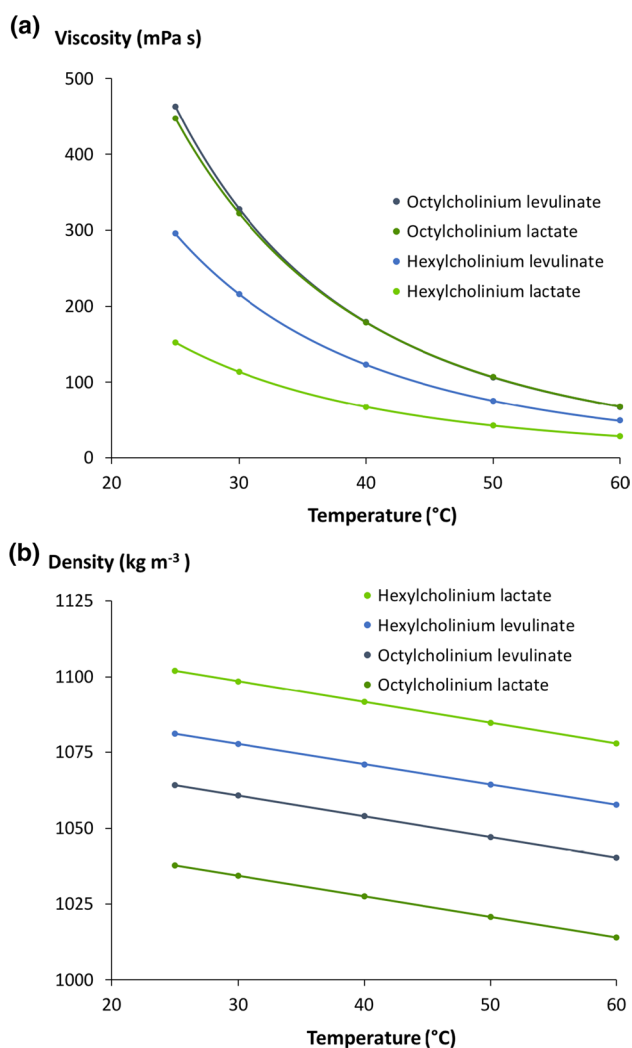


**Fig. 1** **a** Esterification of choline chloride with hexanoic ( $n=4$ ) or octanoic ( $n=6$ ) acid catalyzed by methylsulfonic acid and **b** metathesis reactions with perchlorate salt to exchange chloride anion followed by a second metathesis with potassium levulinate or potassium lactate ( $n=4$  or  $6$ )

## Physicochemical analysis

The density and viscosity of the ionic liquids are reported in Fig. 2. The viscosity and density data were fitted to Vogel–Fulcher–Tammann (VFT) functions in the case of viscosity and to appropriate polynomials in the case of the density.

The study of the physical properties of the solvent involved in absorption process is of crucial interest as to be used as an absorbent a solvent should present not to high viscosity (less than 700 mPa s at 30 °C) (Rodríguez Castillo et al. 2018). In our case, all the studied ionic liquids show viscosity less than 330 mPa s at this temperature. We could also observe that viscosity decreases exponentially



**Fig. 2** Experimental values of the **a** viscosity and **b** density of the ionic liquids. The lines represent the Vogel–Fulcher–Tammann (VFT) correlation fitting for viscosity and appropriate polynomials in the case of the density. At 25 °C, all the studied solvents have viscosities lower than 500 mPa s, while at 60 °C, all solvents have viscosities close or lower than 100 mPa s

with temperature. As absorption is an exothermic process, it is usually performed at temperature less than 60 °C. At this temperature, viscosity is less than 100 mPa s. Considering ionic liquids based on the same anion, the viscosity increased with alkyl chain elongation. Ionic liquids and deep eutectic solvents present viscosity values in the same order of magnitude (206 and 305 mPa s for ChCl/Lev and ChCl/Lac at 30 °C, respectively), Chol-C<sub>6</sub>-Lac presenting the lowest viscosity (Francisco et al. 2013; Moura et al. 2017). We could notice that all the ionic liquids present a density > 1. The obtained density was also > 1 (1.1345 and 1.1761) for ChCl/Lev and Chol/Lac at 30 °C, respectively (Francisco et al. 2013; Moura et al. 2017).

The solid–liquid transition temperatures of ionic liquids can be below ambient temperature and as low as –100 °C. The most efficient method for measuring their transition temperatures is differential scanning calorimetry (DSC) (Anthony et al. 2002). From –100 to 30 °C, no melting point was observed. It has been already reported that many ionic liquids have no melting points, instead exhibiting a glass transition temperature (Zhou et al. 2014). In our case, glass transition curves with T<sub>g</sub> at –79.8, –82.59, –73.07 and –68.69 °C were observed for Chol-C<sub>6</sub>-Lev, Chol-C<sub>8</sub>-Lev, Chol-C<sub>6</sub>-Lac and Chol-C<sub>8</sub>-Lac, respectively.

## Polarity study

Nile Red was used as a probe to evaluate the respective polarity of the ionic liquids and deep eutectic solvents. As Nile Red is a positive solvatochromic dye, when it is solubilized in increasingly polar media, the wavelength of its visible absorption maximum ( $\lambda_{\max}$ ) moves to longer wavelengths (lower energies) (Gabriele et al. 2019). Changes in the  $\lambda_{\max}$  of the dye suggested that the polarity of the ionic liquids decreased in the order Chol-C<sub>6</sub>-Lac > Chol-C<sub>6</sub>-Lev  $\approx$  Chol-C<sub>8</sub>-Lac > Chol-C<sub>8</sub>-Lev ( $E_{\text{NR}}$  values of 52.54, 52.92, 52.99 and 53.88 kcal/mol, respectively). The four ionic liquids presented higher  $E_{\text{NR}}$  values compared to the studied deep eutectic solvents ( $E_{\text{NR}}$  values of 49.79 and 48.02 for ChCl/Lev and ChCl/Lac, respectively), meaning that they are less polar. This difference could be attributed to the presence of an alkyl chain (C6 or C8) and to better ion–ion interactions in the ionic liquids. The  $E_{\text{NR}}$  value of the ionic liquids with a similar alkyl chain is always lower for the lactic acid derivative, meaning a higher polarity of the solvent. This observation is coherent with the log*P* values of lactic acid (–0.72) and levulinic acid (–0.49).

## Partition coefficient

The affinity of the pollutant with the absorbent liquid phase is the key to the process. The efficiency and operating costs are thus governed by the pollutant/absorbent pair. As the

solubility increases with decreasing temperature, absorption is favored by low temperatures, and the determination of the partition coefficient  $K$  was therefore realized at 30 °C. The obtained values of the different VOCs in water and in the studied solvents are presented in Table 2 along with the value of the ratio defined in Eq. (3). A ratio > 1 means that the VOC is better solubilized in the solvent compared to water.

$$\text{Ratio} = \frac{K_{\text{water}}}{K_{\text{solvent}}} \quad (3)$$

As given in Table 2, Chol-C<sub>8</sub>-Lev is the most efficient solvent for toluene absorption with a ratio of 156. The alkyl chain elongation leads to a better solubilization of toluene as well as the use of levulinic acid instead of lactic acid. The deep eutectic solvents based on levulinic acid present also better ratio than the one based on lactic acid. The same tendency is observed for dichloromethane. These results are in good agreement with the  $E_{\text{NR}}$  values. Concerning methyl ethyl ketone, none of the studied solvents performed better than water. This is coherent with the water solubility (573, 10,950 and 761,000 mg/L) and  $\log P$  (2.73, 1.25 and 0.29) values of toluene, dichloromethane and methyl ethyl ketone, respectively.

We recently investigated the use of deep eutectic solvents as absorbent for VOCs (Moura et al. 2017). The values obtained with Chol-C<sub>8</sub>-Lev are in the same order of magnitude than those obtained with deep eutectic solvents based on tetrabutylammonium or phosphonium bromide and carboxylic acids for toluene and dichloromethane. These values are also in the same order of magnitude than the one obtained in silicone oil (0.0033 and 0.0144 for toluene and dichloromethane, respectively, at 31.8 °C) (Poddar and Sirkar 1996), or to 1-butyl-1-methylpyrrolidinium dicyanamide or 1-butyl-3-methylimidazolium acetate (Fourmentin et al. 2016) but higher than those for 1-butyl-3-methylimidazolium hexafluorophosphate or bis(trifluoromethylsulfonyl) amide ionic liquids (Quijano et al. 2011) for toluene. These results confirm that the type of anion plays a role in the absorption capacities of ionic liquids. However, as discussed

previously some ionic liquids based on methylimidazolium or methylpyrrolidinium are still expensive or classified as carcinogenic restricting their use.

No data could be found in the literature concerning methyl ethyl ketone. As the ratio of  $K_{\text{water}}/K_{\text{solvent}}$  is close to 1 for all the studied solvent, this means that the presence of methyl ethyl ketone in the gaseous effluent will lead to absorption efficiency close to water. Therefore, the new solvents are able to solubilize hydrophobic VOC while exhibiting as good efficiency than water for hydrophilic VOCs. As exhausted gases are generally composed of a mixture of hydrophobic and hydrophilic VOCs, this means that the ionic liquids are versatile absorbent suitable for the treatment of VOCs emissions.

Increasing amounts of toluene were then added to Chol-C<sub>8</sub>-Lev in order to explore its absorption capacities for various VOC concentrations. No saturation was detected up to an initial VOC concentration of 3000 g/m<sup>3</sup>. At 3000 g/m<sup>3</sup>, Chol-C<sub>8</sub>-Lev presented an absorption capacity of 14.3 mg<sub>VOC</sub>/g<sub>DES</sub> for toluene. Absorption processes are usually used for gas streams containing VOC concentrations from 10 to 1000 g/m<sup>3</sup>. Therefore, these solvents could be suitable for such applications.

From an economical and green point of view for industrial applications, recycling of the solvent is an important criterion. This parameter was therefore evaluated by performing several absorption/desorption cycles. The absorbed VOC could be released by heating the mixtures at 60 °C during 48 h. This was proven by analyzing the samples after the regeneration process as no VOC was detected in the headspace under these conditions. The absorption capacities of the solvent were stable after five cycles. For example, Chol-C<sub>8</sub>-Lev was able to absorb 99.4% of toluene in the first cycle and 99.5% during the fifth cycle.

## Conclusion

In this work, we successfully synthesized four ionic liquids from environmentally friendly chemicals as starting materials. These new solvents were fully characterized and their

**Table 2** Partition coefficient ( $K$ ) of toluene, dichloromethane and methyl ethyl ketone in water and in the studied bio-based ionic liquids and ratio of  $K_{\text{water}}/K_{\text{solvent}}$  at 30°C

	Toluene		Dichloromethane		Methyl ethyl ketone	
	$K$	Ratio	$K$	Ratio	$K$	Ratio
Water	0.251	1	0.139	1	0.0068	1
Chol-C <sub>6</sub> -Lev	0.0021	120	0.0090	15	0.0055	1.2
Chol-C <sub>8</sub> -Lev	0.0016	156	0.0071	20	0.0051	1.3
Chol-C <sub>6</sub> -Lac	0.0028	91	0.0141	10	0.0067	1
Chol-C <sub>8</sub> -Lac	0.0020	125	0.0109	13	0.0062	1.1
ChCl/Lev	0.0045	56	0.0105	13	0.0066	1
ChCl/Lac	0.0101	25	0.0211	7	0.0098	0.7

use as absorbent for VOC evaluated by determining the partition coefficient of three VOCs in these solvents. We demonstrated that the ionic liquids were able to solubilize hydrophobic VOCs as well as hydrophilic ones. Results obtained are promising and could be related to the physicochemical properties of both ionic liquids and VOCs. Therefore, the solvent properties can be tuned depending on the target VOC. This work demonstrated that VOCs capture with these versatile ionic liquids as absorbent is efficient and effective. These bio-based ionic liquids could also find applications in other applications like solubilization or extraction of bioactive compounds (cellulose, lignin).

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