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ORIGINAL PAPER

Deep eutectic solvents as green absorbents of volatile organic pollutants

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Abstract Volatile organic compounds are a major source of air pollutants. Absorption is an effective solution to treat polluted air loaded with volatile organic compounds, but most actual absorbents are often toxic and non-biodegradable. Here, we tested eutectic solvent mixtures for the absorption of volatile organic compounds for the first time. The affinity of solvent mixtures for toluene, acetaldehyde and dichloromethane was determined by measuring vapour–liquid partition coefficients and liquid phase absorption capacities. Results show that the vapour–liquid partition coefficients vary, at 30 °C, from close to zero for acetaldehyde in the mixtures choline chloride:urea, choline chloride:glycerol and tetrabutylphosphonium bromide:glycerol to 0.124 for dichloromethane in the choline chloride:urea eutectic mixture. These values are similar or even superior to those published for ionic liquids and organic solvents. Solvents based on choline chloride, a food additive, and urea, can solubilize up to 500 times more volatile organic compounds compare to water. Moreover, deep eutectic solvents are easier to prepare and more biodegradable than ionic liquids, which are also toxic. Deep eutectic solvents are more biodegradable than silicone oils, which are also expensive. Furthermore, in terms of recycling, the absorption capacities of the tested solvents remained unchanged during five absorption–desorption cycles. These findings are patented.

Keywords Air pollution · Absorption · Deep eutectic solvent · Green chemistry · Remediation

Introduction

Volatile organic compounds (VOC) are an important class of gaseous pollutants encountered both in industrial facilities and in domestic indoors (Khan and Ghoshal 2000). They include a wide range of chemicals which may have harmful health and environmental effects. However, despite their harmfulness, it is often difficult to replace them especially as solvents or cleaning agents (Wang et al. 2007). Several international protocols and European legislations aim to limit their emissions, pushing scientists to develop more efficient, less costly and greener technologies (Parmar and Rao 2009).

Absorption, used to remove VOC from gas streams by contacting the contaminated air with a liquid solvent, can provide an effective solution for VOC abatement with a removal efficiencies reaching 95–98%. The key factor of this method is the choice of a suitable liquid absorbent. However, most of VOC are hydrophobic and their low water solubility prevents the use of aqueous solutions. Various studies have, therefore, investigated the ability of organic solvents to treat gas effluent loaded with hydrophobic VOC (Darracq et al. 2010; Heymes et al.

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2006). Nevertheless, these absorbents present several drawbacks like their high price, toxicity or high volatility. In the last decade, ionic liquids were also investigated (Bedia et al. 2013; Quijano et al. 2011, 2013). Although their use leads to very good recovery, they present some disadvantages linked to their synthesis, which requires purification steps, and to a certain toxicity, which limits their use (Kudłak et al. 2015).

Deep eutectic solvents (DES) have recently emerged as a greener alternative to ionic liquids (Francisco et al. 2013; Smith et al. 2014; Zhang et al. 2012). They can be obtained by mixing two components with an appropriate molar ratio. The most common deep eutectic solvents are generally based on the mixture of an ammonium or phosphonium salt and a hydrogen bond donor, which are able of associating with each other through hydrogen bond interactions. This combination forms a liquid with a melting point significantly lower than that of each individual component. Deep eutectic solvents share many properties with ionic liquids but are cheaper to produce, often made of naturally occurring chemical, less toxic and mostly biodegradable (Paiva et al. 2014). For example, the EC_{50} values (mM) for *E. Coli* vary from 275 to 232 for choline chloride-based deep eutectic solvent (Wen et al. 2015) while they vary from 0.3 to 40 for imidazolium-based ionic liquids (Pham et al. 2010). Due to their above-mentioned characteristics, they have gained increasing scientific interest with various applications in chemistry or pharmaceutical industry (Ferreira et al. 2015; Jérôme et al. 2014; Smith et al. 2014; Zhang et al. 2012). Many of the requirements for VOC removal could be fulfilled by an absorption system containing liquid room-temperature deep eutectic solvents (low vapour pressure, nonflammability, low viscosity and low price).

To the best of our knowledge, no authors have ever evaluated deep eutectic solvents for VOC absorption. We believe that they could be an ecological alternative to the conventional VOC absorbents. In this paper, the vapour–liquid partition coefficients as well as the absorption capacities of seven deep eutectic solvents were determined to evaluate their efficiency facing three model VOC. We also evaluated whether they can be regenerated and reused.

Experimental

Materials

Choline chloride (98%), tetrabutylammonium bromide (98%), tetrabutylphosphonium bromide (98%), urea (99%), levulinic acid (99%), decanoic acid (98%), glycerol (99.5%), ethylene glycol (99.8%), toluene (99.8%), acetaldehyde (99.5%) and dichloromethane (99.8%) were purchased from Sigma-Aldrich. Choline chloride was dried by placing it at 60 °C for 2 weeks prior to use, and the other compounds were used as received.

Preparation of the eutectic mixtures

Deep eutectic solvents were prepared by stirring the two components at the desired molar ratio and up to 80 °C until a homogeneous colourless liquid was obtained. Then, an accurate mass of solvent (about 3.4 g) was placed in headspace vials of 20 mL for further use. The seven solvents prepared are listed in Table 1.

Density and viscosity measurements

Density and viscosity measurements were carried out on a U-shaped vibrating tube densimeter (Anton Paar, model DMA 5000 M) operating in a static mode. All measurements were performed at atmospheric pressure and at temperatures between 30 and 60 °C.

Vapour–liquid partition coefficients

The tendency of a species to distribute between two phases in equilibrium can be expressed as the ratio of the concentrations of the component in each phase. For a liquid mixture in equilibrium with its vapour, this constant is normally called K, the vapour–liquid partition coefficient is expressed as (Kolb and Ettre 2006):

$$K = \frac{C_G}{C_L} \tag{1}$$

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 two temperatures for the three VOC in the seven solvents was determined experimentally by static headspace–gas chromatography (SH-GC) using a combination of the phase ratio variation method for the VOC in water and the vapour phase calibration method for the VOC in the solvents. All measurements were carried out with an Agilent G1888 headspace sampler coupled with a PerkinElmer Autosystem XL gas chromatography equipped with a flame ionisation detector and a DB624 column using nitrogen as carrier vector. The GC column temperature was set at 80 °C for toluene and 40 °C for dichloromethane and acetaldehyde. The headspace settings were as follows: an oven temperature of 30 or 60 °C and an equilibrium time of 120 or 240 min, respectively. The transfer line temperature was set at 250 °C.

For the determination of K in water, several headspace vials were prepared containing different amounts of water to which the same amount of VOC was added. Using essentially the phase ratio variation method as described by

Table 1 Deep eutectic solvents prepared during this work

Hydrogen bond acceptor	Amount (g)	Hydrogen bond donor	Amount (g)	Ratio
Choline chloride	18.0	Urea	15.5	1:2
Choline chloride	15.1	Ethylene glycol	13.5	1:2
Choline chloride	15.1	Glycerol	19.9	1:2
Choline chloride	19.0	Levulinic acid	16.6	1:2
Tetrabutylphosphonium bromide	15.1	Glycerol	4.1	1:1
Tetrabutylphosphonium bromide	10.1	Levulinic acid	20.5	1:6
Tetrabutylammonium bromide	13.1	Decanoic acid	13.9	1:2

Kolb and Ettre (2006), the values of K were determined 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):

$$\frac{1}{AV_L} = \frac{1}{\alpha}\frac{V_G}{V_L} + \frac{1}{\alpha K} \quad (2)$$

where A is the peak area, α is a constant incorporating several parameters.

For the study of the VOC in the deep eutectic solvents, the vapour phase calibration method was used. First, several vials with a same water volume and different VOC amounts were prepared in order to draw a calibration curve relating the concentration of VOC in the vapour phase with the area under the chromatographic peak (A) using the previously determined K values in water.

$$C_G = \frac{n_{VOC}K}{V_L + KV_G} \quad (3)$$

where n_{VOC} is the total amount of VOC added to each vial. Since 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 VOC were added to vials containing the same solvent amount. These vials were then sealed and incubated at 30 or 60 °C, under stirring for 24 h, to obtain well-equilibrated solutions, before their analysis by static headspace–gas chromatography. The experimental chromatographic peak areas allowed the determination of C_G, the concentration of the VOC in the solvent, C_{DES}, being calculated from the mass balance. The vapour liquid partition coefficients of the VOC in the different solvents were calculated using these two concentrations. All the experiments were performed in triplicate, and the partition coefficients did not vary more than 5%.

Determination of the absorption capacity of the solvents

Various amounts of VOC (from 59 to 1000 g/m^3) were added to vials containing the different solvents. The amount of VOC solubilised in each vial could be determined from C_{DES} and the volume of the solvent solution.

Regeneration of solvent solutions

After analysis, vials containing the different solvents were uncapped and stirred at 60 °C during 48 h. We verified using static headspace–gas chromatography that there was no detectable VOC in the headspace of these vials after another 24 h of equilibration time. Then, the absorption capacities of the solvents were evaluated by putting them in contact with the VOC following the procedure described above. The absorption/desorption cycles were repeated five times.

Results and discussion

The measured densities and viscosities of the deep eutectic solvent studied were fitted to appropriate polynomials in the case of the density and to Vogel–Fulcher–Tammann (VFT) functions in the case of viscosity (Fig. 1). At 30 °C, only two of the studied solvents have viscosities lower than 100 mPa s (the choline chloride:ethylene glycol with 33.62 mPa s and the tetrabutylphosphonium bromide:levulinic acid with 60.351 mPa s), but at 60 °C, all solvents have viscosities close or lower than 100 mPa s.

Since the kinetics of the vapour–liquid equilibrium is linked to viscosity, the absorption capacity of the most viscous solvent, choline chloride:urea, towards toluene was first recorded as a function of time. Stirring the solvent during 24 h was necessary to fulfil the equilibrium at 30 and 60 °C, before placing the samples in the headspace oven. Accordingly, the partition coefficients of the three VOC are listed in Table 2.

The values obtained in water are close to values from the literature (Blach et al. 2008; Fourmentin et al. 2007; Staudinger and Roberts 2001). The significant decrease in K for the studied solvents, compared to water, indicates that a greater amount of VOC is solubilised in these solvents. We can observe a 251-fold decrease at 30 °C and 654-fold at 60 °C for toluene in tetrabutylammonium

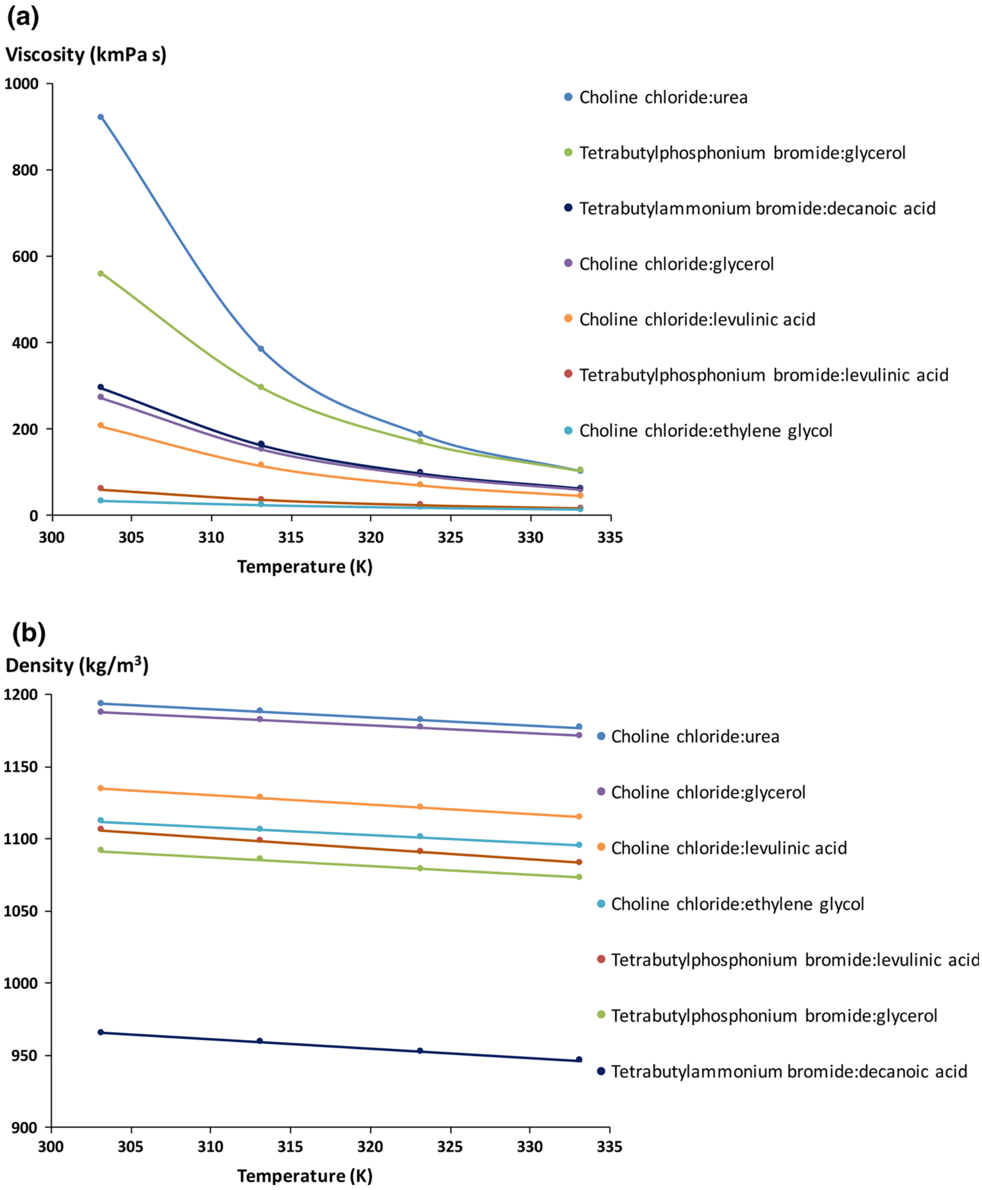

Fig. 1 Experimental values for **a** the viscosity and **b** the density of the deep eutectic solvents. The *lines* represent the Vogel–Fulcher–Tammann (VFT) correlation fitting for viscosity and appropriate polynomials in the case of the density. At 30 °C, only two of the studied solvents have viscosities lower than 100 mPa s (the choline chloride:ethylene glycol and the tetrabutylphosphonium bromide:levulinic acid) while at 60 °C, all solvents have viscosities close or lower than 100 mPa s

Table 2 Vapour–liquid partition coefficients (K) of toluene, acetaldehyde and dichloromethane in water and in seven different solvents at 30 and 60 °C

	Toluene		Acetaldehyde		Dichloromethane	
	30 °C	60 °C	30 °C	60 °C	30 °C	60 °C
Water	0.251	0.654	0.005	0.017	0.139	0.260
Choline chloride:urea	0.096	0.180	<0.001	<0.001	0.124	0.143
Choline chloride:ethylene glycol	0.022	0.005	<0.001	<0.001	0.034	0.010
Choline chloride:glycerol	0.054	0.185	<0.001	<0.001	0.037	0.121
Choline chloride:levulinic acid	0.004	0.025	<0.001	<0.001	0.008	0.028
Tetrabutylphosphonium bromide:glycerol	0.004	0.005	<0.001	<0.001	0.005	0.002
Tetrabutylphosphonium bromide:levulinic acid	0.001	0.005	<0.001	0.001	0.006	0.015
Tetrabutylammonium bromide:decanoic acid	0.001	0.001	<0.001	0.001	0.005	0.007

bromide:decanoic acid, making it the most effective absorbent for this VOC. The K values obtained for toluene are in the same order of magnitude than the ones observed for some imidazolium-based ionic liquids (Quijano et al. 2013) or with common solvents like silicone oil (Salar-García et al. 2017). Concerning dichloromethane,

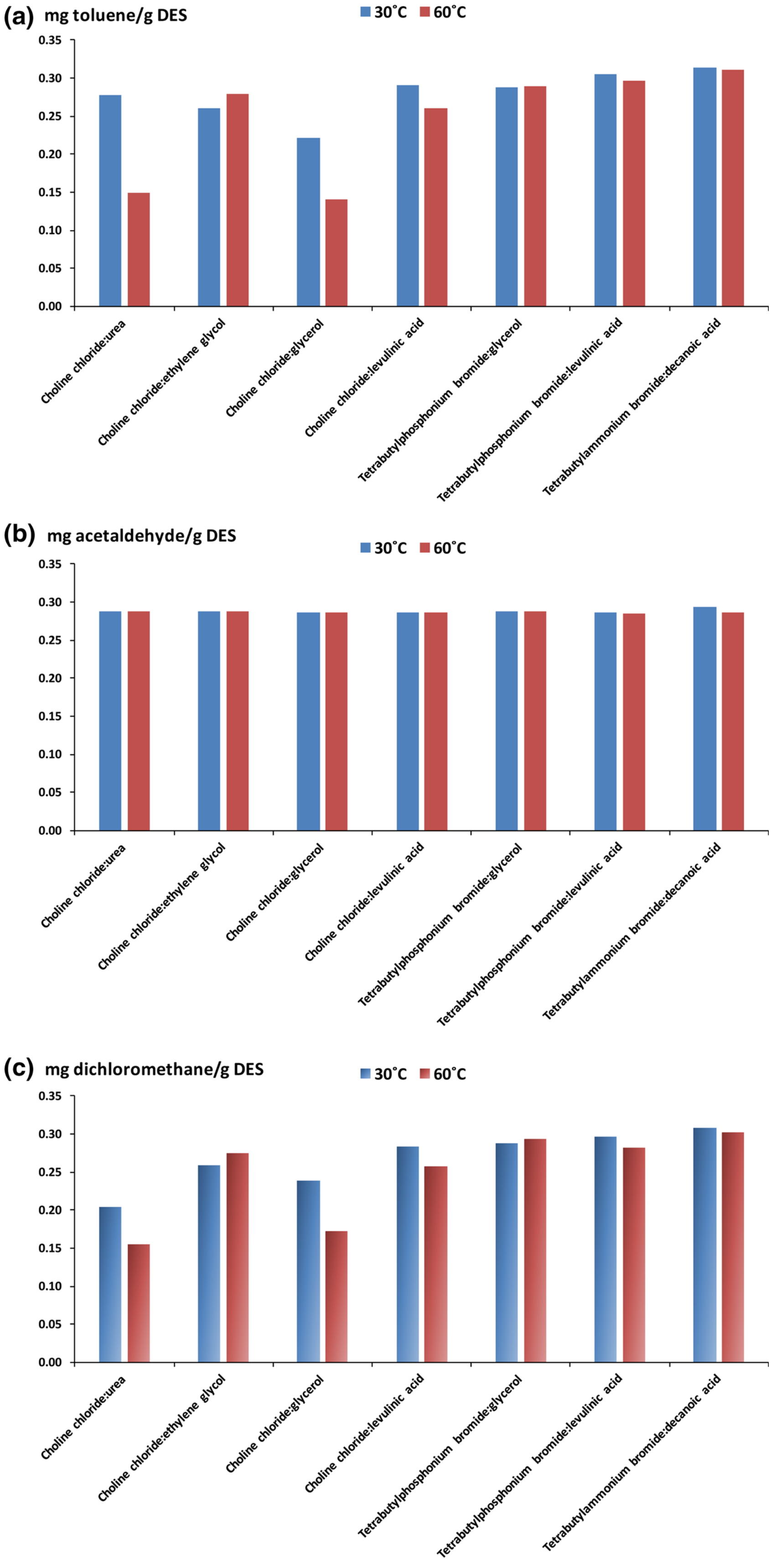

Fig. 2 Absorption capacities of the studied deep eutectic solvents at 30 and 60 °C for **a** toluene, **b** acetaldehyde and **c** dichloromethane. The concentration of the volatile organic compounds was 59 g/m^3. The solvents present various absorption capacities for toluene and dichloromethane while they present similar absorption capacities for acetaldehyde (corresponding to 99.9% absorption of the initial VOC amount). The results obtained with some of the solvents are not affected by temperature. DES stands for deep eutectic solvent

tetrabutylammonium bromide:decanoic acid and tetrabutylphosphonium bromide:levulinic acid are the most effective sorbents leading to a 28- and 23-fold decrease compared to water at 30 °C, while for acetaldehyde choline chloride:urea is the most effective with a 510- and 560-fold decrease at 30 and 60 °C, respectively. To the best of our knowledge, there is no data available in the literature concerning the absorption of acetaldehyde and dichloromethane.

The absorption capacities of the different solvents obtained at 30 and 60 °C are presented in Fig. 2 for an initial amount of VOC of 59 g/m^3. While for toluene and dichloromethane, we could observe significant differences for the studied solvents, and for acetaldehyde, they have quite the same absorption capacities which correspond to a 99.9% absorption of the initial VOC amount introduced in the vial. The results obtained with some of the solvents underlined their efficiency whatever the temperature. As the temperature of the industrial gas stream is not always stable, this trend is of utmost importance for an industrial application of these green solvents as absorbents because it prevents additional energy expenses used for controlling the temperature of the gas stream prior to treatment.

In order to explore the absorption capacities, increasing amounts of VOC were added to the selected solvents. In all cases, solvents showed high loading capacities for the studied VOC since saturation could not be reached up to an initial VOC concentration of 1000 g/m^3. At 1000 g/m^3, the choline chloride:urea solvent presented an absorption capacity of 4.12, 4.86 and 4.05 mgVOC/gDES for toluene, acetaldehyde and dichloromethane, respectively. No saturation was observed for the other solvents too. Absorption processes are usually used for gas streams containing VOC concentrations from 10 to 1000 g/m^3. Therefore, these solvents could be suitable for such applications.

Finally, we evaluated the reversibility of the absorption/desorption process. The ability to reprocess the solvent is an essential criterion from an economical and green point of view for industrial applications. The absorbed VOC could be released by heating the mixtures at 60 °C during 48 h. This was proven by analysing the samples after the regeneration process. No VOC was detected in the headspace under these conditions. The absorption capacities were stable after five cycles.

Conclusion

The absorption of three VOC by seven deep eutectic solvents was studied under different temperatures and VOC concentrations. The vapour–liquid partition coefficients obtained are significantly lower compared to water. The VOC absorption capacities of the solvents increase linearly as the initial concentration of VOC increases up to 1000 g/m^3. The absorbed VOC could be easily desorbed by heating, and the solvents exhibit very good reusability. The high absorption capacities coupled with an easy desorption process as well as the fact that they are cheap, easy to prepare and have a low environmental impact enable deep eutectic solvents to be excellent candidates to be used in VOC absorption processes.

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