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Review

Hydrophobic (deep) eutectic solvents (HDESs) as extractants for removal of pollutants from water and wastewater – A review

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ABSTRACT

Deep eutectic solvents (DESs) are a new generation of solvents that attracted increasing attention in diverse applications. In last years, growing number of studies on hydrophobic (deep) eutectic solvents (HDESs) as an alternative extractants for various chemicals from aqueous environments have been reported. This article provides an overview on the usage of HDESs in liquid–liquid extraction (LLE) of different pollutants from water and wastewater, where purified water tends to be further used or released into the environment. Discussed applications were developed for several emerging organic pollutants, such as pharmaceuticals (including antibiotics – ciprofloxacin, sulfamethoxazole, trimethoprim and vasoprotectant – calcium dobesilate), pesticides (neonicotinoids – imidacloprid, thiamethoxam, nitenpyram, acetamiprid), phenolic compounds, metal ions, among others. The particular attention was given to discuss chemical stability of HDESs after contact with water. On this basis, a matrix of possible water stable DESs was proposed. Furthermore, simple protocols to control HDESs solubility were suggested. Finally, the suggestions and guidelines for future research were provided, with focus on most important physicochemical properties of HDESs playing a key role in presented application. A perspective on their future was discussed suggesting that such HDESs-based LLE should be mainly used for pretreatment of wastewater with high pollution load, followed by adsorption or biological treatment process for removal of HDES traces. This review also highlights a serious environmental issue related to application of HDESs for sample preparation (microextraction) in analytical chemistry. Waste aqueous samples can contain hazardous – HDES related – substances and their utilization should be done with proper care on this aspect.

1. Introduction

Ever since in 2003 Abbott et al. defined a deep eutectic solvent (DES) as a liquid mixture of compounds that exhibits a significant decrease of melting point of>100 °C compared to its pure compounds[1], this new class of solvents has quickly attracted the scientific community. Straightforward preparation method of DESs which consists of simply mixing hydrogen-bond donors (HBDs) and hydrogen-bond acceptors (HBAs) is one of their big advantages over conventional solvents and especially ionic liquids (ILs)[2–3]. Moreover, the compounds used in preparation of DESs are abundant, inexpensive, biodegradable, biocompatible, and very often come from natural sources, as for example choline chloride (ChCl), carbohydrates, amino acids, among others. Another important properties of DESs are their low melting point and volatility, ability to dissolve various substances, and "designer solvent" character[4–5]. The possibility of obtaining liquids just by mixing solid compounds with high melting points caused a big excitement among scientist, and thereafter the number of publications on DESs and their applications significantly increased. Over the years they have been applied in a diverse fields, including analytical chemistry[6–8],

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biocatalysis[9–11], biomass processing[12–13], and also they were used as extractants for biomolecules[14–15], traditional fuels[16–17], and specialty solvents in gas chromatography[18], pharmaceutical[19] and cosmetic industries[20].

Until 2015 only hydrophilic DESs were reported, however their use in some important fields such as in water and wastewater treatment was not possible since they dissolve rather easily in an aqueous environment. This scenario changed when hydrophobic (deep) eutectic solvents (HDESs) were first introduced[21]. The first reported HDESs were a mixtures of long-chain tetraalkylammonium bromide salts combined with long-chain organic acids, which displayed a low melting temperature ranging from −16.65 to 8.95 °C[21]. At the similar time Marrucho's group developed HDESs composed of two neutral compounds, DL-menthol and carboxylic acids[22]. In the following years the interest in this type of DESs have been exponentially growing, however a very small number of HDESs has been proposed to date due to the limited number of available and low-cost HBAs and HBDs that can form HDESs with melting points close to room temperature. Overall, most of the reported hydrophobic DESs are representants of two categories: ionic HDESs and non-ionic, neutral HDESs based on the ionic nature of HBA [3,23]. Ionic HDESs are mainly a combination of quaternary ammonium salts with long alkyl chains with several long-chain alcohols, fatty alcohols, saturated acids, and unsaturated acids as hydrophobic HBDs [3,23–24]. On the other hand, non-ionic HDESs are way less diverse and are generally composed of terpenoid-based compounds such as DL-menthol, L-menthol, and thymol as HBAs, and carboxylic acids, natural compounds such as camphor or menthol, and therapeutical compounds (e.g., lidocaine) as HBDs[3,23–25]. Furthermore, according to this division there are also differences in the magnitude of the melting-point depression of ionic and neutral HDESs[3]. In general, for HDESs a deep depression in the melting point is usually not obtained, and in fact only large and small depressions are observed[3]. This difference in melting point depression of ionic and neutral HDESs is due to the presence of charged salts in case of ionic HDESs even if their charges are screened by the long hydrocarbon alkyl chains[3]. Meanwhile for neutral HDESs only small depressions in the melting points are observed and they are in fact eutectic mixtures[3].

Irrespective of this fact, as well as the lack of some fundamental knowledge about HDESs, these solvents have been tested in several applications. Especially, the one of the advantages of HDESs has been exploited – their water immiscibility. Contrary to hydrophilic DESs, this property allows their use in extractions and separations of compounds from aqueous phases. Nevertheless, envisaging the application of HDESs in water treatment, it is of pivotal importance to guarantee the chemical stability of these fluids in contact with water, in order to ensure that there is no contamination of the water with HDESs or HBAs and HBDs, as well as any loss of HDESs. According to main research groups in the area of HDESs, to obtain stable solvent both compounds used in its preparation must be hydrophobic, otherwise, the hydrophilic component will leak into the aqueous phase according to its water solubility[21,26]. Usually, if starting materials with very low water solubility are used, the prepared HDES also has a negligible solubility in water[3].

Over the years several review articles have been published in which the preparation methods, fundamental physicochemical properties, toxicity and major areas of interest for DESs and HDESs were thoroughly discussed[2–3,5,23–24,27–31]. However, with increased interest in HDESs as solvents and extraction media, and their more often use in water purification, it is important to give a perspective on how HDESs have been performing in water treatment processes. Recently, one excellent review on application of DESs in water treatment was published[24]. Nevertheless, it discusses a wide range of processes with little to none emphasis on the important property from the point of view of applicability of these solvents in water treatment – their water stability.

The major focus of this paper will be directed towards the use of HDESs in extraction of different pollutants from water for large scale applications, where purified water tends to be further used or released into the environment. The particular attention will be paid to whether the stability of HDES has been confirmed after contact with water. Furthermore, simple protocols to control solubility of used solvents will be proposed. Finally, the existing research gaps in the field are highlighted, and suggestions and guidelines for future research are proposed.

2. HDESs in extraction for water treatment

Irrespective to the fact that HDESs are not so well-studied as their hydrophilic counterparts and there is still missing important information on these solvents from the fundamental point of view, they were tested in a fair amount of applications and the usage of these solvents is already a flourishing field. In particular, HDESs became a promising solvents in extraction applications for water treatment processes, in which it was possible to take advantage of their poor water solubility or water immiscibility. HDESs have been already tested both as extractants in liquid–liquid extraction (LLE) processes and sorbents in solid-phase extraction. However, the focus of this paper will be directed towards the use of HDESs in large scale LLE. Throughout the subsequent sections, applications of HDESs in extraction of different pollutants from water for industrial scale applications will be discussed. The summary of up-to-date studies on the liquid–liquid extraction of pollutants from aqueous environments is presented in Table 1. In the following subsections, the extraction capacity of HDESs-based systems for several pollutants is evaluated through the distribution coefficients (D) and extraction efficiencies (EE%) values. D is defined as:

$$D = \frac{c_{0,solute}^{aq} - c_{1,solute}^{aq} \times \left(\frac{V_1^{aq}}{V_0^{aq}}\right)}{c_{0,solute}^{aq}} \quad (1)$$

where $c_{0,solute}^{aq}$ and $c_{1,solute}^{aq}$ are the concentrations of the solute before extraction and after extraction, while V_0^{aq} and V_1^{aq} are the volumes of the aqueous phase before and after extraction[32]. Note that volume correction was added due to transfer of some of the water to the HDES phase during contact.

Furthermore, log D was calculated using the following equation:

$$log_{10}D = log_{10}\frac{c_{solute}^{HDES}}{c_{solute}^{aq}} \quad (2)$$

where c_{solute}^{HDES} and c_{solute}^{aq} are concentrations of the solute in HDES and aqueous phases, respectively.

The extraction efficiency (EE%) is defined according to:

$$EE\% = \frac{c_{0,solute}^{aq} - c_{1,solute}^{aq}}{c_{0,solute}^{aq}} \times 100\% \quad (3)$$

where $c_{0,solute}^{aq}$ and $c_{1,solute}^{aq}$ are the concentrations of the solute before extraction and after extraction, respectively.

It is worth to mention here that not all HDESs are suitable for extraction in large scale applications. It is mainly related to the high cost of some available HDESs. For instance, HDESs that are prepared using long alkyl chain HBAs and HBDs are usually quite expensive. Furthermore, melting point of HDESs increases with increasing length of the alkyl chain. Thus, it imposes the usage of higher temperature of extraction process, further increasing the cost which is a key issue for industry.

LLE is a popular separation technique that uses the partitioning of a solute between two immiscible liquid phases (usually an organic solvent and aqueous sample), without a chemical reaction[33]. Usually, the solute partitions from aqueous phase to organic phase as a result of a chemical potential mechanism[24]. For the separation to occur, the solvent and the raffinate must be immiscible, that generally means that they have opposite polarities[24]. To the main advantages of LLE belongs its flexibility, universality, low energy consumption and

Table 1
Applications of HDESs in liquid–liquid extraction of pollutants from water and wastewater.

Pollutant	HDES	Evaluation of HDES stability in water	Main results	Ref.
Acetic acid, propionic acid, butyric acid	$[N_{8881}]Br:C_{10}$ (1:2)	Yes	EE% of 29.7%, 63.4%, 83.1% for acetic, propionic and butyric acid, respectively.	[21]
	$[N_{8888}]Br:C_{10}$ (1:2)		EE% of 30.6%, 65.9%, 87.4% for acetic, propionic and butyric acid, respectively.	
	$[N_{7777}]Cl:C_{10}$ (1:2)		EE% of 32.0%, 76.5%, 91.5% for acetic, propionic and butyric acid, respectively.	
	$[N_{8881}]Cl:C_{10}$ (1:2)		EE% of 38.0%, 70.5%, 89.8% for acetic, propionic and butyric acid, respectively.	
	$[N_{8888}]Cl:C_{10}$ (1:2)		EE% of 25.0%, 52.7%, 81.3% for acetic, propionic and butyric acid, respectively.	
$CoCl_2$, $NiCl_2$, $FeCl_2$, $MnCl_2$, $ZnCl_2$, $CuCl_2$, NaCl, KCl, LiCl	lidocaine:C_{10} (1:2)	Yes	$D \geq 0.992$ for Co, Cu, Fe, Mn, Ni, Zn ions.	[32]
	lidocaine:C_{10} (1:3)		$D \geq 0.991$ for Co, Cu, Fe, Mn, Zn ions.	
	lidocaine:C_{10} (1:4)		$D \geq 0.991$ for Cu, Fe, Zn ions.	
Pertechnetate ($^{99m}TcO_4^-$)	$[P_{14,666}]Cl:C_{10}$ (1:2)	No	EE%>99%	[37]
	$[N_{8888}]Br:C_6$ (1:2)		EE%>99%	
	$[N_{8888}]Br:C_{10}$ (1:2)		EE%>99%	
Imidacloprid, Thiamethoxam, Nitenpyram, Acetamiprid	DL-menthol:C_8 (1:1)	Yes	EE% of 72.72%, 43.66%, 66.44%, 39.61% for Imidacloprid, Thiamethoxam, Nitenpyram and Acetamiprid, respectively.	[26]
	DL-menthol:C_{10} (1:1)		EE% of 53.06%, 7.18%, 45.00%, 27.10% for Imidacloprid, Thiamethoxam, Nitenpyram and Acetamiprid, respectively.	
	DL-menthol:C_{12} (2:1)		EE% of 66.64%, 26.00%, 77.45%, 16.69% for Imidacloprid, Thiamethoxam, Nitenpyram and Acetamiprid, respectively.	
Ciprofloxacin	$C_{12}:C_8$ (1:3)	Yes	EE%≈60%	[38]
	$C_{12}:C_{10}$ (1:2)	Yes	EE%≈90%	[38]
	DL-menthol:C_8 (1:1)	Yes	EE%≈60%	[38]
	DL-menthol:C_{10} (1:1)	Yes	EE%≈90%	[38]
	DL-menthol:C_{12} (2:1)	Yes	EE%≈90%	[38]
	$[N_{7777}]Br:C_{10}$ (1:2)	Yes	EE%≈5%	[38]
	$[N_{8881}]Br$:DL-menthol (1:2)	Yes	EE%≈5%	[38]
	$[N_{8881}]Br:C_8$ (1:2)	Yes	EE%≈20%	[38]
	$[N_{8881}]Br:C_{10}$ (1:2)	Yes	EE%≈15%	[38]
	$[N_{8888}]Br:C_{10}$ (1:2)	Yes	EE%≈2%	[38]
	thymol:C_8 (0.33:0.66)	No	EE%=99.92%	[39]
	thymol:C_{10} (0.44:0.56)	No	EE%=99.92%	[39]
	thymol:C_{12} (0.56:0.44)	No	EE%=99.92%	[39]
Trimethoprim, Sulfamethoxazole	thymol:C_8 (0.33:0.66)	No	EE% of 99.64%, 97.02% for Trimethoprim and Sulfamethoxazole, respectively.	[39]
	thymol:C_{10} (0.44:0.56)		EE% of 99.50%, 96.49% for Trimethoprim and Sulfamethoxazole, respectively.	
	thymol:C_{12} (0.56:0.44)		EE% of 99.82%, 96.16% for Trimethoprim and Sulfamethoxazole, respectively.	
Calcium dobesilate	$[N_{8881}]Cl:BrCH_2COOH$ (2:1)	No	EE%≈73%	[40]
	$[N_{8881}]Cl:BrCH_2COOH$ (1:1)		EE%≈99%	
	$[N_{8881}]Cl:BrCH_2COOH$ (1:2)		EE%≈48%	
	$[N_{8881}]Cl:BrCH_2COOH$ (1:3)		EE%≈52%	
	$[N_{8881}]Cl:BrCH_2COOH$ (1:4)		EE%≈47%	
	$[N_{8881}]Cl:Cl_2CHCOOH$ (2:1)		EE%≈77%	

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Table 1 (*continued*)

Pollutant	HDES	Evaluation of HDES stability in water	Main results	Ref.
	[N_{8881}]Cl: $Cl_2CHCOOH$ (1:1)		EE%≈93%	
	[N_{8881}]Cl: $Cl_2CHCOOH$ (1:2)		EE%≈56%	
	[N_{8881}]Cl: $Cl_2CHCOOH$ (1:3)		EE%≈45%	
	[N_{8881}]Cl: $Cl_2CHCOOH$ (1:4)		EE%≈34%	
	[N_{8881}]Cl: Cl_3CCOOH (2:1)		EE%≈73%	
	[N_{8881}]Cl: Cl_3CCOOH (1:1)		EE%≈72%	
	[N_{8881}]Cl: Cl_3CCOOH (1:2)		EE%≈30%	
	[N_{8881}]Cl: Cl_3CCOOH (1:3)		EE%≈18%	
	[N_{8881}]Cl: Cl_3CCOOH (1:4)		EE%≈12%	
Bisphenol-A	DL-menthol:C_1 (1:1)	No	EE%=99.0%	[41]
	DL-menthol:C_2 (1:1)	No	EE%≈95%	[41]
	DL-menthol:C_3 (1:1)	No	EE%=98.2%	[41]
	DL-menthol:C_6 (1:1)	No	EE%≈65%	[41]
	DL-menthol:C_8 (1:1)	No/No	EE%≈65%, EE%=99.94%	[41–42]
	DL-menthol:C_8 (1:2)	No	EE%=81.65%	[43]
	DL-menthol:C_{10} (1:1)	No	EE%≈80%	[41]
	DL-menthol:C_{10} (1:2)	No	EE%=92.43%	[43]
	[N_{7777}]Br:C_8 (1:2)	No	EE%=94.91%	[43]
	[N_{7777}]Br:C_{10} (1:2)	No	EE%=97.10%	[43]
	[N_{8881}]Br:C_8 (1:2)	No	EE%=84.24%	[43]
	[N_{8881}]Br:C_{10} (1:2)	No	EE%=91.99%	[43]
	[N_{8881}]Br:DL-menthol (1:2)	No	EE%=91.45%	[43]
	[N_{8888}]Br:C_8 (1:2)	No	EE%=90.48%	[43]
	[N_{8888}]Br:C_{10} (1:2)	No	EE%=97.61%	[43]
	DL-menthol: camphor (3:2)	No	EE% >99.95%	[42]
	DL-menthol:C_4OH (1:1)	No	EE%≈96%	[41]
	DL-menthol:$C_{10}OH$ (1:1)	No	EE%≈90%	[41]
	DL-menthol:$C_{18}OH$ (1:1)	No	EE%≈80%	[41]
Phenol	DL-menthol:C_8 (1:1)	Yes/No/No	EE%=87.46%, EE%=85.2%, EE%>99%	[44–46]
	DL-menthol:C_9 (1:1)	Yes	EE%>94%	[47]
	DL-menthol:C_{10} (1:1)	Yes/No/Yes/No	EE%=88.78%, EE%=86.1%, EE%>93%, $\log D_{HDES-water}$=0.94	[44–45,47–48]
	DL-menthol:C_{12} (1:1)	Yes	EE%>92%	[47]
	DL-menthol:C_{12} (2:1)	No	EE%=88.9%	[45]
	DL-menthol:C_{18} (1:1)	Yes	EE%>91%	[47]
	C_{12}:C_8 (1:3)	Yes	EE%=75.78%	[44]
	C_{12}:C_{10} (1:2)	Yes	EE%=67.84%	[44]
	thymol:C_8 (1:2)	No	EE%>98%	[46]
	DL-menthol:thymol (1:1)	No	EE%>98%	[46]
	[N_{8888}]Br:C_{10} (1:2)	No	$\log D_{HDES-water}$=1.70	[48]
	[N_{8888}]Cl:C_{10} (1:2)	No	$\log D_{HDES-water}$=2.07	[48]
2-chlorophenol	DL-menthol:C_6 (1:2)	No	EE%=97.90%	[49]

(*continued on next page*)

Table 1 (*continued*)

Pollutant	HDES	Evaluation of HDES stability in water	Main results	Ref.
	DL-menthol:C_8 (1:1)	Yes/No	EE%=97.02%, EE%>99%	[44,46]
	DL-menthol:C_8 (1:2)	No	EE%=97.73%	[49]
	DL-menthol:C_{10} (1:1)	Yes	EE%=97.04%	[44]
	DL-menthol:C_{10} (1:2)	No	EE%=97.18%	[49]
	C_{12}:C_8 (1:3)	Yes	EE%=98.42%	[44]
	C_{12}:C_{10} (1:2)	Yes	EE%=98.00%	[44]
	thymol:C_8 (1:2)	No	EE%>99%	[46]
	DL-menthol:thymol (1:1)	No/No	EE%>98%, EE%=95.51%	[46,49]
	DL-menthol:thymol (1:2)	No	EE%=94.68%	[49]
	DL-menthol:thymol (1:3)	No	EE%=94.14%	[49]
	DL-menthol:thymol (1:4)	No	EE%=94.23%	[49]
2-nitrophenol	DL-menthol:C_8 (1:1)	No	EE%>99%	[46]
	thymol:C_8 (1:2)		EE%>99%	
	DL-menthol:thymol (1:1)		EE%>95%	
3-chlorophenol,2,4-dichlorophenol	DL-menthol:thymol (1:1)	No	EE% of 99.25%, 95.55% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	[49]
	DL-menthol:thymol (1:2)		EE% of 96.31%, 95.41% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	
	DL-menthol:thymol (1:3)		EE% of 97.22%, 95.12% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	
	DL-menthol:thymol (1:4)		EE% of 95.53%, 95.08% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	
	DL-menthol:C_6 (1:2)		EE% of 99.76%, 96.02% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	
	DL-menthol:C_8 (1:2)		EE% of 97.79, 96.13% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	
	DL-menthol:C_{10} (1:2)		EE% of 97.92, 96.00% for 3-chlorophenol and 2,4-dichlorophenol, respectively.	
o-cresol	DL-menthol:C_8 (1:1)	Yes	EE%=96.49%	[44]
	DL-menthol:C_{10} (1:1)		EE%=96.80%	
	C_{12}:C_8 (1:3)		EE%=93.52%	
	C_{12}:C_{10} (1:2)		EE%=92.03%	
Guaiacol, syringol	DL-menthol:C_8 (1:1)	No	EE% of 84.1%, 69.0% for guaiacol and syringol respectively.	[45]
	DL-menthol:C_{10} (1:1)		EE% of 90.0, 73.8% for guaiacol and syringol respectively.	
	DL-menthol:C_{12} (2:1)		EE% of 93.5, 76.4% for guaiacol and syringol respectively.	
Benzoic acid, chlorobenzene, phthalic acid, salicylic acid, toluene, toluic acid	DL-menthol:C_{10} (1:1)	No	log$D_{HDES–water}$ of 1.49, 2.15, 0.088, 1.86, 1.94, 2.03 for benzoic acid, chlorobenzene, phthalic acid, salicylic acid, toluene and toluic acid, respectively.	[48]
	[N_{8888}]Br:C_{10} (1:2)		log$D_{HDES–water}$ of 1.77, 2.55, 1.91, 2.81, 1.74, 2.50 for benzoic acid, chlorobenzene, phthalic acid, salicylic acid, toluene and toluic acid, respectively.	
	[N_{8888}]Cl:C_{10} (1:2)		log$D_{HDES–water}$ of 2.21, 2.70, 1.75, 2.92, 1.68, 2.99 for benzoic acid, chlorobenzene, phthalic acid, salicylic acid, toluene and toluic acid, respectively.	
Adipic acid, levulinic acid, succinic acid	TOPO:C_{10} (1:1)	No	EE% of 84.58%, 82.32%, 58.55% for adipic, levulinic and succinic acid, respectively.	[50]
	TOPO:C_{12} (1:1)		EE% of 83.79%, 66.73%, 77.08% for adipic, levulinic and succinic acid, respectively.	
Furfural	[N_{6666}]Br:C_{10} (1:3)	Yes	EE%=85%	[51]
	[N_{6666}]Br:C_{12} (1:3)		EE%=85%	
	[N_{8888}]Br:C_{10} (1:3)		EE%=80%	
	[N_{8888}]Br:C_{12} (3:1)		EE%=80%	
Estriol, estrone, 17α-ethynylestradiol, 17α-estradiol, 17β-estradiol	DL-menthol:C_8 (1:1)	No	EE% of 99.07%, 99.90%, 99.90%, 99.90%, 99.93% for estriol, estrone, 17α-ethynylestradiol, 17α-estradiol and 17β-estradiol, respectively.	[52]

(*continued on next page*)

Table 1 (*continued*)

Pollutant	HDES	Evaluation of HDES stability in water	Main results	Ref.
	DL-menthol:C_{10} (1:1)		EE% of 98.61%, 99.86%, 99.89%, 99.87%, 99.91% for estriol, estrone, 17α-ethynylestradiol, 17α-estradiol and 17β-estradiol, respectively.	
	DL-menthol:C_{12} (1:1)		EE% of 98.63%, 99.86%, 99.88%, 99.87%, 99.91% for estriol, estrone, 17α-ethynylestradiol, 17α-estradiol and 17β-estradiol, respectively.	
	C_{10}:C_8 (1:1)		EE% of 98.50%, 99.88%, 99.85%, 99.84%, 99.89% for estriol, estrone, 17α-ethynylestradiol, 17α-estradiol and 17β-estradiol, respectively.	
	C_{12}:C_8 (1:1)		EE% of 98.45%, 99.85%, 99.84%, 99.84%, 99.89% for estriol, estrone, 17α-ethynylestradiol, 17α-estradiol and 17β-estradiol, respectively.	
	C_{12}:C_{10} (1:1)		EE% of 97.66%, 99.79%, 99.79%, 99.77%, 99.81% for estriol, estrone, 17α-ethynylestradiol, 17α-estradiol and 17β-estradiol, respectively.	

possibility of recycling[34–36]. Despite all of these favorable characteristics, this technique has a several disadvantages that make it not suitable for some of the applications. For instance, it is time-consuming, requires large amounts of solvents[34–36]. Furthermore, the used solvents are mostly toxic organic solvents, which additionally showed some limitations in terms of their selectivity towards certain solutes[34–36]. Envisaging the application of LLE in water treatment, it is necessary to use hydrophobic solvents. HDESs became great candidates as extraction solvents because of their easy preparation, high extraction efficiency, recyclability, among others. Moreover, HDESs have highly tunable nature since through the manipulation of different types of HBAs, HBDs and molar ratios, it is possible to modify their biological and physicochemical properties to make them suitable extraction solvents for the wide range of solutes present in water.

2.1. Carboxylic acids

The first application of HDESs in water treatment has already taken place in the pioneering work of van Osch et al.[21]. The authors prepared HDESs based on methyltrioctylammonium chloride ([N_{8881}]Cl), tetraheptylammonium chloride ([N_{7777}]Cl), tetraoctylammonium chloride ([N_{8888}]Cl), methyltrioctylammonium bromide ([N_{8881}]Br) and tetraoctylammonium bromide ([N_{8888}]Br) as HBAs, and decanoic acid (C_{10}) as HBD, and used them in extraction of volatile fatty acids (acetic, butyric and propionic acid) from diluted aqueous solution[21]. Due to possible future application of the studied HDESs in water treatment processes, the authors also verified the stability of these solvents after contact with water (details can be found in section 3). The studied HDESs revealed superior extraction efficiencies for the volatile acids compared to the trioctylamine (TOA), representative of amine-based extractants that are conventionally used for the extraction of carboxylic acids. Such better performance was attributed to hydrogen bonding ability of HDES components[21]. The best extractability of all volatile fatty acids (VFAs) was obtained when using [N_{8881}]Cl:C_{10} (1:2) HDES with 38.0%, 70.5% and 89.8% extraction efficiency for acetic, propionic and butyric acid, respectively[21]. These results were explained as a consequence of increased accessibility of both the VFAs and the water to this HDES due to the lower steric hindrance effect of the alkyl chains [21]. Furthermore, when a symmetric salt was used as HBA e.g. [N_{8888}]Cl and [N_{7777}]Cl, the decrease in extraction efficiencies with the increase of the alkyl chain of the salt was observed[21]. It was also reported that the studied HDESs displayed better extractants performance for VFA with longer alkyl chain length since extraction efficiency increased with the increase in the alkyl chain length of the acid[21]. However, for these solvents to be used as extractants for carboxylic acids and to assure sustainability of the overall process, it is necessary to study solvents regeneration and reuse. Furthermore, it is very important to study biodegradability of such long alkyl chain salts in order to guarantee the removal of its traces from water phase after extraction.

In 2020, Riveiro et al.[50] prepared two HDESs composed of trioctylphosphine oxide (TOPO) as HBA and decanoic, dodecanoic (C_{12}) acids as HBDs and used them as extractants in LLE for adipic acid, levulinic acid, and succinic acid. The extraction experiments revealed that when the initial concentration of the acid is increased, the extraction efficiencies usually increased as well[50]. In general, at initial concentration of 10 g/L 84.58%, 82.32%, 57.05% extraction efficiency using TOPO:C_{10} HDES, and 83.14%, 65.87%, 62.19% using TOPO:C_{12} HDES for adipic, levulinic and succinic acid, respectively, were obtained[50]. Hence, the following order of the extractability of HDESs for the extracted acids was deducted: adipic acid > levulinic acid > succinic acid and explained by the easier solvation of acids in water in the presence of shorter chains and carboxylic groups that can form hydrogen bonds with water molecules[50]. Furthermore, regarding the effect of the HBD on extraction efficiency, it was discovered that an increase in the HBD chain length led to an increase in the extraction efficiency, in particular at lower concentration of the extracted acid[50]. Nevertheless, it was also shown that both studied HDESs were characterized by lower extractability compared to TOPO alone. This better performance of TOPO over TOPO-based HDESs was attributed to the fact that for TOPO there is possible the hydrogen bonding between the oxygen of the P = O group in TOPO and the –OH group of the extracted acid, while in HDESs this P = O group is already occupied through hydrogen bonds formed during formation of HDES[50]. In view of these result, it can be concluded that extraction of these carboxylic acids is ruled by the ability to hydrogen bonding of the solvents used as extractants. This is in agreement with the results obtained in the study of van Osch and coworks[21], where hydrogen bonding ability of HDES components was also responsible for improved extraction efficiency of other carboxylic acids. Therefore, in order to find the best HDES for separation of organic acids from aqueous environment, it should be composed of HBA and HBD highly prone to form hydrogen bonds with solutes. However, due to formation of the hydrogen bonds between solute and HBA and/or HBD, there is a possibility that hydrogen bonds between HBA and HBD might be weakened and it may result in destruction of the hydrogen bond framework of the HDES and leakage of its components into the aqueous phase. This aspect should be addressed in future papers when selecting proper HDES.

2.2. Alkali and transition metal ions

In another study van Osch et al.[32] proposed the use of a HDES based on decanoic acid and lidocaine for the removal of alkali and transition metal ions from water. Some of the metal ions are toxic and their presence in water make it undrinkable, therefore the removal of

such ions from contaminated water is needed. They prepared hydrophobic DESs composed of decanoic acid and lidocaine in 2:1, 3:1 and 4:1 molar ratios[32]. Afterwards, the authors measured distribution coefficients (D) for the ions of the metal salts: cobalt chloride ($CoCl_2$), nickel chloride ($NiCl_2$), iron chloride ($FeCl_2$), manganese chloride ($MnCl_2$), zinc chloride ($ZnCl_2$), copper chloride ($CuCl_2$), sodium chloride (NaCl), potassium chloride (KCl) and lithium chloride (LiCl). It was observed that with the investigated HDESs all transition metal ions, in experiments with only single metal salts in water phase, could be removed with high D values ($D \rightarrow 1$)[32]. High removal ($D \rightarrow 1$) was achieved for both pure transition metal salt solution and a mixed metal salt solution[32]. On the other hand, the extraction of the alkali metal ions in such a mixture of metal ions was rather low (D up to 0.266), which was explained by the preference of fatty acids to bind with transition metals and not with alkali metals[32]. Moreover, the whole process of extraction was very fast because the same D were achieved within 5 s of shaking as after shaking for 1 h[32]. An ion exchange process, in which the positively charged metal ion is exchanged with the partially positively charged lidocaine was put forward as a possible extraction mechanism[32]. It was confirmed during NMR analysis of water phase in which the presence of lidocaine was observed[32]. The obtained results were further compared to those obtained with ILs based on fatty acids and quaternary ammonium salts and it was found out that when pH was not controlled, HDESs surpassed ILs in metal ion extraction, while they performed worse for chloride ions[32]. On the other hand, similar results for removal of metal ions were obtained when the pH of the water phase was adjusted[32]. Finally, the authors evaluated the possibility of HDES regeneration with $Na_2C_2O_4$ as a stripping solution and checked HDES reusability[32]. D values of approximately 0.85–0.90 were achieved for the regeneration of Co^{2+} into the water phase[32]. Furthermore, extraction experiments after regeneration revealed that it was possible to reuse HDES with high efficiency for the HDES with a higher decanoic to lidocaine ratio (3:1 and 4:1)[32]. Nevertheless, some turbidity of the water phase after reaching phase equilibrium was noted[32]. On the other hand, in the case of HDES with 2:1 ratio of decanoic acid to lidocaine, the D was only 0.706 after regeneration[32]. Moreover, a decrease in the volume of the HDES after extraction was observed, meaning that some of HDES leaked to the water phase[32]. All of these observations means that HDES composed of lidocaine and decanoic acid might not be the most suitable extraction solvents for metal ion removal. It is related to the fact that during the extraction, an ion exchange occurs and lidocaine is leaked to the water phase. Such leaching of lidocaine into the aqueous phase results in difference in the HBA:HBD ratio of the HDES after regeneration, which is reflected in changes in extraction ability. It means that HDES cannot be used in many extraction cycles. This highly limits such a proposed application for industrial practice.

The extractive removal of metal anion – pertechnetate ($^{99m}TcO_4^-$) – from aqueous media using HDESs was also reported by Phelps et al.[37]. Pertechnetate is a chemically stable, toxic, and mobile anion, that is released into the environment by technetium-99, a radionuclide produced during artificial nuclear fission[37]. Most importantly tetra-oxo anions and radionuclides are listed as priority pollutants by the U.S. Environmental Protection Agency, therefore it is necessary to remove low levels of TcO_4^- from contaminated groundwater. Three HDESs were prepared with various HBAs, namely trihexyltetradecylphosphonium, $[P_{14,666}]Cl$, or $[N_{8888}]Br$ and fatty acid as HBDs (hexanoic acid (C_6) or C_{10}), combined in a 1:2 molar ratio[37]. All the studied HDESs showed high extraction capacity of $^{99m}TcO_4^-$ (>99%) when using equivolume (1:1, v/v) mixtures of HDES and aqueous phase containing of a variety of competing anions, such as HCO_3^-, Cl^-, NO_3^-, $H_2PO_4^-$, and SO_4^{2-}[37]. On the other hand, the ReO_4^- anion suppressed $^{99m}TcO_4^-$ extraction when present in stoichiometric amounts relative to the HDES[37]. The reason for that was most probably saturation of the HDES phase with perrhenate, which is an oxyanion with similar characteristics to pertechnetate, thus leading to decreased extraction of the latter[37]. In general, the extraction efficiency was dependent upon factors such as the nature of the competing anion(s), type of HBD, and pH[37]. Overall, distribution ratios in the 100–8000 and 50–2000 ranges for 1:1 and 1:50 (v/v) extraction systems were obtained in this work[37]. The obtained results were found to be similar or even better than those obtained using other extraction methods. For instance, distribution ratios of 100–500 and 400–700 for pertechnetate using crown ether (dicyclohexano-18-crown-6) containing hydrophobic ionic liquids[53] and using aqueous biphasic systems containing chaotropic ionic liquids[54] were reported, respectively. Aiming at HDES recycling, a removal of pertechnetates from the HDES using back extraction into an aqueous phase was also tested. For that purpose, a series of aqueous media containing organic cosolvents, acids, bases, reducing agents, or high ionic strength were employed, and it was found out that the aqueous solutions at pH 5 containing citrate and tin(II) chloride ($SnCl_2$) as a reducing agent were most effective for pertechnetate removal with back extraction efficiency of 57–69%[37]. None of the tested solutions was found to completely remove ^{99m}Tc from HDESs previously used to extract $^{99m}TcO_4^-$ from water. These results means that there is a need for more efficient HDESs regeneration method, because reuse of a HDES containing even a very small amount of ^{99}Tc would be practically impossible, as it may possess high risk to the environment.

2.3. Pesticides

HDESs were also used as extraction solvents for pesticides present in water[26]. Pesticides are commonly used in agriculture to combat insects. Hence, it is possible that some of them can pass through the soil and subsoil and lead to contamination of water, posing a potential risk to living beings. Florindo et al.[26] prepared HDESs based on DL-menthol as HBA, and octanoic (C_8), decanoic and dodecanoic acid as HBDs. The stability of the studied solvents in water was evaluated using NMR analysis and no leaking of HDESs components to the water phase was observed[26]. These water stable HDESs were further tested in extraction of four neonicotinoids (Imidacloprid, Thiamethoxam, Nitenpyram, and Acetamiprid) and extraction efficiencies up to 80% were obtained [26]. The highest extraction efficiency was observed for Imidacloprid (~80% EE), followed by Acetamiprid (~75% EE), while much lower effectiveness of HDESs in extraction of Thiamethoxam (~40% EE) and Nitenpyram (~35% EE) was attained[26]. These results were explained by the observation that pesticides hydrophobicity was the key property influencing their extraction from water since extraction efficiencies followed the inverse order of their water solubility[26]. Furthermore, no correlation was found between the extractions efficiency of the pesticides and their octanol–water partition coefficient (K_{ow} defined as: $K_{ow} = \frac{c_{solute}^{octanol}}{c_{solute}^{water}}$, where $c_{solute}^{octanol}$ and c_{solute}^{water} are concentrations of the solute in octanol- and water-rich phases, respectively)[26]. The obtained results further revealed that there was no relationship between the extraction efficiencies of the pesticides and the increase of hydrophobicity of the HDESs which resulted from the alkyl chain length of the HBD[26]. Overall, DL-menthol:C_8 HDES showed the best performance as extractant for 3 of the studied pesticides, namely Imidacloprid, Thiamethoxam and Nitenpyram[26]. On the other hand, for Acetamiprid the best suitable solvent was DL-menthol:C_{12}, followed up very closely by DL-menthol:C_8[26]. Comparing the extraction efficiencies of HDESs to the values obtained using hydrophobic ILs, namely $[C_2MIM][NTf_2]$, $[C_4MIM][NTf_2]$, and $[C_6MIM][NTf_2]$, it was observed that these obtained for HDESs were lower than those obtained when ILs were used (EE% up to 90%)[26]. Moreover, the authors showed that it was possible to reuse the prepared HDESs, demonstrating their potential as sustainable solvents in water treatment applications. Nevertheless, it is still necessary to study HDESs regeneration, since it was seen that in the following extraction cycles the extractability decreased. It should be also noted that in this work the experiments were not performed using the real samples and relatively high concentrations of pesticides (0.025 g/L) in

the starting aqueous solutions were used. Therefore, it would be interesting to see how the studied HDESs would perform with much lower concentrations of pesticides.

2.4. Active pharmaceutical ingredients (APIs)

In another work of Florindo et al.[38] HDESs were also applied in extraction of ciprofloxacin from water environments. Ciprofloxacin is an active pharmaceutical ingredient (API) that can be found up to μg/L levels in the aquatic environment and is identified as one of the top 10 priority micropollutants present in water environments. HDESs prepared using natural neutral components, such as menthol and fatty acids, and also using quaternary ammonium salts and natural fatty acids were studied as potential extractants[38]. The authors chose eutectic mixtures that had low water and high ciprofloxacin solubility thus being promising candidates to separate ciprofloxacin from water. It was observed that neutral HDESs had up to 3 wt% of water solubility, and that water solubility of ionic HDESs varied between 3 wt% and 8 wt% [38]. In liquid–liquid extraction several experimental variables that can influence the extraction of ciprofloxacin were investigated, and it was observed that pH was a very crucial for the extraction with higher extraction efficiencies obtained when ciprofloxacin was in its anionic form[38]. On the other hand, the temperature, the stirring speed and HDES/water phase ratio did not have significant impact on the extraction efficiencies[38]. Furthermore, the obtained results revealed that HDESs that contained natural and neutral compounds in their composition offered the best extraction efficiencies[38]. In particular, HDES composed of dodecanoic and decanoic acid (molar ratio 1:2) was the best extractant from the studied solvents[38]. These results were assigned to high solubility value of ciprofloxacin and low water solubility of this HDES, as ciprofloxacin extraction was linked to the hydrophobicity of the HDES, in particular to the water solubility in the HDES[38]. Finally, a reusability and a recyclability of the HDES was assessed. It was showed that C_{12}:C_{10} HDES kept its extraction properties and removed ciprofloxacin from the water with similar efficiency for at least four cycles[38]. For purpose of HDES recycling (see Fig. 1), adsorption using activated carbon was proposed. The obtained results showed that this approach was a viable, and slightly higher removal extraction efficiencies of ciprofloxacin (82%) than those obtained with fresh HDES (76%) were achieved[38]. This higher extraction efficiency has been assigned to possible removal of some impurities present in the components of the HDES during contact with the activated carbon[38]. On top of that, adsorption with activated carbon is already implemented and available in water treatment plants, hence it is very good choice from practical and industrial point of view. Furthermore, in the proposed by the authors approach there is no contact of activated carbon with water, which limits some possible health and environmental problems associated with the ingestion of microparticles.

An attempt to remove another type of API – calcium dobesilate – was also carried out by Zhu et al.[40]. Calcium dobesilate is a vascular protective drug used to improve microcirculation. However, it was also was found to have serious adverse effects on human health such as gastrointestinal diseases, central and peripheral nervous system disorders, as well as skin and appendages damages[40]. Therefore, the excreted calcium dobesilate may enter into water environment and pose serious threat to living beings. For purpose of removal of this drug from water, the researchers selected acidic HDESs composed of $[N_{8881}]Cl$ as HBA and dichloroacetic acid ($Cl_2CHCOOH$), bromoacetic acid ($BrCH_2COOH$) and trichloroacetic acid (Cl_3CCOOH) as HBDs[40]. The obtained results revealed that all 3 HDESs extracted calcium dobesilate from aqueous solution with high efficiency above 70%[40]. The following order of extraction efficiency of HDESs was deducted: $[N_{8881}]Cl$:$BrCH_2COOH$ > $[N_{8881}]Cl$:$Cl_2CHCOOH$ > $[N_{8881}]Cl$:Cl_3CCOOH, which was consistent with the order of pKa values in water of the acids [40]. Furthermore, for each type of HDES the effect of HBD:HBA molar ratio was studied. It was found out that the HDESs with the ratio of 1:1 showed the highest extraction efficiency[40]. The decrease in extraction efficiency with increased proportion of HBD (molar ratios of 1:1, 1:2, 1:3 and 1:4) was observed[40]. The same was valid when increased proportion of $[N_{8881}]Cl$ (molar ratio of 2:1) was used, most likely due to high viscosity of this HDES that affected the mass transfer rate between the two phases in the extraction process[40]. $[N_{8881}]Cl$:$BrCH_2COOH$ (1:1) HDES was selected as the best extractant from the studied solvents and used in the optimization experiments in which the effect of pH, extraction temperature, mixing time, interferential inorganic salts and organic coexists, were systematically investigated. It was observed that pH had very small effect on the extraction efficiency (97.45–99.03% extraction efficiency in the pH range from 1.2 to 9.2), and extraction efficiency slightly diminished under alkaline condition due to calcium dobesilate instability in alkaline solution[40]. Similarly, the temperature also had small influence on the extraction and from 10 °C to 40 °C, the extraction efficiency increased slightly by 2.8%, thus room temperature was adopted as optimal one[40]. Furthermore, it was observed that extraction efficiencies increased with increasing vortex time and became stable after 150 s of shaking[40]. Lastly, it was showed that common inorganic salts up to 1.0 mol/L and high concentration of common organic compounds did not interfere with the extraction[40]. The studies on extraction mechanism revealed that it involved the breakage of the hydrogen bond between Cl^- in $[N_{8881}]Cl$ and H on the carboxyl group of $BrCH_2COOH$ followed by formation of the complex between the big anion of calcium dobesilate, $[N_{8881}]^+$ and $BrCH_2COO^-$ through electrostatic and hydrogen bonding interactions [40]. Moreover, the HDES was successfully regenerated using hydrochloric acid as back extraction solvent and then reused in the next extraction cycles, and such regenerated HDES maintained high extraction efficiency[40]. It was deducted that in this process hydrochloric acid protonates hydroxybenzenesulfonate and $BrCH_2COO^-$ further leading to destroying electrostatic interaction between protonated hydroxybenzenesulfonate and $[N_{8881}]^+$ [40]. At the same time, Cl^- ions enter into HDES phase and combined with $[N_{8881}]^+$ create hydrogen bonds with $BrCH_2COOH$ resulting in re-formation of HDES[40].

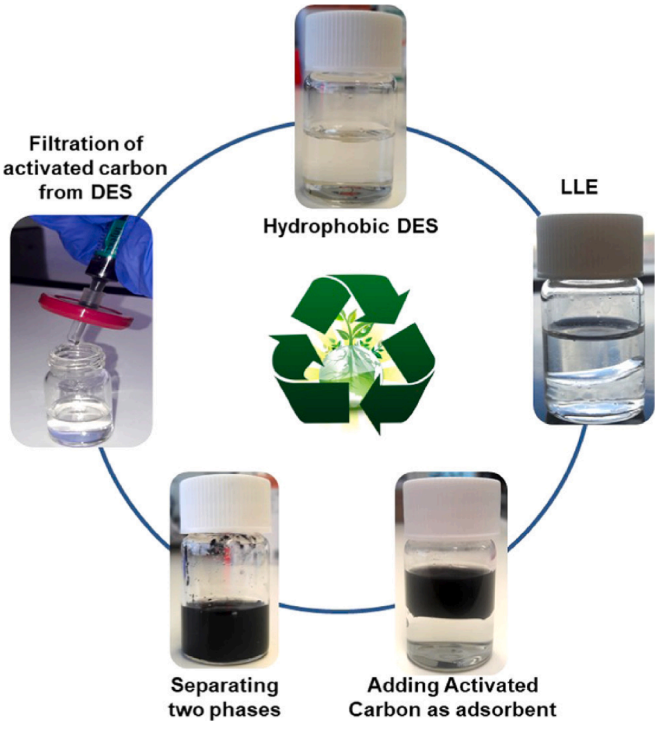

Fig. 1. Schematic representation of the circular approach for recycling and reuse of hydrophobic DESs contaminated with ciprofloxacin. Reprinted with permission from [38]. Copyright (2019) American Chemical Society.

Nevertheless, it has to be pointed out that using strong acid for back extraction is not the best approach taking into consideration sustainability of the whole process.

More recently, another group of researchers tested the HDESs composed of thymol and fatty acids in extraction of APIs (antibiotics) from ultrapure water and hospital wastewater[39]. These solvents were selected based on the screening of solvents using COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS) approach. Afterwards, antibiotics extraction experiments were performed and the influence of the HDES/water ratio, aqueous matrix, and pH was analyzed. It was observed that for trimethoprim and ciprofloxacin HDESs surpassed the conventional solvents at any pH and matrix, and significantly higher overall extraction yields were achieved[39]. Moreover, the extraction results followed the order of the HDESs hydrophobicity and extractability decreased in the order: thymol:C_{12} > thymol:C_{10} > thymol:C_8[39]. These results were explained as an effect of decreased hydrophobicity when reducing the alkyl chain length of the carboxylic acid that led to increase of the partial solubility of the acid in water, decreasing the pH of the aqueous phase and favoring the presence of the charged form of these antibiotics[39]. The studies on the effect of water matrix on the extraction of trimethoprim and ciprofloxacin revealed that higher extraction efficiencies were achieved when using the feed in hospital wastewater, suggesting that the other substances present in the matrix favored the transfer of antibiotics into the organic phase, which might be caused by salting-out effect[39]. On the other hand, for sulfamethoxazole the extraction efficiency increased as the length of the alkyl chain of the carboxylic acid diminished[39]. This was most probably due to the decreasing hydrophobicity and consequently higher pH value and the concentration of the sulfamethoxazole in its neutral state, which was found to favor this antibiotic extraction into HDES phase[39]. In general, it was observed that by reducing the pH value of the feed in the hospital wastewater matrix higher extraction efficiencies were obtained[39]. Finally, it was also found out that higher extraction efficiency was achieved while using ultrapure water matrix[39]. It was hypothesized that solutes present in the hospital wastewater matrix favored the solvation of sulfamethoxazole in the aqueous phase, decreasing its transfer to the organic phase[39]. Overall, comparing the results obtained for trimethoprim and ciprofloxacin to these obtained for sulfamethoxazole, both pH and matrix had more impact on sulfamethoxazole extraction[39]. Furthermore, HDESs were found out more effective in the extraction of ciprofloxacin and trimethoprim (extraction yields up to 99.92% and 99.82%, respectively) than in the extraction of sulfamethoxazole (extraction yields up to 96.16%)[39]. However, it was also observed that after the contact with water the change in pH of the raffinate took place[39]. This change in pH means that some part of dodecanoic acid, decanoic acid, and octanoic acid leaked into the aqueous phase, however the exact amount of acid was not determined. Moreover, when thymol was used as extraction solvent, around 0.12–0.15% of it transferred to the aqueous phase[39], thus similar amounts of thymol may be expected when HDES is used. Nevertheless, thymol showed considerably lower losses of solvent than conventional solvents such as ethyl acetate and methyl isobutyl ketone[39]. All of these observations regarding HDES components losses and comparable extraction efficiencies of terpenoids and HDES, indicate that in the case of studied HDESs it is more beneficial to use pure terpenoids instead of eutectic mixtures, as it will simplify the extraction process and solvent regeneration.

2.5. Bisphenol-A

In another attempt Florindo et al.[43] used non-ionic HDESs composed of DL-menthol as HBA and octanoic acid, decanoic acid as HBDs, as well as ionic HDESs composed of [N_{8888}]Br), [N_{7777}]Br, [N_{8881}]Br as HBA and octanoic acid and decanoic acid as HBD to remove bisphenol-A (BPA) from aqueous solutions. Bisphenol-A (BPA) is largely used as a plasticizer from food and drink plastic packaging to plastic medical devices and is an emerging micropollutant detected in increasing concentrations globally in water sources. It also has ability to mimic the estrogen hormone, having an impact on the normal development and function of human and wildlife reproductive system. Thus, its harmful effects make it necessary to remove BPA from water sources. The used HDESs showed good extraction efficiencies (>85%) of BPA from water due to high hydrophobicity of these solvents and very low water solubility and a high octanol–water partition coefficient (K_{ow}) of BPA, which together resulted in high affinity for hydrophobic DES phase [43]. It was further noticed that quaternary ammonium salts based HDES extracted BPA with higher efficiency than DL-menthol based HDESs showing that the extraction efficiencies depend on the choice of the components of HDES[43]. Moreover, it was observed that the extraction efficiencies were highly affected by different HBD used and increased with the increase of the alkyl chain length in the fatty acid [43]. The increase in extraction efficiencies was also discovered with the increase of the alkyl chain in the quaternary ammonium salt, once again confirming that HDES hydrophobicity played a major role in extraction of BPA[43]. Under optimal conditions (BPA (0.1 g/L), HDES/water ratio (1/1), temperature (25 °C), and contact time (10 min)) [N_{8888}]Br:C_{10} HDES was the best extractant from the studied solvents and almost 98% of BPA present in water was removed[43]. Overall, the following order of extraction efficiencies of BPA was depicted: [N_{8888}]Br:C_{10} > [N_{7777}]Br:C_{10} > [N_{7777}]Br:C_8 > DL-menthol:C_{10} > [N_{8881}]Br:C_{10} > [N_{8888}]Br:C_8 > [N_{8881}]Br:C_8 > DL-menthol:C_8[43]. Very important observations were made from large scale application perspective because the HDES/water mass ratio did not have a significant influence on the HDES extraction efficiencies of BPA and a small amount of solvent was needed to process large volumes of BPA contaminated water[43]. However, in this study considerably high concentrations of BPA in the range of 0.025–0.1 g/L were used, while in water environments BPA can be found at very low concentrations, usually ranging from ng/L to mg/L. Since, it was shown that the extraction efficiency of HDESs decreased with decreased initial concentration of BPA in water, it would be important to evaluate the potential of the used solvents in removal of BPA from real samples. Furthermore, the reuse of HDES was evaluated and the solvent during five cycles did not lose any of its BPA extraction capability due to around five hundred times higher solubility of BPA in HDES than in water[43].

More recently, the BPA extraction from water using HDESs was also studied by An et al.[41] In this work, DL-menthol was used as HBA and combined with a series of different carboxylic acids (hexanoic acid, propionic acid, decanoic acid, acetic acid, octanoic acid, formic acid) and alcohols (n-butyl alcohol, oleyl alcohol, 1-dodecanol) as HBD in the 1:1 molar ratio to form HDES[41]. The obtained results revealed that the extraction efficiency was greatly affected by the HBD used. DL-menthol: propionic acid and DL-menthol:formic acid were the best extractants and 98.2% and 99.0% extraction efficiencies using 0.75 mL of HDES, 4 mL of spiked water, BPA concentration of 100 μg/L, and 3 min extraction time were achieved[41]. In general, the extraction efficiencies for alcohol-based HDESs followed the order of n-butyl alcohol > 1-dodecanol > oleyl alcohol, while for the carboxylic acid-based HDESs the efficiency increased as follows: formic acid > propionic acid > acetic acid > decanoic acid > hexanoic acid > octanoic acid[41]. Even though, the extractions efficiencies presented in this work are quiet promising, a stability in water of the studied HDESs may raise some concerns. The stability of solvents after contact with water was not evaluated, however on the basis of previous works on this topic, it is safe to assume that for HDESs prepared with small alkyl chain length alcohols or carboxylic acids a significant loss of the alcohol or acid takes place, hindering application of some of these solvents in water treatment.

In another study Rodríguez-Llorente et al.[42] evaluated the possibility of extractive removal and recovery of BPA using menthol:camphor and menthol:C_8 HDESs. It was found out that among these two solvents, menthol:camphor showed better extraction efficiency than menthol:C_8[42]. The menthol:camphor HDES extracted BPA with efficiency above >99.00% over the entire initial BPA concentration range, while

menthol:C_8 HDES was able to remove above >97.40% of BPA present in aqueous solution[42]. Furthermore, the extraction efficiencies with the two HDESs were higher than those obtained with citronellol and α-terpineol[42]. Additionally, menthol:camphor HDES showed comparable performance to terpenoids (eucalyptol and geraniol) and better performance than conventional solvents (methyl isobutyl ketone and diisopropyl ether)[42]. Interestingly, comparing the results obtained in this study to those obtained in previous works, it was observed that menthol:C_8 HDES extracted BPA with superior efficiency compared to the results reported by Florindo et al.[43] using the same HDES and also another HDESs prepared from medium chain fatty acids and menthol or quaternary ammonium bromides. Having in mind the sustainability of the whole extraction process, the reusability and regeneration of solvents was also evaluated. It was found out that menthol:camphor HDESs almost entirely kept its extractability and extraction efficiency after 6 cycle was still above 97.5%[42]. Finally, the regeneration of solvent through NaOH back extraction was performed and the chemical stability of the HDES after regeneration process was confirmed through FTIR. Furthermore, such regenerated solvent showed similar extraction efficiencies to those obtained with fresh solvent[42]. The proposed by the authors process of BPA extraction, solvent regeneration and reuse, and BPA recovery is shown in Fig. 2. As it can be seen, in this process the authors proposed to use back extraction with strong base (NaOH) for HDES regeneration and precipitation with strong acid (HCl) for BPA recovery, however such a scheme is highly unsustainable due to addition of acids and bases. Furthermore, the choice of back extraction is also not preferable as it will difficult purification process and produce some other waste streams. In general, the performance of HDESs in these works showed that these solvents are very promising candidates as extractants for BPA not only because of their excellent performance in bisphenol A extraction but also due to their easy preparation from readily available compounds that are low cost and low toxic.

2.6. Phenolic compounds

HDESs were also used as extractants for removal of phenolic compounds from water[44–47,49]. Phenolic compounds pose major threat to the society since they are toxic and produce adverse effects on the environment and human health when they are consumed even at low concentrations. Because of that phenolic compounds are considered as top priority pollutants with the threshold quantity in wastewaters of 1 mg/L and less than 0.001 mg/L in potable water. In the first reported work HDESs composed of menthol and thymol as HBAs and organic acids (C_8, C_{10}, C_{12}) as HBDs and HBAs were prepared and applied to remove phenol, o-cresol, and 2-chlorophenol from water[44]. The authors demonstrated that it was possible to extract >70% of all phenolic compounds present in water[44]. It was also showed that extraction efficiency followed the order of the hydrophobicity of phenolic compounds: 2-chlorophenol > o-cresol > phenol[44]. Furthermore, the extraction efficiencies increased with the increased HDES hydrophobicity as a consequence of a lower water-solute interaction, and increased solute–solvent interaction[44]. Consequently, HDESs based on menthol presented higher extraction efficiencies than those based on dodecanoic acid. No major differences in extraction efficiencies were observed for different menthol-based HDESs, while for the C_{12}-based HDESs higher extraction efficiencies were achieved with C_{12}:C_8 HDES than with C_{12}:C_{10} HDES[44]. Overall, it was demonstrated that for initial concentrations below 10 mg/L of 2-chlorophenol and o-cresol it was possible to reach the legal limit for phenolic compounds in wastewater in only one extraction cycle using menthol:C_8, menthol:C_{10} and C_{12}:C_8 HDESs[44]. On the other hand, three extraction cycles were needed to reach the legal limit for phenol[44]. Moreover, for C_{12}:C_{10} HDES which displayed the lowest extraction efficiencies from the studied solvents, the number of extraction cycles that were necessary for all studied phenolic compounds in order to reach the legal limit allowed in wastewaters was higher[44]. Nevertheless, all of the studied HDESs showed promising potential as extractants of phenols either when present in water separately or as a mixture of all three studied phenols.

Phenolic compounds (2-chlorophenol, 3-chlorophenol and 2,4-dichlorophenol) were also extracted from water by HDESs in the study of Adeyemi et al.[49]. In this work menthol-based HDESs were prepared, specifically menthol:thymol, menthol:C_6, menthol:C_8, menthol:C_{10}[49]. The stability of solvents in water was not studied experimentally in this here, however a possible contamination of water phase with HDESs was predicted using COSMOThermX modeling tool[49]. It was predicted that 0.00063495 g from starting amount of 1.012 g of menthol, and 0.00297711 g from starting amount of 0.98 g of thymol transfer into water phase[49]. Simple re-scaling of these values for the amount of HDES needed to treat hundreds of cubic meters of wastewater per day clearly indicates high risk of such solution to the environment. Moreover, the choice of these HDESs was also justified by their safe character as menthol and thymol are naturally occurring compounds, often present in oral and skin prescriptions. Similarly, carboxylic acids are widely represented in nature. Therefore, the prepared HDESs were considered suitable for water treatment purposes. The studied solvents showed good extraction efficiencies above 94%[49]. In the case of thymol-based HDESs the extraction of chlorophenols followed the order 3-chlorophenol > 2,4-dichlorophenol > 2-chlorophenol, whereas for alkanoic acid-based HDESs the order was as follows: 3-chlorophenol > 2-chlorophenol > 2,4-dichlorophenol[49]. It was further discovered that the best extraction capability for all chlorophenols was displayed by menthol:C_6 HDES with almost 99% extraction efficiency[49]. Overall, HDESs prepared using alkanoic acid as HBD demonstrated higher extraction efficiencies than those with thymol as HBD[49]. This higher efficiency was assigned to the fact that alkanoic acids are more polar and tend to create hydrogen bonds more than thymol-based HDESs[49]. Consequently, these HDESs displayed enhanced hydrogen bonding between them and chlorophenols resulting in higher extraction efficiency [49].

In another study, Gonzalez and co-workers[45] evaluated the extractive potential for phenols (phenol, guaiacol and syringol) of HDESs composed of menthol as HBA and three organic acids (C_8, C_{10} and C_{12}) as HBDs. In the extraction process optimization, it was discovered that the highest extraction efficiencies were obtained when HDES/water ratio of 1/1 was used[45]. Furthermore, the increase in efficiency with an increase in the initial phenol concentration was observed[45]. The highest extraction percentages were achieved using HDES composed of organic acid with the longest chain – menthol:C_{12}[45]. Using this solvent, extraction efficiencies up to 98.8, 94.4 and 92.5% for guaiacol, syringol and phenol, respectively, were achieved [45]. Moreover, it was observed that extraction efficiencies were linked to hydrophobicity of the solvents and the more hydrophobic HDES the higher extraction capacity (menthol:C_{12} > menthol:C_{10} > menthol:C_8) [45]. In regards to the effect of the chemical structure of phenols, the following order for the extraction efficiency was observed: guaiacol > phenol > syringol[45]. The observed trend was explained as a results of two distinct effects – hydrophobicity of the solutes and the molecular volume[45]. Consequently, the most hydrophobic of the studied phenols – guaiacol – was easier to extract than syringol and phenol. On the other hand, the higher extraction efficiency for phenol than for syringol (although the latter is more hydrophobic) was assigned to the increase of the molecular volume due to the presence of additional methoxy groups, which also promoted steric hindrance ultimately leading to less effective solute–solvent interactions and molecular packing in the extract phase [45].

Furthermore, Rodriguez-Llorente et al.[46] studied the potential use of hydrophobic eutectic solvents composed of thymol, menthol and C_8 (menthol:thymol, menthol:C_8, thymol:C_8) in the separation of phenol, 2-nitrophenol, and 2-chlorophenol from water. These 3 eutectic mixtures were chosen as promising solvents basing on initial screening using the COSMO-RS method. The experimental results from extraction studies revealed that in case of phenol separation and using HDES/water ratio

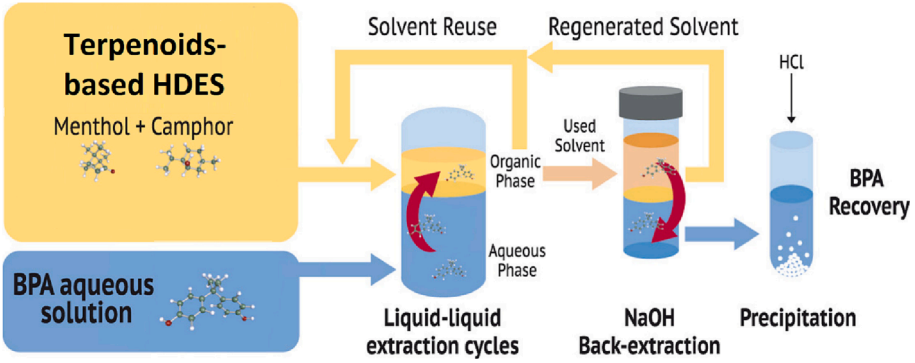

Fig. 2. Schematic representation of the process flow diagram for recycling and reuse of DL-menthol:camphor (3:2) HDES, and BPA recovery. Adapted with permission from [42]. Copyright (2021) Elsevier.

1/1, the extraction efficiencies followed the order of: menthol:C_8 > menthol:thymol > thymol:C_8[46]. Overall, for all the studied HDESs extraction efficiencies above 90% were achieved, however even better separation was observed when citral, geraniol, and linalool were used [46]. For 2-chlorophenol extraction efficiencies higher than 99.5% were obtained at high HDES/water ratios using both C_8-based HDESs[46]. On the other hand, menthol:thymol was able to remove up to 95.5% of 2-chlorophenol[46] and the obtained values were found similar to those reported in the work of Adeyemi et al.[49]. Moreover, the studied HDESs showed better or similar extraction capability as conventional solvent – diisopropyl ether[46]. In a case of 2-nitrophenol, very good extraction efficiencies above 99.5% were obtained using menthol:C_8, thymol:C_8[46]. Once again, these two HDESs exceeded diisopropyl ether performance in 2-nitrophenol extraction, however the third of the studied HDESs – menthol:thymol – performed worse than conventional solvents e.g. toluene and diisopropyl ether[46]. Although, both of the C_8-based HDESs showed quite good extraction efficiencies for all phenols, they were found not chemically stable in alkali back extraction due to the formation of octanoate ion, and thus they were not further considered in the other studies[46]. Moreover, menthol:thymol HDES was also discarded for further studies due to its lower extraction efficiency than conventional solvents[46].

Liquid–liquid extraction using HDESs was shown to be promising approach for removal of phenol from wastewater[47]. In the work conducted by Cheng et al.[47] the extraction of ultra-high-concentrated phenol (~54,000 mg·L^{-1}) from actual industrial wastewater was carried out. For that purpose, eight HDESs prepared using DL-menthol as HBA and various fatty acids (nonanoic acid (C_9), C_{10}, C_{12}, oleic acid (C_{18})) as HBD were selected and the effects of various parameters, such as HBA/HBD molar ratio, HDES/wastewater mass ratio, and initial concentration of phenol in wastewater, on extraction efficiencies were evaluated [47]. Before extraction experiments, the stability of prepared HDESs in water was assessed. It was confirmed that after reaching phases equilibrium the volume of the HDES phase did not decrease at all[47]. Nevertheless, this is macroscale assessment and it is not enough to conclude on HDES stability after contact with water, therefore the ^{1}H NMR analysis of water phase was performed and it was found that no new peaks appeared, which further verified the stability of the studied HDESs in water[47]. From all HDESs, DL-menthol:C_9 (2:1) showed the highest extraction efficiency of 97.48 % within 5 min at room temperature when HDES/wastewater mass ratio of 2:1 was used[47]. Furthermore, it was observed that the extraction efficiencies followed the reversed order of HBD hydrophobicity and with the increased alkyl chain length the extraction efficiencies decreased (DL-menthol:C_9 > DL-menthol:C_{10} > DL-menthol:C_{12} > DL-menthol:C_{18}) [47]. The formation of new hydrogen bonds between HDES and phenol molecules was put forward as the major driving force of extraction according to the results of FTIR and ^{1}H NMR experiments[47]. Moreover, the possibility of regeneration and reuse of HDESs was studied using activated carbon, and it was demonstrated that it is possible to carry out up to 10 successive extractions with very little loss of HDES extraction capacity (>72 %)[47].

Finally, hydrophobic DESs composed of menthol, [N_{8888}]Br and [N_{8888}]Cl as HBAs and C_{10} as HBD were also used for the extraction of a series of simple, substituted benzene derivatives from water[48]. The obtained results showed that there was a straightforward relationship between partitioning in HDES–water and octanol–water systems and compounds displaying higher hydrophobicity also showed high-$D_{HDES-water}$ values[48]. This observation means that the absolute magnitude of solute partition coefficient determines the efficiency with which this solute is extracted, making it possible to predict if a particular HDES is suitable for extraction of a given solute. Furthermore, it was noted that the partitioning of the studied solutes between HDES and water was very dependent on the aqueous phase pH, with higher distribution ratios being observed under conditions where the neutral form of the solute predominates[48]. For the different HDESs, the obtained values of $D_{HDES-water}$ for several organic solutes varied with the HDES composition, and for example for toluene and phenol was only 1 (0.04 log units) using [N_{8888}]Br:C_{10} HDES, while using menthol:C_{10} HDES it was >10 (1 log unit)[48]. Likewise, significant differences were observed for the chlorobenzene–toluene separation factor, which was 0.8 log units using [N_{8888}]Br:C_{10} HDES, and only 0.2 log units using menthol:C_{10} HDES[48]. All of these observations clearly showed highly tunable nature of the studied HDESs in order to meet specific extraction problem.

2.7. Others

The suitability of HDESs composed of different N-quaternary ammonium bromide salts ([N_{4444}]Br, [N_{5555}]Br, [N_{7777}]Br, [N_{8888}]Br) as HBA and C_{10} and C_{12} as HBD for removal of furfural present in water was carried out by McGaughy et al.[51]. LLE extraction experiments were done for systems of HDES made from decanoic and dodecanoic acid using [N_{6666}]Br and [N_{8888}]Br, at a 3:1 molar ratio[51]. The reason for that was the fact that the extraction systems with [N_{4444}]Br- and [N_{5555}]Br-based HDESs were found not stable after contact with water [51]. In case of HDESs that contained HBA with longer alkyl chain, higher furfural removal was obtained for [N_{6666}]Br-based HDES which exhibited 85% extraction efficiency (compared to 80% for [N_{8888}]Br) [51]. This higher extraction efficiency was achieved despite the fact that there was very high water uptake for [N_{6666}]Br systems (67 mol %/13.7 mass % water with decanoic acid and 63 mol %/ 12.7 mass % water with dodecanoic acid)[51]. Therefore, it was hypothesized that this additional water uptake may be beneficial for furfural extraction and that by increasing the ammonium salt's alkyl chain length ability of hydrogen bonding decreases[51]. Furthermore, no clear impact of the HBD on extraction was observed, suggesting that the salt is primarily responsible for furfural removal[51]. In general, the experimental results agreed

with above 95% accuracy with computational predictions from COSMOtherm modeling and it was shown that HDESs can successfully remove furfural from aqueous water even at its very low concentrations (0.1 mol%)[51].

Recently, HDESs were also applied in removal of estrogens from water[52]. It is important to eliminate natural and artificially synthesized estrogens from water and wastewater because even at minimal concentrations these substances are posing potential risk to humans and wildlife. Moreover, estrogens can remain in water systems since they are not completely removable by current strategies that are employed by wastewater treatment plants (WWTPs). Therefore, alternative approaches are constantly sought and LLE using HDESs was considered as one of the possible solutions to this problem. In the work of Hlozek et al. [52] a series of HDESs based on a combination of menthol with natural organic acids (C_8, C_{10} and C_{12}) were tested in extraction of five estrogens namely estrone, 17α-estradiol, 17β-estradiol, 17α-ethynylestradiol and estriol. In the extraction, various experimental conditions were studied such as HDESs composition, molar ratio, extraction time, extraction rate. It was observed that under the optimal conditions (extraction time 15 min, shaking speed 2000 rpm, molar ratio HBA/HBD 1:1) HDESs showed high efficiency for estrogen removal and they were eliminated from the water at low levels of 10 and 20 μg/mL[52]. From the studied eutectic mixtures, menthol:C_8 (1:1) was found to be the most efficient in extraction of all estrogens studied, achieving up to 99.9% extraction efficiency for spiked water samples and up to 97.9% extraction efficiency for real and wastewater[52]. Furthermore, slightly lower efficiency was exhibited by the other menthol-based HDESs (menthol:C_{10} and menthol:C_{12}) and these prepared using combination of two organic acids (C_8:C_{10}, C_8:C_{12} and C_{10}:C_{12})[52]. Generally, better results than using conventional solvents such as hexane and chloroform, and comparable results to those obtained using *tert*-butyl methyl ether were attained with HDESs as extractants, while they are greener and more sustainable than organic solvents[52]. Finally, the authors showed that HDESs can be applied in up to 3 consecutive extraction cycles without significant loss of solvent extraction capacity and no need of solvent regeneration[52]. However, in order to use HDESs to extract estrogens from wastewater in more cycles, the regeneration of solvent is necessary as at about four to five cycles the extraction capacity of the HDES is exhausted[52].

In summary, it can be concluded that HDESs are effective extractants for various pollutants present in water. It is possible to obtain almost 100% extraction efficiencies using relatively low amounts of solvents that can be further regenerated and reused without significant losses in their extraction capacity. Furthermore, such HDESs very often were shown to be more effective than conventional solvents, while being greener and more environmental friendly alternative. However, it is also clear that there is rather small diversity as far it comes to the composition of HDESs used for extraction. Most of them are composed of the same starting materials and used in removal of different pollutants. What is more, there are some studies (see Table 1) in which water stability of the used HDESs was not evaluated. Since after the extraction the purified water tend to be further used, it requires for it to be without any traces of HDES or its components, making it necessary to study HDESs stability in water and eventually to remove the traces of HDESs after extraction process.

3. Stability of HDESs in water and critical evaluation of the methods used for HDESs stability determination

Considering the use of HDESs as solvents for extraction of pollutants present in water and its further use or release into the environment, it is of pivotal importance to guarantee the chemical stability of HDESs, ensuring that there is no HDESs solubility in water, or that there is no contamination of water with HDESs components. In general, it is considered that to obtain stable HDESs both HBA and HBD used in their preparation must be hydrophobic, and if the hydrophilic component is used, it will leak into the aqueous phase according to its water solubility [21,26]. Therefore, if starting materials with very low water solubility are used, the prepared HDES also has a negligible solubility in water[3]. In this section, the stability of HDESs in water will be discussed. The main focus will be directed towards HDESs used in studies described in section 2.1. Furthermore, an attention will be given to the methodology used for determination of the stability of HDESs in water and some of the constraints of these methods will be pointed out. The stability in water of HDESs previously used as solvents in LLE for water treatment is summarized in Table 2.

As can be seen in Table 2, in most of the studies where chemical and water stability of HDESs was evaluated, the nuclear magnetic resonance (NMR) spectroscopy analysis of the water phase was used. In Fig. 3, results of NMR analysis of both phases for the systems containing three different DESs is shown. Taking into consideration that the sensitivity of NMR is quite low and that the substances used in HDES preparation have some solubility in water, clearly there is a risk that some amounts of HDES or its components will contaminate the water phase. Due to above mentioned fact, it seems too simple and insufficient to withdraw conclusions about HDES stability in water basing exclusively on the results of the NMR spectroscopy. The HDES stability in water should be tested using more sensitive techniques. For example, in works of van Osch and co-workers, ion chromatography (IC) was used in order to determine the quantity of salt that leached into water phase. Even though, this method is very sensitive, it is only suitable to detect ions, thus is not appropriate for all types of HDESs. In a lot of cases it only allows to quantify one of the HDESs components. It is also worth to mention that sometimes for purpose of assessing water stability of HDESs the researchers use Karl Fisher titration to measure the amount of water present in HDES after extraction experiments. The concept is based on the studies of Hammond et al.[55] and Gabriele et al.[56] in which the effect of water on deep eutectic solvents was studied. It was concluded that in order to disrupt the hydrogen bonds between the HBD and HBA of the DESs and the structure of the DES between 42 wt% and 51 wt%, or 50 wt% and 75 wt% of water was needed. As it can be seen, in this method water stability of HDESs is not assessed in direct manner and in our opinion the conclusions withdrawn by measuring water content in HDESs are not sufficient to claim whether HDESs is stable in water or not.

Regarding the water stability of HDESs, it was firstly determined for quaternary ammonium salt-based HDESs in the work of van Osch et al. [21]. For that purpose, the aqueous phase after mixing with HDES was analyzed and the content of salt that leached was measured using IC. It was found out that [N_{7777}]Cl:C_{10} (1:2) and [N_{8888}]Cl:C_{10} (1:2) after mixing with water had leaked salt to the water and around 2.3 and 1.9% ($m_{salt,leached}/m_{salt,DES}$) of the salt moved into the water phase, respectively[21]. Furthermore, [N_{7777}]Cl:C_{10} (1:2) HDES released a higher amount of salt compared to [N_{8888}]Cl:C_{10} (1:2) HDES, because the longer the alkyl chain length the higher the hydrophobicity of the prepared solvent[21]. [N_{8881}]Br:C_{10} (1:2) HDES was shown the least stable HDES with around 5.2% of the salt transferred to the water-rich phase [21]. These results showed that some solubility of HDESs in water should be always expected. Nevertheless, these values confirm the high hydrophobicity and relatively good stability in water of these solvents. For example, when [N_{4444}]Cl was used as HBA, analysis of water samples by IC revealed that around 34.8% of the salt leached to the water phase[21]. Similar observations were made in another work and >70% for [N_{4444}]Br and >55% for [N_{5555}]Br when paired with either decanoic or dodecanoic acid leached to the water phase[51]. Furthermore, longer alkyl chains drastically decreased the amount of leaked salt, with less than 1 mol % of [N_{6666}]Br and [N_{7777}]Br and 4.3–5.8% of [N_{8888}]Br leaching into the aqueous phase[51].

Some solubility in water of HDES composed of decanoic acid and lidocaine was demonstrated[32]. It was showed that after extraction process a small amount of decanoic acid was present in the water phase [32]. Moreover, higher amounts of lidocaine were detected after analysis of water phase using ^{1}H NMR[32]. The reason of that was most

Table 2
The stability in water of HDESs considered in this review.

HDES	Determination method	Results	Ref.
$[N_{6666}]Br:C_{10}$ (1:3)	COSMOThermX modeling	0.05% of HBA leached, 0.017% of HBD leached	[51]
$[N_{6666}]Br:C_{12}$ (1:3)	COSMOThermX modeling	0.05% of HBA leached, 0.017% of HBD leached	[51]
$[N_{7777}]Br:C_{10}$ (1:3)	COSMOThermX modeling	0.05% of HBA leached, 0.017% of HBD leached	[51]
$[N_{7777}]Br:C_{12}$ (1:3)	COSMOThermX modeling	0.05% of HBA leached, 0.017% of HBD leached	[51]
$[N_{8881}]Br:C_8$ (1:2)	Karl Fisher titration	~7% of H_2O after contact	[38]
$[N_{8881}]Br:C_{10}$ (1:2)	Ion chromatography	0.0231 $m_{salt,leached}/m_{salt,DES}$ [g·g^{-1}]	[21]
	Karl Fisher titration	6.938% of H_2O after contact	
$[N_{8888}]Br:C_{10}$ (1:2)	Ion chromatography	0.0523 $m_{salt,leached}/m_{salt,DES}$ [g·g^{-1}]	[21]
	Karl Fisher titration	2.005% of H_2O after contact	
$[N_{8888}]Br:C_{10}$ (1:3)	COSMOThermX modeling	4.3% of HBA leached, 0.017% of HBD leached	[51]
$[N_{8888}]Br:C_{12}$ (1:3)	COSMOThermX modeling	5.75% of HBA leached	[51]
$[N_{7777}]Cl:C_{10}$ (1:2)	Ion chromatography	0.0232 $m_{salt,leached}/m_{salt,DES}$ [g·g^{-1}]	[21]
	Karl Fisher titration	2.339% of H_2O after contact	
$[N_{7777}]Br:C_{10}$ (1:2)	Karl Fisher titration	~4% of H_2O after contact	[38]
$[N_{8881}]Cl:C_{10}$ (1:2)	Ion chromatography	0.0300 $m_{salt,leached}/m_{salt,DES}$ [g·g^{-1}]	[21]
	Karl Fisher titration	6.222% of H_2O after contact	
$[N_{8888}]Cl:C_{10}$ (1:2)	Ion chromatography	0.0193 $m_{salt,leached}/m_{salt,DES}$ [g·g^{-1}]	[21]
	Karl Fisher titration	1.785% of H_2O after contact	
$[N_{8888}]Br$:DL-menthol (1:2)	Karl Fisher titration	~6.5% of H_2O after contact	[38]
lidocaine:C_{10} (1:2)lidocaine:C_{10} (1:3)lidocaine:C_{10} (1:4)	^{1}H NMRTOC	Small amounts of C_{10} and high amounts of lidocaine present in water phase after extraction.	[32]
DL-menthol:C_2 (1:1)	^{1}H NMR	Water phase contaminated with the HBD - acetic acid.	[26]
DL-menthol:C_6 (1:1)	^{1}H NMR	Water phase contaminated with the HBD – hexanoic acid.	[26]
DL-menthol:C_8 (1:1)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[26,44]
	Karl Fisher titration	~3% of H_2O after contact	[38]
DL-menthol:C_9 (1:1)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[47]
DL-menthol:C_{10} (1:1)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[26,44,47]
	Karl Fisher titration	~2% of H_2O after contact	[38]
DL-menthol:C_{12} (1:1)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[47]
DL-menthol:C_{12} (2:1)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[26]
	Karl Fisher titration	~2% of H_2O after contact	[38]
DL-menthol:C_{18} (1:1)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[47]
C_{12}:C_8 (1:3)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[44]
	Karl Fisher titration	~2% of H_2O after contact	[38]
C_{12}:C_{10} (1:2)	^{1}H NMR	No peak other than water was observed on water phase spectra.	[44]
	Karl Fisher titration	~1% of H_2O after contact	[38]
thymol:C_8 (1:1)	Visual inspection	Cloudy water-rich phase contaminated with thymol.	[44]
thymol:C_{12} (1:1)	Visual inspection	Cloudy water-rich phase contaminated with thymol.	[44]

probably related to the ion exchange process that was pointed out as metal ions extraction mechanism[32]. In this ion exchange the positively charged metal ion was exchanged with the partially positively charged lidocaine hence its presence in the water phase[32]. This was further validated with total organic carbon (TOC) analysis in which it was observed that upon increasing the metal salt concentration supported the TOC value increased[32]. With that, it would be interesting to study the stability of this HDES with non-contaminated water to determine the solubility of this solvent.

The stability in water of DL-menthol-based HDESs was also studied [26,47]. Firstly, the ^{1}H NMR analysis was done for solvents prepared using various acids as HBD, namely acetic, pyruvic, levulinic, butyric, hexanoic, octanoic, decanoic and dodecanoic acid[26]. It was observed that after separation of the phases, the water phase was contaminated with the HBD when acetic, pyruvic, levulinic, butyric and hexanoic acids were used, and that there was no peaks of HBA (DL-menthol)[26]. Moreover, in the case of DL-menthol:C_8, DL-menthol:C_{10}, DL-menthol:C_{12} on ^{1}H NMR water-rich phase spectra, no peak other than water was observed[26]. The leaching of the HBD was found proportional to its hydrophilicity and for DL-menthol:acetic acid a loss of around 90% of the acid to the water-rich phase was observed, which decreased to around 20% for DL-menthol:butyric acid and no loss was observed when DL-Menthol:C_8 was used[26]. Later, information on water stability of DL-menthol:C_9 and DL-menthol:C_{18} HDESs was gathered and both of the these solvents were found stable in water[47]. These results corroborated with observations made by Florindo et al.[26] where it was stated that for DL-menthol-based HDES to be stable, acids with long alkyl chain should be used in HDES preparation (C_8 or longer).

The stability in water of C_{12}:C_8 (1:3), C_{12}:C_{10} (1:2) HDESs was determined by Sas et al.[44]. After analysis of water phase using ^{1}H NMR spectroscopy it was found out that both these solvents were stable in water because there was no peaks of the starting compounds of HDESs [44]. On the other hand, for the biphasic systems prepared using thymol:C_8 (1:1) and thymol:C_{12} (1:1), a cloudy interphase was observed, thus it was concluded that these HDESs are not stable and not suitable for LLE of phenolic compounds from water[44]. Furthermore, the studies on TOPO-based HDESs, namely TOPO:C_{10} and TOPO:C_{12} confirmed the stability in water of these fluids as no evidence of HDESs starting materials or HDESs was observed on spectra of water phase[50].

Taking into account either low sensitivity of the used method or the nature of HDESs components (despite being hydrophobic compounds, all of them are water soluble to some small extent), it is clear that all HDESs present some solubility in water. Therefore, some loss of HDES and/or its components is inevitable. This small loss of HDES might not be a big issue if the components used in HDES preparation are of low cost and come from natural sources, however even small loss might have big

consequences on the sustainability of the process especially when expensive and toxic components are used e.g. long alkyl chain length chain quaternary ammonium salts. The loss of the HDES or its components will require one additional step in the water treatment in which traces of HDES or its components will be removed. Furthermore, preferential leakage of HDES components into the aqueous phase might results in differences in initial molar ratio of HBA:HBD and properties of HDES. With that regeneration and reusability of such solvents might be impossible making the overall process unsustainable from economical point of view. Nevertheless, small solubility of HDESs and thus pollution of water with HDESs or its components, should not exclude their use in water purification. As discussed in earlier sections, HDESs were proved to be very effective in removal of diverse range of pollutants present in water. Therefore, HDESs can be used to reduce the high pollutant load (as chemical oxygen demand (COD)), and if the selected HDESs are biodegradable, it will allow their removal in the next, biological purification step. Furthermore, basing on the information gathered in this review regarding water stability of HDESs, in Fig. 4 we propose a matrix that should be helpful for future researchers in the field and which will allow to easily select HBA and HBD that can possibly form water-stable HDES.

4. Suggestions and guidelines for future research

The literature review and experience of the authors in the field of DESs and water and wastewater treatment processes, incline us to propose a few general rules for the future investigation of HDESs as extractants of pollutants from water. In particular, simple protocols that allow to determine HDESs solubility in water will be suggested. We believe that by following the proposed guidelines will enable to consciously select HDESs suitable for purification of water, granting that there is no water contamination with HDES or its components. The suggestions and guidelines for future research on HDESs in extraction for water treatment are outlined below.

i) Pure HDESs should be characterized as much as possible, in particular their physicochemical properties, such as density, viscosity, polarity, surface tension, water solubility, toxicity. Disregarding these parameters may lead to the selection of the HDESs that will not be best candidates for water treatment.

a) Both viscosity and density are key properties of solvents because they greatly influence dissolution, reactions, and separation processes, determining their viability. For instance, the high viscosity of most HDESs was shown to have a large effect on the extraction process and also on the further analysis of HDES extracts. Therefore, for extraction purposes it is worth considering a usage of low viscous (less than 20 mPa s) HDESs based on fatty acids, menthol and thymol, which were shown to be less viscous than majority of hydrophilic DESs. Besides that, HDESs composed of HBAs and HBDs with long chain in HBA and HBD have a similar density to water, which from point of view of separation and extraction process will mean that more time will be needed for phases to separate.

b) Polarity is another important physicochemical property that should be further studied as it determines the sum of all possible interactions between a solvent and any potential solute, thus highly influencing the extraction capacity. Furthermore, polarity has a big impact on miscibility of HDES in water. Preliminary evaluation of DES polarity can be done using a simple test based on contact angle measurement [57].

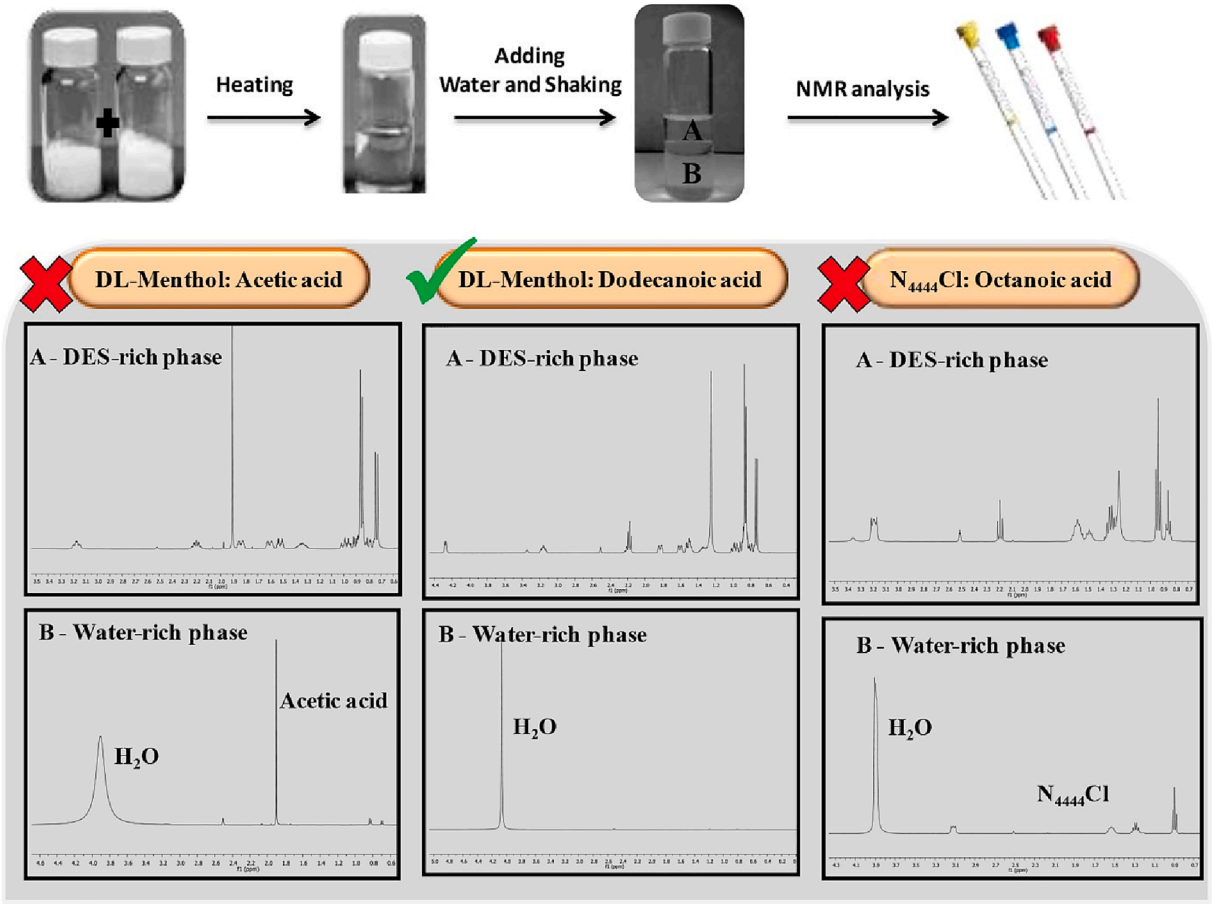

Fig. 3. ^{1}H NMR analysis of HDES stability after liquid–liquid extraction technique. Reprinted with permission from [26]. Copyright (2017) Elsevier.

c) Some HDES may form emulsions, therefore it is necessary to study the surface tension and select only these solvents with high surface tension values. Moreover, higher surface tension values of HDES usually ensure higher extraction efficiency.
d) Low solubility in water of HDES is a very important from a point of view of its applicability for water treatment. Selection of HDES for which there is no loss will ensure that the whole process will be sustainable and no additional environmental and/or economic costs will take place.
e) For HDESs to be widely used in the extraction of pollutants from water, their toxicity should be carefully studied. Some of the components of HDESs are considered as toxic, thus it is necessary to study if after creation of HDESs the toxic effect is diminished or not.
f) Several components of HDES are volatile. Even if their smell does not have odorous character, their presence in water even at ppm level will cause their emission into the air affecting the local air quality [58].
g) On this basis, HDES-based processes seem to be a good solution for pre-treatment of wastewater with high pollution load. Such step should be followed by a biological treatment process for removal of traces of HDES.
h) Selection of HDES components should include above aspects and allow to apply biodegradable components that can be removed at the biological treatment process. It demands a pre-analysis of "compatibility" of DES components with type of bacteria present in activated sludge.
ii) As discussed in section 3 there are various methods used to evaluate the stability of HDESs in water. Nevertheless, all of them have some disadvantages and the obtained results may not be very precise and do not represent the true. Therefore, we decided to suggest some simple protocols to determine stability of HDESs in water by measuring their water solubility.
- Ultraviolet (UV) – in case of HDES components containing chromophore groups, their concentration in water after extraction process can be easily detected at ppm level by simple spectrophotometric measurement. A proper monitored wavelength can be easily selected based on UV–vis spectrum of target components available in the literature.
- High performance liquid chromatography (HPLC) – chromatographic separation can be used prior to detection, on this basis HDES components can be quantified in case of real or more complex matrix.
- Gas chromatography (GC) – for pure water experiments a Direct Aqueous injection (DAI) can be used. In other cases (real, complex matrix), headspace analysis or other sample preparation technique should be used. GC will be very useful in case of HDES volatile components.
- Ion-exchange chromatography – for HDES containing ionic components this method can be useful to determine their content in aqueous phase as previously reported[18].
- TOC – this analysis can be performed in the case of HDES containing organic components as it allows to monitor overall levels of organic compounds present in aqueous systems.
- COSMO-RS modeling – this approach can be used for theoretical estimation of the amount of HDESs components. In this analysis HDESs are treated as combination of distinct components and it is possible to predict the activity coefficient of any compound, having in mind that its solubility in a solvent is inversely proportional to its activity coefficient in the system.

5. Conclusions and outlook

Hydrophobic deep eutectic solvents are emerging subclass of DESs that contrary to their hydrophilic counterparts can be used in water and wastewater treatment processes due to their water immiscibility. Over the last years, the interest in HDESs have been exponentially growing, however a very limited number of HDESs has been proposed to date due to the restricted availability of HBAs and HBDs that can form HDESs with melting points close to room temperature. Furthermore, if we envisage application of these solvents for water purification purposes, even more special attention is needed. For HDES to be suitable for extraction of pollutants from water, its chemical and structural stability in water has to be guaranteed. Throughout this paper, it was showed that HDESs can be used as efficient extractants for various pollutants without contaminating water. However, it is also obvious that there are not a lot of studies reported on the applications of HDESs in liquid–liquid extraction for water treatment and most of them are rather theoretical works. Moreover, most of these works focused on the usage of the same solvents and only the extracted solute was changing. This is mostly related to the fact that, although some of DESs are considered hydrophobic, they are not stable in water. Therefore, in order to design water-

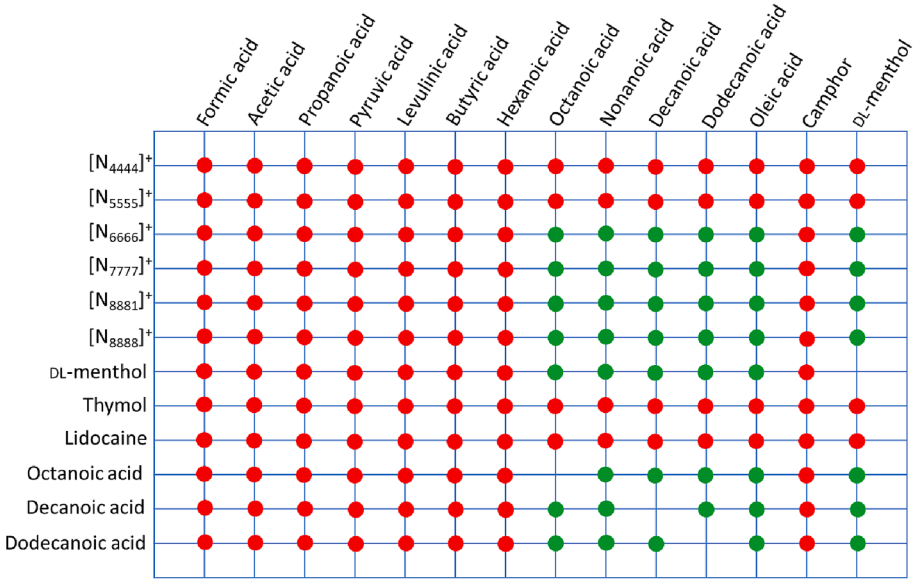

Fig. 4. Matrix of possible water stability of deep eutectic solvents composed of different hydrogen bond acceptors and hydrogen bond donors (– not stable in water and – stable in water). Note that not all the presented combination of HBA and HBD will form DES.

stable HDESs both components need to be hydrophobic and have very low water solubilities. On the other hand, such water-stable HDESs are usually composed of expensive and toxic hydrophobic quaternary ammonium salts, which does not make them the best candidates for water purification due to their considerable impact on the process sustainability. Consequently, further efforts are needed to develop and characterize new HDESs. For example, the use of all-natural compounds in HDESs preparation will be without a doubt of continued interest of the researchers in the field, as they will allow to reduce the cost and may be able to replace toxic, volatile organic compounds, thus fulfilling one of the green chemistry principles. Nevertheless, before it will be possible, there are still a lot aspects that need to be tackled. For instance, studies on physicochemical properties of HDESs such as volatility, viscosity, polarity, surface tension, toxicity are needed. In particular, it is necessary to solve the issue of HDESs safety. Furthermore, the HDESs stability has to be carefully evaluated using the adequate and precise methodology. Our analysis indicated that it is necessary to have an improved, standard protocol for determination of solubility of HDESs in water. In this way, it will be possible to create a database of water-stable HDESs that can be used in water treatment processes. When all of the mentioned issues will be covered, it will be necessary to expand the research from laboratory to industrial scale and solve all the technological issues associated with the usage of HDESs in a large scale. With that being said, a lot of time will most likely pass before HDESs will be considered as real alternative for the conventional solvents. In our opinion, HDESs will probably be more suitable for processing rather small volumes of wastewater with high pollution load or containing specific hazardous pollutants and followed by a biological treatment process for removal of traces of HDESs.

This review proved a serious environmental issue in respect to large scale applications of HDESs for treatment of aqueous phase. Such issue remains also on microscale separations – in analytical chemistry. A large number of papers has been published on applications of HDESs in analytical scale procedures (many of them named as microextraction protocols for sample preparation). Each batch of such analysis of water samples will result in aqueous waste samples polluted with DESs. Thus, their utilization should be done with care, as in many cases they are hazardous wastes.

It is expected that, in a future, the field of HDESs and their application in extraction of pollutants from water will evolve rapidly. With possible many newer HDES combinations and with their flexibility and designer solvent character, their use in water treatment will continue to grow, and they will probably replace others solvents used in water purification applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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