Supramolecular deep eutectic solvents in extraction processes: a review

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REVIEW ARTICLE

Supramolecular deep eutectic solvents in extraction processes: a review

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Abstract

Solvent selection is essential for industrial and analytical extraction processes to ensure environmental safety and neutrality. Nevertheless, toxic and hazardous solvents are often used, due to their cost-effectiveness and ready availability. In green chemistry, alternative solvents such as supramolecular deep eutectic solvents are gaining attention due to their superior performance compared with traditional non-green solvents in certain applications. Here we review the use of supramolecular deep eutectic solvents as a green solvent for analytical and industrial liquid–liquid extraction processes, with focus on physicochemical properties, extraction conditions, the capacity factor, the enrichment factor, fuel desulfurization, extraction of biological active compounds, lignin valorization, and sample preparation.

Keywords Cyclodextrins · Supramolecular deep eutectic solvents · Liquid–liquid extraction processes · Green solvents · SUPRADES

Abbreviations

^{19}F NMR	Fluorine-19 nuclear magnetic resonance spectroscopy
CD	Cyclodextrin
CM-β-CD	Carboxymethyl-β-cyclodextrin
CRYSMEB	Low methylated-β-cyclodextrin
C_{IN}	Initial concentration of analytes
DES	Deep eutectic solvent
DFT	Density functional theory
DM-β-CD	2,6-Di-O-methyl-β-cyclodextrin
EF	Enrichment factor
HP-α-CD	Hydroxypropyl-α-cyclodextrin
HP-β-CD	Hydroxypropyl-β-cyclodextrin
HPLC–PDA	High-performance liquid chromatography equipped with photodiode array detector
HPLC–UV	High-performance liquid chromatography equipped with ultraviolet detector
LOD	Limit of detection
MB-NH_2@CD@DES	Trifluoroacetamide and benzyltrimethylammonium chloride-modified β-cyclodextrin-grafted magnetic beads
Methyl-β-CD	Methyl-β-cyclodextrin
MP	Melting point
PAHs	Polycyclic aromatic hydrocarbons
RAMEB	Randomly methylated-β-CD
RGB	Red–green–blue
$R_{L/S}$	Liquid–solid ratio
SBE-β-CD	Sulfobutylether-β-cyclodextrin
S-β-CD	Sulfated-β-cyclodextrin sodium salt
SUPRADES	Supramolecular deep eutectic solvents
UV–Vis	Ultraviolet–visible spectroscopy
TG	Glass transition temperature

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Introduction

The choice of reagents heavily influences the greenness of the technological procedures. Solvents play a significant role in the industrial separation processes and sample preparation. Many technological processes commonly use toxic organic solvents derived from crude oils. In today's environmentally conscious society, reducing the use of hazardous solvents in academic and industrial settings is crucial. To achieve this goal, two primary strategies can be implemented. First, it is important to reduce the use of solvents by modifying the technology or replacing harmful organic solvents with eco-friendly alternatives [5, 9, 72, 73]. However, organic solvents are necessary for many chemical processes, including extraction and microextraction. Moreover, numerous extraction, purification, and cleaning processes rely heavily on solvents, often requiring substantial excesses to guarantee adequate product purity. Therefore, it is more practical to explore alternative environmentally friendly solvents.

Most academic papers have focused on replacing hazardous and flammable organic solvents with environmentally friendly alternatives, including ionic liquids, deep eutectic solvents (DESs), surfactants, hydrotropes, and bio-based solvents [69]. Among the aforementioned solvents, ionic liquids have gained significant attention as effective extraction solvents because of their non-volatile, non-flammable, and non-explosive characteristics, as well as their ability to customize their physicochemical properties through the selection of cations and anions [95]. However, their high cost, complex synthesis, proven toxicity, and minimal biodegradability have hindered their use in industrial applications [75, 101]. To address these limitations, Abbott et al. introduced an innovative eco-friendly solvent known as a deep eutectic solvent in 2003 [1].

Deep eutectic solvents are created by mixing at least two solid components (typically at elevated temperatures) to form a liquid. The interaction between the components of a deep eutectic solvent is mainly driven by the formation of hydrogen bonds between the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). The first published deep eutectic solvent was choline chloride combined with urea at a 1:2 molar ratio [1]. Components with functional groups capable of forming hydrogen bonds were used to significantly reduce the melting point of the mixture. Deep eutectic solvents are known to have unique properties. Their main advantages include the natural origin of many of the components used for their preparation, low toxicity, and simple, cost-effective preparation. By altering the components of a deep eutectic solvent, a solvent with properties tailored to the specific separation requirements for various systems can be obtained [12, 27, 46, 86, 99]. This makes deep eutectic solvents widely applicable in various fields [88]. Currently, distinct subclasses of deep eutectic solvents exist based on their physicochemical properties and the origin/functionality of their components. These subclasses include hydrophobic, natural, therapeutic, and magnetic deep eutectic solvents [7, 17, 20, 74, 80, 85].

The latest group, first published in 2020, are supramolecular deep eutectic solvents (SUPRADES) [28]. This is a family of deep eutectic solvents containing cyclodextrin (CD), a host molecule which can form inclusion complexes. In SUPRADES, cyclodextrin can be used as hydrogen bond acceptor, in binary supramolecular systems, or as additives within deep eutectic solvents, in ternary supramolecular systems. SUPRADES can combine the advantages of conventional deep eutectic solvents with those of cyclodextrins. Their benefits make it a promising candidate for various industrial and laboratory applications, as demonstrated by the recent papers [41, 42, 52, 58, 98]. However, limited information is available in the literature regarding their physicochemical properties and potential applications.

The extraction process is a crucial area of science used in analytical and large-scale processes. Safety in the extraction process becomes increasingly important when planning conscious processes; therefore, there is a need to replace the toxic organic solvents by greener alternatives. This review summarizes the groundbreaking and innovative use of the SUPRADES, including their properties and applications in the extraction processes. Despite their novelty, SUPRADES already attracted the attention of scientists and few reviews have already been published. The use of deep eutectic solvents in extraction techniques is also a hot topic that has been reviewed (Table 1). However, to the best of our knowledge, this is the first review on the use of SUPRADES in extraction techniques.

The present review summarizes the use of supramolecular deep eutectic solvents, which combine the properties of cyclodextrins and eutectic solvents in a variety of extraction processes (Fig. 1). First, the different cyclodextrins and other compounds used for the preparation of SUPRADES are described. The physicochemical properties of the solvents obtained are detailed, and the price of these new solvents is estimated. Then, the different extraction processes using SUPRADES will be described. Finally, we will critically discuss the future of SUPRADES in extraction processes.

Supramolecular deep eutectic solvents composition and preparation

The key component of SUPRADES is cyclodextrin, a molecule from the oligosaccharide family, obtained by enzymatic degradation of starch [18, 19, 82]. Native cyclodextrins

Table 1 Recent reviews on supramolecular deep eutectic solvents (SUPRADES) or extraction processes using deep eutectic solvents

Topic	Title	Reference
SUPRADES formation	Combination of DES and macrocyclic host molecules: review and perspectives	[56]
General application of SUPRADES in absorption, sample preparation, and supramolecular polymeric adhesive materials	Supramolecular deep eutectic solvents and their applications	[52]
Definitions, properties, characterization, and applications of cyclodextrins-based polymeric deep eutectic solvents	Green materials with promising applications: cyclodextrin-based deep eutectic supramolecular polymers	[98]
Application of conventional deep eutectic solvents in microextraction techniques	Microextraction of bioactive compounds using deep eutectic solvents: a review	[69]
Hydrophobic deep eutectic solvents application for removal of different contaminants from water	Hydrophobic (deep) eutectic solvents (HDESs) as extractants for removal of pollutants from water and wastewater—a review	[65]
Natural deep eutectic solvents for extracting pigments	Sustainable green extraction of anthocyanins and carotenoids using deep eutectic solvents (DES): a review of recent developments	[71]
Hydrophilic deep eutectic solvents for phytochemicals extraction	Hydrophilic deep eutectic solvents: a new generation of green and safe extraction systems for bioactive compounds obtaining from natural oil & fats—a review	[38]
Application of natural deep eutectic solvents in microextraction processes	Applications of (natural) deep eutectic solvents in liquid phase microextraction: a review	[64]
Application of deep eutectic solvents for the extraction of anthocyanins	Application of deep eutectic solvents in the extraction of anthocyanins: stability, bioavailability, and antioxidant property	[33]

These reviews gather the different SUPRADES described up to 2022 as well as their potential applications or highlight the potential of deep eutectic solvents in extraction process. No reviews were published gathering the application of SUPRADES in extraction processes

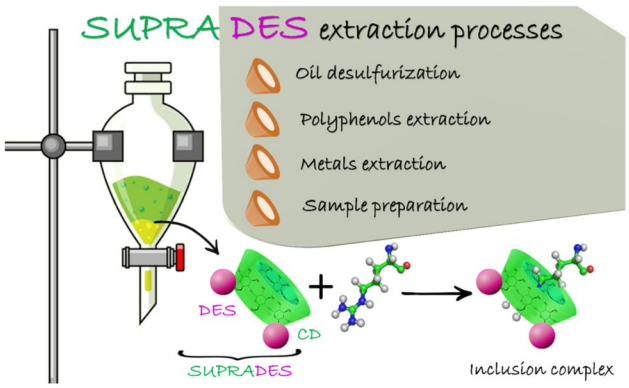

Fig. 1 Various extraction processes concerned by the use of supramolecular deep eutectic solvent (SUPRADES) that combine cyclodextrins and eutectic solvent properties. One of the advantages of these supramolecular solvents is to take benefit of the ability of cyclodextrins to form inclusion complexes with a variety of hydrophobic organic compounds

are molecules composed of six (α-CD), seven (β-CD), or eight (γ-CD) D-glucopyranose units linked by an α-(1–4) bonds [18]. Cyclodextrins are frusto-conical in shape, have a hydrophilic outer surface, and their cavities are relatively hydrophobic. The unusual structure of cyclodextrins (*i.e.,* a hydrophilic outer surface connected to a relatively hydrophobic cavity) makes them capable of forming inclusion complexes in aqueous solutions with numerous molecules of low hydrophilicity and appropriate geometric size (which will allow non-covalent host/guest interaction) [6, 57, 82]. The number of D-glucopyranose molecules determines the size of the hydrophobic cavity (4.7–5.3 Å, 6.0–6.5 Å, and 7.5–8.3 Å for α-CD, β-CD, and γ-CD, respectively) [67]. Naturally occurring cyclodextrins can be modified by amination, esterification, or etherification reactions [21]. In these processes, additional functional groups are introduced: methyl, ethyl, hydroxyl, hydroxypropyl, carboxymethyl, or sulfobutylether.

A summary of the most common cyclodextrins and their modifications is shown in Fig. 2. Possible benefits of modifying cyclodextrins include increasing the solubility in water, changing the volume of the cavity, increasing the stability (resistance to oxygen and/or light), and helping to control the chemical activity of the guest molecules [21]. The presence of cyclodextrins in SUPRADES enables the encapsulation of numerous chemical compounds through the formation of hydrogen bonds and host/guest interactions [22, 23, 68]. The SUPRADES described in the literature are solvents composed mainly of two or three organic substances, called binary and ternary systems, respectively.

Binary SUPRADES are obtained precisely the same route as conventional deep eutectic solvents. This procedure for obtaining them involves magnetic stirring of the two precursor compounds in an appropriate molecular ratio in a closed

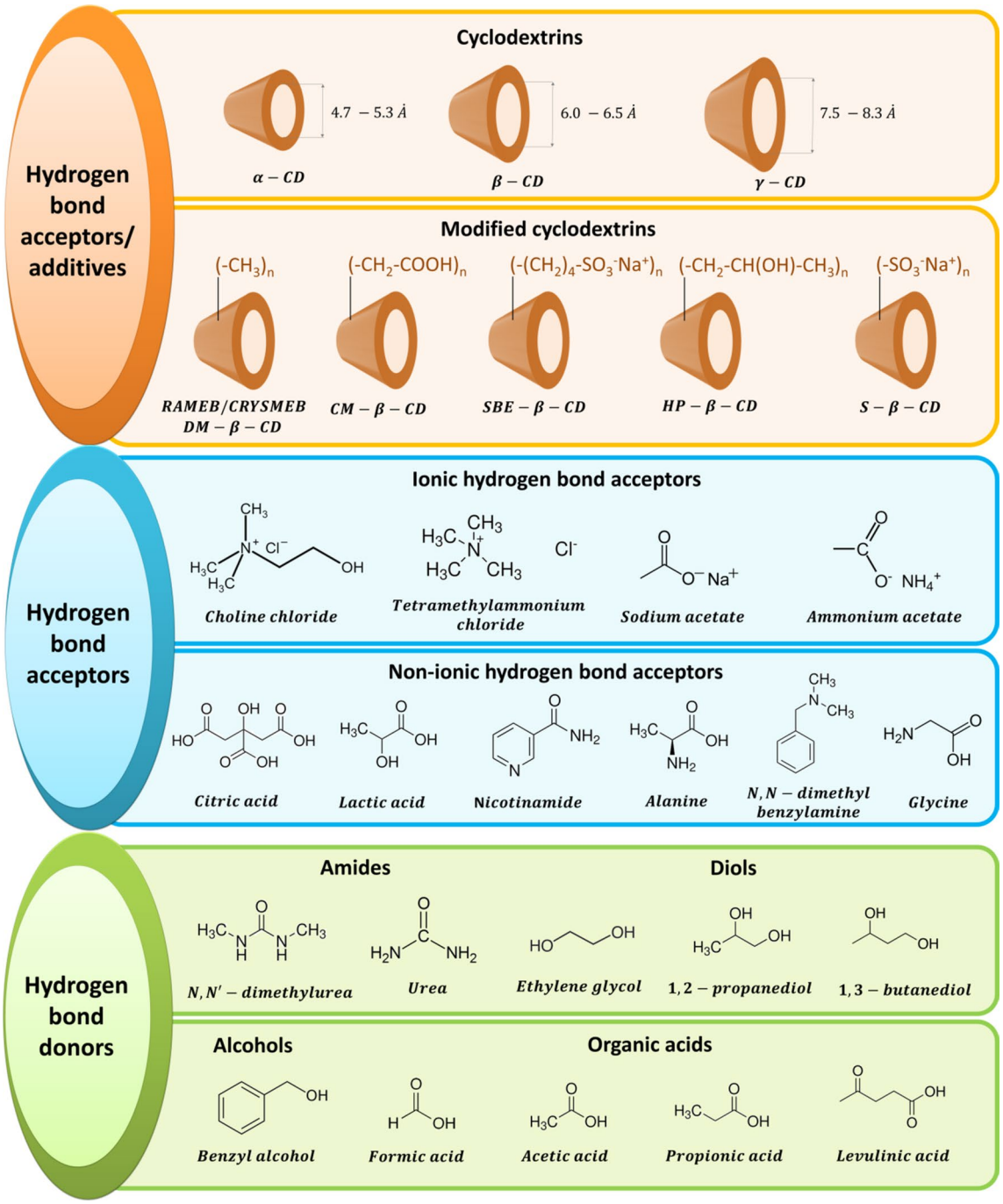

Fig. 2 Commonly used ingredients for preparing supramolecular deep eutectic solvents (SUPRADES). In binary systems, cyclodextrins act as a hydrogen bond acceptor and are associated with a hydrogen bond donor. In ternary systems, cyclodextrins act as additives in a conventional deep eutectic solvent prepared from a hydrogen bond donor and a hydrogen bond acceptor. Different chemical families can play the role of hydrogen bond donor or acceptor. CD: cyclodextrin; CM-β-CD: carboxymethyl-β-cyclodextrin; CRYSMEB: low methylated-β-cyclodextrin; DM-β-CD: 2,6-Di-O-methyl-β-cyclodextrin, HP-β-CD: hydroxypropyl-β-cyclodextrin; RAMEB: randomly methylated-β-CD; SBE-β-CD: sulfobutylether-β-cyclodextrin; S-β-CD: sulfated-β-cyclodextrin

vial at a certain temperature for a certain period of time [1]. The final product is a homogeneous and stable clear liquid at room temperature. The procedure is simple and does not require additional chemicals. In binary SUPRADES, cyclodextrin acts as a hydrogen bond acceptor because of the presence of O-glycosidic bonds in the outer part of its structure. Both native (α-CD, β-CD, γ-CD) and modified cyclodextrins, *i.e.,* sulfobutylether-β-cyclodextrin (SBE-β-CD),

sulfated-β-cyclodextrin sodium salt (S-β-CD), 2,6-Di-O-methyl-β-cyclodextrin (DM-β-CD), carboxymethyl-β-cyclodextrin (CM-β-CD), low methylated-β-cyclodextrin (CRYSMEB), hydroxypropyl-β-cyclodextrin (HP-β-CD), and randomly methylated-β-cyclodextrin (RAMEB), are used to prepare binary SUPRADES. In contrast, the same chemicals used in the preparation of conventional deep eutectic solvents are used as hydrogen bond donors. These compounds include carboxylic acids (*i.e.,* formic acid, levulinic acid, lactic acid, citric acid), alcohols (benzyl alcohol), diols (*i.e.,* ethylene glycol, 1,2-propanediol, 1,3-butanediol), and amides (N,N′-dimethylurea, urea, nicotinamide) [29–31, 39, 41].

Ternary SUPRADES contains conventional deep eutectic solvents in its structure, mainly quaternary ammonium salts, *i.e.,* choline chloride, tetramethylammonium chloride or sodium acetate, and various hydrogen bond donors such as urea, citric acid, L-malic acid, and L-tartaric acid. Cyclodextrin plays the role of additive. Formulating ternary SUPRADES is more challenging than preparing binary SUPRADES. This is because the direct mixing of deep eutectic solvents with cyclodextrin (in the same molar ratios of deep eutectic solvents:cyclodextrin as in binary SUPRADES) does not typically result in the formation of a liquid complex at room temperature. Therefore, a small amount of cyclodextrin is generally added to the deep eutectic solvents. Water can be added to increase the proportion of cyclodextrin in the SUPRADES structure, as it plays a role in forming the deep eutectic solvents-cyclodextrin hydrogen-bonding network, which leads to the formation of supramolecular structures.

Physical properties of supramolecular deep eutectic solvents

The physical properties of SUPRADES depend on the type of cyclodextrin, other organic components, and their stoichiometry. Often, even a small change in the amount of a single ingredient can significantly alter the physicochemical properties of SUPRADES, which can improve or worsen its extraction ability. This section summarizes the crucial physical properties of the SUPRADES described in the literature (Table 2).

Melting point and glass transition temperature

The evaluation of solvents necessitates the determination of their melting points or glass transition temperatures, which are crucial factors for SUPRADES. Melting point is the temperature at which a crystalline material transitions from solid to liquid. In contrast, the glass transition temperature transitions from a glassy state to a highly elastic state. Since most extraction processes are conducted at room temperature, SUPRADES extractants must have a melting point/glass transition temperature lower than room temperature. However, the results show that only a limited number of SUPRADES meet this assumption. This is because of the relatively high melting points of cyclodextrins, which are 507, 501, and 474 °C for α-, β-, and γ-CD, respectively [35]. The modified cyclodextrins exhibit lower melting points, with values of 182, 202, 267, and 260 °C for methyl-β-cyclodextrin, sulfobutylether-β-cyclodextrin, hydroxypropyl-β-cyclodextrin, and hydroxyethyl-β-cyclodextrin, respectively [44]. In addition, cyclodextrins form relatively weak non-covalent interactions with other components, such as van der Waals or electrostatic interactions. In most cases, hydrogen bonds, which play a major role in lowering the melting point, are formed in insufficient amounts to create a liquid extractant at room temperature.

Notably, the formation of cyclodextrin—hydrogen bond donor inclusion systems—did not significantly reduce the melting point. Theoretically, increasing the cyclodextrin content in the SUPRADES structure should increase its melting point too. This theory was confirmed for binary SUPRADES composed of α-, β-, and γ-CD as hydrogen bond acceptor and carboxylic acids, *i.e.,* citric acid, L-(-)-malic acid, and L-(+)-tartaric acid (1:10) [90]. However, in different works, comparing binary SUPRADES containing the same compounds in different proportions showed an opposite trend. In the CRYSMEB:*N,N′*-dimethylurea and RAMEB:*N,N′*-dimethylurea systems, increasing the proportion of cyclodextrin from 3:7 to 7:3 decreased the melting point from 92 to 71 °C and from 91 to 51 °C, respectively. By contrast, increasing the proportion above 80% m/m significantly increased the melting point above 100 °C [31]**.** To obtain binary SUPRADES with melting point/freezing point below 25 °C, the cyclodextrin content of the complex structure must be significantly reduced. For example, for binary systems composed of levulinic acid, *i.e.,* HP-β-CD:levulinic acid (1:32), RAMEB:levulinic acid (1:27), CRYSMEB:levulinic acid (1:25), and SBE-β-CD:levulinic acid (1:44), the glass transition temperature is -73.3, -74.3, -73.5, and -67.8 °C, respectively [29]. Similar glass transition temperature values of -80, -78.4, and -79.6 °C were obtained for ternary SUPRADES that consist of thymol:heptanoic acid (2:1) + DM-β-CD, thymol:heptanoic acid (2:1) + RAMEB, thymol:heptanoic acid (2:1) + HP-β-CD, respectively [97].

Decomposition temperature

The decomposition temperature of SUPRADES is a crucial factor in determining its suitability for high-temperature processes. In particular, for extraction processes, the decomposition temperature plays a vital role in solvent regeneration

Table 2 Physical properties and estimated price of supramolecular deep eutectic solvent (SUPRADES) used for extraction in the literature

SUPRADES (molar ratio)	Water content (%)	Viscosity (temp, °C) [mPa·s]	Density (temp, °C) [kg/m^3]	MP/TG [°C]	Decomposition temp. [°C]	Hydrophobicity	Price per 1 kg	Reference
Binary SUPRADES								
Sulfobutylether-*β*-cyclodextrin:levulinic acid (1:44)	3.9	1300 (30 °C)	1234.3 (30 °C)	− 67.8	127.6	No	55.93 €	[29]
Low methylated-*β*-cyclodextrin:levulinic acid (1:25)	3.3	480 (30 °C)	1207.5(30 °C)	− 73.5	137.7	No	246.94 €	[29]
Hydroxypropyl-*β*-cyclodextrin:levulinic acid (1:32)	2.7	600 (30 °C)	1204.7 (30 °C)	− 73.3	130.4	No	130.4 €	[29]
Randomly methylated-*β*-cyclodextrin:levulinic acid (1:27)	2.5	212.9 (30 °C)	1184.5 (30 °C)	− 74.3	117.6	No	71.4 €	[29]
α-Cyclodextrin:*N,N'*-dimethylurea (3:7)	–	1436 (90 °C)	–	86	–	No	134.19 €	[31]
β-Cyclodextrin:*N,N'*-dimethylurea (3:7)	–	1165 (90 °C)	–	91	–	No	70.49 €	[31]
β-Cyclodextrin:*N,N'*-dimethylurea (1:1)	–	434 (90 °C)	–	67	–	No	74.49 €	[31]
γ-Cyclodextrin:*N,N'*-dimethylurea (3:7)	–	1096 (90 °C)	–	91	–	No	181.54 €	[31]
Hydroxypropyl-*α*-cyclodextrin:*N,N'*-dimethylurea (3:7)	–	163 (90 °C)	–	87	–	No	2619.81 €	[31]
Hydroxypropyl-*β*-cyclodextrin:*N,N'*-dimethylurea (3:7)	–	205 (90 °C)	–	91	–	No	2382.45 €	[31]
Hydroxypropyl-*γ*-cyclodextrin:*N,N'*-dimethylurea (3:7)	–	208 (90 °C)	–	94	–	No	2942.73 €	[31]
Low methylated-*β*-cyclodextrin:*N,N'*-dimethylurea (3:7)	–	445 (90 °C)	–	92	–	No	1406.73 €	[31]
Low methylated-*β*-cyclodextrin:*N,N'*-dimethylurea (1:1)	–	103 (90 °C)	–	79	–	No	2301.95 €	[31]
Low methylated-*β*-cyclodextrin:*N,N'*-dimethylurea (7:3)	–	45,500 (90 °C)	–	71	–	No	1406.73 €	[31]
Randomly methylated-*β*-CD:*N,N'*-dimethylurea (3:7)	–	235 (90 °C)	–	91	–	No	1604.73 €	[31]
Randomly methylated-*β*-cyclodextrin:*N,N'*-dimethylurea (1:1)	–	196 (90 °C)	–	71	–	No	2781.95 €	[31]
Randomly methylated-*β*-CD:*N,N'*-dimethylurea (7:3)	–	834 (90 °C)	–	51	–	No	3869.17 €	[31]
Randomly methylated-*β*-cyclodextrin:ethylene glycol (1:40)	3.12	175 (20 °C)	1179.64 (20 °C)	–	–	No	15.66 €	[41]
Randomly methylated–*β*-cyclodextrin:1,2-propanediol (1:40)	2.38	305 (20 °C)	1111.48 (20 °C)	–	–	No	23.73 €	[41]
Randomly methylated-*β*-cyclodextrin:1,3-butanediol (1:40)	2.08	476.78 (20 °C)	1005.3 (20 °C)	–	–	No	62.7 €	[41]
Randomly methylated-*β*-cyclodextrin:benzyl alcohol (1:40)	1.78	22.78 (20 °C)	1076.25 (20 °C)	–	–	No	51.3 €	[41]
α-Cyclodextrin:formic acid (1:3)	–	5.3 (30 °C)	–	–	–	No	131.9 €	[39]
β-Cyclodextrin:formic acid (1:3)	–	3.6 (30 °C)	–	–	–	No	79.3 €	[39]
γ-Cyclodextrin:formic acid (1:3)	–	3.3 (30 °C)	–	–	–	No	171.05 €	[39]
Methyl-*β*-cyclodextrin:formic acid (1:3)	–	42.8 (30 °C)	–	–	–	No	529.86 €	[39]

Table 2 (continued)

SUPRADES (molar ratio)	Water content (%)	Viscosity (temp, °C) [mPa·s]	Density (temp, °C) [kg/m^3]	MP/TG [°C]	Decomposition temp. [°C]	Hydrophobicity	Price per 1 kg	Reference
Methyl-β-cyclodextrin:acetic acid (1:3)	–	88.9 (30 °C)	–	–	–	No	769.48 €	[39]
Methyl-β-cyclodextrin:propionic acid (1:3)	–	44.1 (30 °C)	–	–	–	No	500.83 €	[39]
β-Cyclodextrin:lactic acid (1:4)	0.79	818 (21.3 °C)	–	–	–	No	38.12 €	[30]
Hydroxypropyl-β-cyclodextrin:citric acid (1:14)	20	7800 (30 °C)	1360 (30 °C)	–	220	No	452.51 €	[10]
Hydroxypropyl-β-cyclodextrin:lactic acid (1:35)	14.5	98 (30 °C)	1150 (30 °C)	–	140	No	244.14 €	[10]
Hydroxypropyl-β-cyclodextrin:choline chloride (2:35)	20	320 (30 °C)	1110 (30 °C)	–	270	No	306.62 €	[10]
α-Cyclodextrin:citric acid (1:5)	–	$5.2{\cdot}10^5$ (25 °C)	–	−33	258.3	No	93.2 €	[90]
α-Cyclodextrin:citric acid (1:10)	–	$1{\cdot}10^4$ (25 °C)	–	−43	225.2	No	51.04 €	[90]
α-Cyclodextrin:L-(-)-malic acid (1:5)	–	$8.5{\cdot}10^4$ (25 °C)	–	−29	282.2	No	489.79 €	[90]
α-Cyclodextrin:L-(-)-malic acid (1:10)	–	$2.05{\cdot}10^4$ (25 °C)	–	−50	276.7	No	507.63 €	[90]
α-Cyclodextrin:L-(+)-tartaric acid (1:5)	–	$1.28{\cdot}10^4$ (25 °C)	–	−23	271.1	No	132.84 €	[90]
α-Cyclodextrin:L-(+)-tartaric acid (1:10)	–	$4{\cdot}10^5$ (25 °C)	–	−36	262.3	No	118.12 €	[90]
β-Cyclodextrin:citric acid (1:5)	–	$1.1{\cdot}10^6$ (25 °C)	–	−24	225.2	No	58.06 €	[90]
β-Cyclodextrin:citric acid (1:8)	2 mL	125 (20 °C)	1423.4 (20 °C)	–	–	No	48.2 €	[16]
β-Cyclodextrin:citric acid (1:10)	–	$2.5{\cdot}10^3$ (25 °C)	–	−41	207.9	No	31.89 €	[90]
β-Cyclodextrin:L-(-)-malic acid (1:5)	–	$5{\cdot}10^7$ (25 °C)	–	2	284.8	No	454.65 €	[90]
β-Cyclodextrin:L-(-)-malic acid (1:10)	–	$3.2{\cdot}10^6$ (25 °C)	–	−44	346.9	No	488.49 €	[90]
β-Cyclodextrin:L-(+)-tartaric acid (1:5)	–	$4{\cdot}10^7$ (25 °C)	–	−25	270.1	No	97.71 €	[90]
β-Cyclodextrin:L-(+)-tartaric acid (1:10)	–	$3.6{\cdot}10^6$ (25 °C)	–	−29	264.6	No	98.98 €	[90]
γ-Cyclodextrin:citric acid (1:5)	–	$5.2{\cdot}10^7$ (25 °C)	–	−30	264.8	No	119.34 €	[90]
γ-Cyclodextrin:citric acid (1:10)	–	$8.4{\cdot}10^5$ (25 °C)	–	−41	243.9	No	89.11 €	[90]
γ-Cyclodextrin:L-(-)-malic acid (1:5)	–	$6{\cdot}10^{10}$ (25 °C)	–	−22	287.7	No	515.94 €	[90]
γ-Cyclodextrin:L-(-)-malic acid (1:10)	–	$6{\cdot}10^5$ (25 °C)	–	−40	278.5	No	521.9 €	[90]
γ-Cyclodextrin:L-(+)-tartaric acid (1:5)	–	$1.1{\cdot}10^8$ (25 °C)	–	−18	279.6	No	159.0 €	[90]
γ-Cyclodextrin:L-(+)-tartaric acid (1:10)	–	$7.9{\cdot}10^5$ (25 °C)	–	−40	260.1	No	132.38 €	[90]
Ternary SUPRADES								
Choline chloride:urea (1:2) + 2% α-cyclodextrin	–	668 (30 °C)	1198.9 (30 °C)	–	–	No	45.38 €	[39]
Choline chloride:urea (1:2) + 10% α-cyclodextrin	–	746 (30 °C)	1216.1 (30 °C)	–	–	No	69.56 €	[39]
Choline chloride:urea (1:2) + 2% β-cyclodextrin	–	758 (30 °C)	1197.8 (30 °C)	–	–	No	45.38 €	[39]
Choline chloride:urea (1:2) + 10% β-cyclodextrin	–	661 (30 °C)	1214.2 (30 °C)	–	–	No	48.52 €	[39]
Choline chloride:urea (1:2) + 10% β-cyclodextrin	–	639 (30 °C)	1212.7 (30 °C)	–	–	No	48.52 €	[26]

Table 2 (continued)

Ternary SUPRADES								
Choline chloride:urea (1:2) + 20% *β*-cyclodextrin	0.667	2104 (21.3 °C)	–	–	–	No	52.44 €	[30]
Choline chloride:urea (1:2) + 2% *γ*-cyclodextrin	–	775 (30 °C)	1198.1 (30 °C)	–	–	No	52.72 €	[39]
Choline chloride:urea (1:2) + 10% *γ*-cyclodextrin	–	1127 (30 °C)	1215.2 (30 °C)	–	–	No	85.22 €	[39]
Choline chloride:urea (1:2) + 2% hydroxypropyl-*β*-cyclodextrin	–	802 (30 °C)	1197.2 (30 °C)	–	–	No	199.56 €	[39]
Choline chloride:urea (1:2) + hydroxypropyl-*β*-cyclodextrin	–	1487 (30 °C)	1210.1 (30 °C)	–	–	No	264.14 €	[39]
Choline chloride:urea (1:2) + 2% low methylated-*β*-cyclodextrin	–	666 (30 °C)	1196.9 (30 °C)	–	–	No	134.51 €	[39]
Choline chloride:urea (1:2) + 10% low methylated-*β*-cyclodextrin	–	257 (30 °C)	1204.2 (30 °C)	–	–	No	494.14 €	[39]
Thymol:heptanoic acid (2:1) + 2,6-di-O-methyl-*β*-cyclodextrin	–	–	–	− 80.0	196.17	Yes	260.89 €	[97]
Thymol:heptanoic acid (2:1) + randomly methylated-*β*-cyclodextrin	–	–	–	− 78.4	197.31	Yes	622.30 €	[97]
Thymol:heptanoic acid (2:1) + hydroxypropyl-*β*-cyclodextrin	–	–	–	− 79.6	194.83	Yes	851.54 €	[97]
Choline chloride:lactic acid:hydroxypropyl-*β*-cyclodextrin (17.5:35:2)	8.5	760 (30 °C)	1180 (30 °C)	–	270	No	438.09 €	[10]
Citric acid:Lactic acid:hydroxypropyl-*β*-cyclodextrin (14:35:2)	8.2	4265 (30 °C)	1290 (30 °C)	–	220	No	423.37 €	[10]
Choline chloride:citric acid:hydroxypropyl-*β*-cyclodextrin (17.5:14.5:2)	20	1020 (30 °C)	1230 (30 °C)	–	220	No	454.59 €	[10]

Binary SUPRADES are obtained by mixing one cyclodextrin with one hydrogen bond donor, while ternary SUPRADES are obtained by adding one cyclodextrin in an already prepared deep eutectic solvent. The cyclodextrin is therefore considered as an additive in this case. Density plays a significant role in separation processes, particularly in extraction as well as viscosity since high viscosity of the extractants could impede the mass transfer process. The water content could affect these physicochemical properties

MP melting point, *TG* glass transition temperature

and sample preparation processes, such as direct solvent dispensing into the hot injector of a gas chromatograph. At high temperatures, the structure of SUPRADES may undergo phase changes, breakdown of hydrogen bonds, and electrostatic interactions between hydrogen bond acceptor, hydrogen bond donor, and cyclodextrin. Therefore, an assessment of the thermal stability of SUPRADES provides valuable information on the temperature at which the solvent can be used without undergoing structural changes [50, 76].

Thermogravimetric analysis curves for the binary SUPRADES indicated two distinct weight losses. The first, which was relatively minor, occurred between 100 °C and 140 °C. This was attributed to the loss of water from the SUPRADES structures, including those that were not intentionally hydrated [37]. However, cyclodextrins' characteristic cavity structure facilitates water adsorption and hinders its removal. The second weight loss corresponded to the decomposition of SUPRADES and occurred at temperatures ranging from 207 to 287.7 °C. Nevertheless, the exact values varied depending on the components and stoichiometry of SUPRADES. As the cyclodextrin content in the SUPRADES structure increased from 1:10 to 1:5 (cyclodextrin:hydrogen bond donor), the decomposition temperature increased [90]. This can be attributed to the high decomposition temperatures of cyclodextrins and the strong bonds between hydrogen bond donor and cyclodextrin. SUPRADES based on levulinic acid and lactic acid exhibited relatively low decomposition temperatures

of 127.6, 137.7, 130.4, 130.4, and 120 °C for SBE-β-CD:levulinic acid (1:44), CRYSMEB:levulinic acid (1:25), HP-β-CD:levulinic acid (1:32), and RAMEB:levulinic acid (1:27), HP-β-CD:lactic acid (1:35), respectively [29]. The lower boiling points of both acids likely contributed to their lower decomposition temperatures. For binary SUPRADES, much less data are available in the literature. However, it can be observed that the approximate degradation temperatures for binary SUPRADES range from 195 to 270 °C. In addition, an increased number of components in eutectic mixtures are associated with increased steps associated with distinct T-onset values [10, 97].

Density

Solvent density is a crucial thermophysical property that plays a significant role in separation processes, particularly in extraction. To effectively separate the phases, the density of SUPPRADES needs to be either higher or lower than the density of the sample matrix. Conventionally, deep eutectic solvents have a higher density than water, ranging from 1.0 g/cm^3 to 1.35 g/cm^3 at 20 °C [27, 63]. The majority of the binary and ternary SUPRADES have similar densities. Their densities range from 1.1 to 1.36 g/cm^3 at 20 °C [10, 26, 29, 39, 41]. Only RAMEB:1,3-butanediol (1:40) has a much lower density of 1.01 g/cm^3, which results from the density of the butanediol [41]. In this case, the cyclodextrin content was minimal and only slightly changed the density of SUPRADES. Increasing the cyclodextrin content in the deep eutectic solvents structure increased its density. To lower the density, it is possible to add water to SUPRADES. However, this modification is limited to hydrophilic SUPRADES. Temperature is another parameter that significantly influences the density. A decrease in temperature results in a reduction of the kinetic energy of SUPRADES molecules, which leads to an increase in density (Fig. 3). This is because, at low temperatures, the decrease in the movement of SUPRADES molecules and the consequent reduction of the molar volume of the eutectic complexes can be observed [2, 15]. However, economic considerations make many industrial processes require temperatures close to room temperature. Additionally, in the extraction process, a change in the temperature of the solvent also affects the temperature of the second phase, which does not improve phase separation.

Viscosity

Viscosity is a critical factor for several SUPRADES applications. The low viscosity of SUPRADES simplifies the management of solvents and reduces energy costs. However, the high viscosity of the extractants impedes the mass transfer process. Main conventional deep eutectic solvents exhibit high viscosities (greater than 100 mPa·s at room temperature and normal pressure). Unfortunately, the viscosity of major SUPRADES is even higher [1, 27, 61, 63, 79]. Compared to choline chloride: urea (1:2), with a viscosity of 1358 mPa·s, SUPRADES based on the same deep eutectic solvent containing β-CD exhibited a higher value of 2104 mPa·s [30]. This increased viscosity in SUPRADES can be attributed to several factors, such as the strong hydrogen bonds between the cyclodextrins and hydrogen bond donor, which restrict the mobility of free species within the eutectic molecule. Additionally, the larger size of the cyclodextrins molecules and smaller empty volumes contributed to increased viscosity. This phenomenon is known as the steric effect. It can be quantified using hole theory, which takes into account the strong electrostatic and van der Waals interactions between cyclodextrins and hydrogen bond donors [2, 45, 61].

The viscosity of SUPRADES is mainly influenced by the type and amount of cyclodextrin in its structure. In binary SUPRADES systems composed of neat cyclodextrins, the viscosity increased in the following order for a same hydrogen bond donor: α-CD < β-CD < γ-CD. The differences in viscosities were almost an order of magnitude. Furthermore, as the SUPRADES content increased, its viscosity increased significantly by up to three orders of magnitude after changing the molar ratio from 1:10 to 1:5 (cyclodextrin:hydrogen bond donor) [90]. However, replacing neat cyclodextrins with modified cyclodextrins can significantly reduce the viscosity of SUPRADES. Compared to the viscosity of β-CD:*N,N′*-dimethylurea (1165 mPa·s), replacing β-CD by hydroxypropylated or methylated β-cyclodextrins leads to significantly reduced viscosity, with values of 205, 445, and 235 mPa s, respectively [31]. Furthermore, it is possible to add water to ternary SUPRADES to decrease its dynamic viscosity. As the water content in the system increases, the viscosity decreases. This decrease in viscosity can be attributed to the lower viscosity of water than that of the deep eutectic solvents. Moreover, the viscosity of SUPRADES decreases considerably as the temperature increases, which can be attributed to either the Arrhenius or Vogel-Fulcher-Tammann model (Fig. 3). This occurs because an increase in temperature results in a surge in the average velocity of the SUPRADES components in the liquid phase, which diminishes intermolecular forces, lowering the fluid resistance to flow and altering viscosity [45].

Furthermore, it is crucial to determine whether the new extraction solvents are Newtonian or non-Newtonian. Newtonian fluids maintain a constant viscosity regardless of the shear rate, making their behavior predictable and straightforward to model [70]. This characteristic can be beneficial in processes where consistent fluid behavior is essential, such as in specific liquid–liquid extraction procedures that require precise control over mixing and separation. Although few studies have explored this parameter, all the experiments conducted to date have displayed Newtonian properties [10, 29, 90].

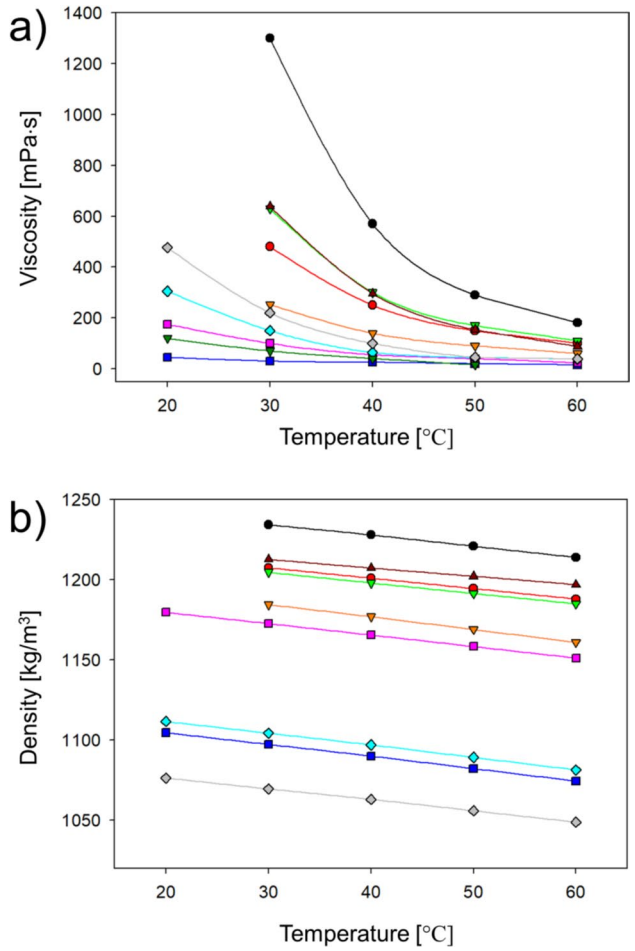

Fig. 3 **a** Viscosity and **b** density of supramolecular deep eutectic solvents at various temperatures [16, 26, 29, 41]. The viscosity of SUPRADES decreases considerably as the temperature increases, which can be attributed to either the Arrhenius or Vogel-Fulcher-Tammann model. A decrease in temperature results in a reduction of the kinetic energy of SUPRADES molecules, which leads to an increase in density. (—●—) Sulfobutylether-*β*-cyclodextrin:levulinic acid (1:44); (—●—) Low methylated-*β*-cyclodextrin:levulinic acid (1:25); (—▼—) Hydroxypropyl-*β*-cyclodextrin:levulinic acid (1:32); (—▼—) Randomly methylated-*β*-cyclodextrin:levulinic acid (1:27); (—■—) Randomly methylated-*β*-cyclodextrin:benzyl alcohol (1:40); (—■—) Randomly methylated-*β*-cyclodextrin:ethylene glycol (1:40); (—◆—) Randomly methylated-*β*-cyclodextrin:1,2-propanediol (1:40); (—◇—) Randomly methylated-*β*-cyclodextrin:1,3-butanediol (1:40); (—▲—) Choline chloride:urea (1:2) + 10% *β*-cyclodextrin; (—▼—) *β*-cyclodextrin:citric acid (1:8)

Hydrophobicity and hydrophilicity

When selecting an extraction solvent, it is essential to consider its compatibility with the sample matrix. An ideal solvent should have minimal solubility in the matrix or not dissolve in it at all. Extraction solvents can be classified into two categories: hydrophobic and hydrophilic solvents. Hydrophobic substances do not attract water and typically reject water. Solvents that absorb more than 0.2% of their weight in water are generally categorized as hydrophilic [94]. Most SUPRADES are hydrophilic solvents because of the strong hygroscopic nature of the cyclodextrins. The water solubilities of individual cyclodextrins at 25 °C were 145, 18.5, 232, > 600, > 500, > 500, and > 500 mg/mL for *α*-CD, *β*-CD, *γ*-CD, HP-*β*-CD, SBE-β-CD, RAMEB, and HP-*γ*-CD, respectively [11]. Despite the hydrophobic cavity of cyclodextrins, non-covalent bonds are more easily formed with other hydrophilic substances because of the hydrophilic properties of the outer layer of the cyclodextrins. In most cases, to obtain a liquid at room temperature, the prerequisite is using hydrophilic hydrogen bond donors or hydrogen bond acceptor:hydrogen bond donor. The combination of two or three hydrophilic substances allows SUPRADES to be dissolved in water in any proportion and can easily absorb water from the air, causing significant changes in the physicochemical properties of SUPRADES. However, a major disadvantage is that SUPRADES cannot be used to extract substances from water or wastewater.

The current scientific literature has only reported a single paper that has investigated hydrophobic SUPRADES composed of thymol:heptanoic acid (1:1) and its derivatives, including 2,6- DM-*β*-CD, HP-*β*-CD, and RAMEB. The hydrophobic properties of SUPRADES were assessed based on the wetting angle. The initial water contact angle of RAMEB-thymol:heptanoic acid (1:1) was 31.25°; however, upon interaction with the alkaline proton donor, the contact angle of RAMEB- thymol:heptanoic acid (1:1) increased to 110.05°, indicating the strong hydrophobicity of the prepared SUPRADES. Additionally, the results of the aforementioned study demonstrated that the hydrophobicity/hydrophilicity of SUPRADES could be adjusted by altering the pH [97].

Price of supramolecular deep eutectic solvents

The cost of organic solvents is a critical factor for industrial applications. However, the commercial availability of SUPRADES has not yet been established, necessitating estimating their cost by considering the expenses associated with individual cyclodextrins, hydrogen bond acceptors, and hydrogen bond donors on a laboratory scale. Consequently, the price of SUPRADES tends to be relatively high. The prices were estimated following the methods employed in previous studies [60], in which SUPRADES prices were calculated by averaging the market prices (per kilogram) of commonly sold chemicals. The cost of SUPRADES was then determined based on the stoichiometry of the individual components. The prices for high-purity (98% or greater) SUPRADES components were estimated. The price varies from €15.66 to €3869.17 per kilogram, primarily influenced by the type and amount of cyclodextrins present. As the concentration of the cyclodextrins increased, the overall cost of the solvent increased significantly. Consequently, SUPRADES that utilize

cyclodextrins as additives are less expensive. Moreover, the cost heavily depends on the type of cyclodextrin used in preparing the new solvent. SUPRADES derived from modified cyclodextrins are generally more costly because of their higher unit price, attributed to the intricate synthesis process involved. Although bulk purchases are typically associated with lower costs, it is widely accepted that the expense of industrial-grade solvents is only 10% of that of laboratory-grade extractants [32]. Nevertheless, reducing the purity of SUPRADES components may result in decreased costs. However, this approach could hurt the physicochemical properties of SUPRADES and the extraction procedure. Further studies are required to investigate this hypothesis.

Applications of supramolecular deep eutectic solvents in extraction processes

Fuel desulfurization

Supramolecular deep eutectic solvents are adequate for the desulfurization of fuels, particularly in removing difficult-to-extract organosulfur compounds such as thiophene, benzothiophene, dibenzothiophene, and 4,6-dimethyl dibenzothiophene. Numerous studies have demonstrated the high removal efficiency of thiophenes using conventional deep eutectic solvents [3, 14, 40, 62, 83] and aqueous solutions of cyclodextrins [25, 59]. However, the use of SUPRADES for oxidative desulfurization and extractive desulfurization of fuels was first reported in 2022 [39]. The authors tested eight different binary SUPRADES systems using neat and methylated-β-cyclodextrin as hydrogen bond acceptors and carboxylic acids, such as formic acid, acetic acid, and propionic acid, as hydrogen bond donors. The efficiency of eliminating sulfur compounds with SUPRADES based on oxidative desulfurization was higher than that with extractive desulfurization. Under the optimal experimental conditions, the desulfurization rate of SUPRADES prepared using methylated-β-cyclodextrin and formic acid reached 99.6%. The conventional extraction process demonstrated an extraction efficiency of less than 10%. This suggests that the desulfurization performance of dibenzothiophene is insufficient in the absence of oxidants, such as H_2O_2. This is primarily due to deep eutectic solvents's high catalytic oxidation capacity, and to polar sulfones that are more soluble in methylated-β-cyclodextrin:formic acid (1:3), indicating that the oxidant plays a crucial role in desulfurization. Density functional theory (DFT) calculations revealed that the reaction barrier for hydrogen peroxide to oxidize acid groups to peroxy-acid decreased by 81% in SUPRADES, demonstrating the exceptional catalytic performance of cyclodextrins. Furthermore, the density functional theory results suggest that the structure of dibenzothiophene is disrupted during its interaction with SUPRADES [39].

Another study presented a novel strategy involving the utilization of β-CD as the hydrogen bond acceptor and citric acid as the hydrogen bond donor. Additionally, carbon quantum dots were incorporated into the oxidative desulfurization. This study demonstrates that adding a carbon quantum dots solution enhances the catalytic performance of β-CD: citric acid/carbon quantum dots and improves their H-bonding stability, making them more convenient to store. By adjusting the content of the carbon quantum dots solution, the viscosity of β-CD:citric acid/carbon quantum dots can be easily modified without altering the eutectic nature of the SUPRADES. The sulfur removal efficiency of β-CD:citric acid/carbon quantum dots was 99.32% at 50 °C. The researchers confirmed that the powerful interaction between the β-CD:citric acid/carbon quantum dots and dibenzothiophene diminished the aromaticity of dibenzothiophene and made it prone to oxidation. In addition, the carboxylic acids in β-CD:citric acid/carbon quantum dots can be oxidized by H_2O_2 to form peracids, which can be simultaneously utilized as oxidants for sulfur compounds [16]. A summary of the application of SUPRADES in fuel desulfurization is summarized in Table 3.

Extraction of biologically active compounds

Georgantzi et al. prepared a novel SUPRADES consisting of L-lactic acid:nicotinamide (7:1) and 1.5% (w/v) β-CD. This SUPRADES was further tested as an extraction solvent in ultrasound-assisted extraction to extract polyphenols from Greek medicinal plants (Thyme, Oregano, Greek sage, and sage). The performance of SUPRADES in extracting polyphenols was significantly higher than that achieved with 60% (v/v) aqueous ethanol/water and conventional deep eutectic solvents. This study revealed that polyphenols may exhibit properties of hydrogen bon donors and interact with the hydrogen bond acceptor of SUPRADES, potentially leading to some form of antagonism. This may result from β-cyclodextrin-weakening polyphenol-hydrogen bond acceptor interactions due to the strong hydrogen bond formation associated with β-CD/polyphenol inclusion complex formation. However, β-cyclodextrin also increases the solubility of less polar polyphenols by entrapping them, thereby influencing the overall outcome [36]. Similar results were obtained for the extraction of polyphenols from Fenugreek Seeds (*Trigonella foenum-graecum*) using choline chloride:glycerol with β-CD and from *Olea europaea* leaf using lactic acid:ammonium acetate (7:1) with β-CD as the extraction solvents. The results of the aforementioned studies revealed that the incorporation of β-CD led to a marked enhancement in the efficiency of polyphenol extraction [13, 34]. Polyphenols were also successfully extracted

from *Olea europaea* leaves using SUPRADES based on glycerol:glycine:water (7:1:3) and methyl-β-cyclodextrin. The results revealed that the extraction efficiency of polyphenols using SUPRADES was considerably more significant than that achieved using aqueous ethanol. Furthermore, SUPRADES extract exhibited enhanced antioxidant properties, which could not be solely attributed to the higher concentration of polyphenols. The authors suggested that the interactions of polyphenols with cyclodextrin may have played a significant role [8].

According to Jovanović et al., nine different SUPRADES were examined as extractants for anthocyanins (cyanidin-3-O-glucoside, cyanidin-3-O-galactoside, cyanidin-3-O-arabinoside, and total anthocyanins) from chokeberry fruits using ultrasound-assisted extraction. They discovered that a deep eutectic solvent composed of choline chloride and malic acid was the most effective for extracting chokeberry anthocyanins. The study revealed that the extraction efficiency was significantly enhanced by using HP-β-CD at concentrations up to 3% (w/w), whereas increasing the concentration to 6% (w/w) diminished this effect. The enhanced anthocyanin extraction was ascribed to the formation of inclusion complexes, which increased their stability and solubility. However, the increased concentration of HP-β-CD resulted in a decrease in the extraction efficiency owing to the increase in viscosity caused by adding this sugar compounds. Density functional theory analysis indicated that cyanidin molecules interacted with choline chloride and malic acid through conventional and carbon-hydrogen bonds and cation-π interactions. Moreover, chloride anions and water molecules interact with ligands and solvent molecules, acting as bridges between them [53].

Zhang et al. described an application of switchable SUPRADES (*N,N*-dimethylbenzylamine:acetic acid + 5.5% wt percent β-CD) to extract flavonoids (baicalin, wogonoside, and baicalin) from *Scutellariae Radix*. Flavonoids were investigated using high-performance liquid chromatography equipped with UV detector (HPLC–UV), and the results demonstrated that SUPRADES exhibited a superior extraction yield of total flavonoids, amounting to 157.95 mg/g, compared to pure deep eutectic solvents, which yielded 135 mg/g, and traditional organic solvents, such as 60% ethanol, which produced 104.87 mg/g. As in previous research, the incorporation of β-CD led to the capture of flavonoids through host/guest interactions, significantly improving the extraction yield. In addition, homogeneous extraction and rapid two-phase separation were achieved thanks to the distinct polarity-switching properties of SUPRADES [100].

In another investigation, researchers studied the extraction of secoiridoids, including gentiopicroside, loganic acid, swertiamaroside, and sweroside, from the roots and rhizomes of *Gentiana Rigescens*. They used β-CD as the booster and a glycine:glycerol solvent mixture in a 1:3 ratio, along with ultrasound-assisted extraction. The results of this study indicate that in an aqueous deep eutectic solvents, β-CD interacts with secoiridoids via non-covalent and hydrogen bonds, and that the four secoiridoids compounds fit well into the hydrophobic cavity of β-CD. The number of hydrogen bonds between the secoiridoids and β-CD was substantial. The extraction process yielded 39.82 mg/g of gentiopicroside, 6.61 mg/g of loganic acid, 0.79 mg/g of swertiamaroside, and 0.57 mg/g of sweroside. Overall, the proposed method demonstrated that aqueous SUPRADES extraction was more effective than conventional solvents for secoiridoid compounds from *G. rigescens* [93].

Sample preparation and microextraction

Sample preparation is an essential aspect of green analytical chemistry, as it helps minimize the utilization of organic solvents or replace them with environmentally harmful alternatives. The use of SUPRADES as extraction solvents in combination with liquid–liquid microextraction and solid–liquid microextraction techniques single-drop microextraction, dispersive liquid–liquid microextraction, homogeneous liquid–liquid microextraction, and solid-phase microextraction has gained significant attraction in analytical sample preparation [54].

In 2021, a first study was published that focused on testing of SUPRADES as extractants for the microextraction of 18 aromatic organic pollutants, including UV filters, polycyclic aromatic hydrocarbons, alkylphenols, plasticizers, and food ingredients from aqueous samples, [30]. In this study, headspace single-drop microextraction technique was used. The authors compared the pollutant extraction efficiencies achieved for SUPRADES and conventional deep eutectic solvents. Although the enrichment factors for individual analytes were higher for the tetrabutylammonium chloride:lactic acid (1:2) deep eutectic solvent compared to the tested β-CD:lactic acid (1:4) SUPRADES, the enrichment factor values obtained for choline chloride:urea + 20 wt% β-CD were significantly higher than those of the conventional choline chloride:urea (1:2) deep eutectic solvents. The results show that the presence of cyclodextrins effectively influenced the extraction efficiency of the analytes. The calibration curves for the analytes using SUPRADES showed excellent linearity ($R^2 > 0.983$) and low limit of detection values for all analytes (< 14.6 µg/L). To attain the most favorable outcomes, the process required a solvent microdroplet of 6.5 µl, a stirring rate of 1000 revolutions per minute, a salt concentration of 30% (w/v), and a temperature of 40 °C [30].

A novel method for concentrating parathion methylene in water, juice, tea, and vinegar was explored using dispersive liquid–liquid microextraction. This study used hexanoic acid:menthol (1:1) as the extractant and an aqueous solution

Table 3 Application of supramolecular deep eutectic solvent (SUPRADES) in extraction processes for various type of analytes

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
Fuel desulfurization	Dibenzothiophene Benzothiophene 4,6-Dimethyl dibenzothiophene	methyl-β-CD:formic acid (1:3)	Model oil based on n-octane	Liquid–liquid extraction: 4 h; 30 °C $m_{SUPRADES}$ = 0.87 g C_{IN} = 500 µg/mL	Gas chromatography-mass spectrometry	0.057 mg/g 0.041 mg/g 0.052 mg/g	– – –	[39]
	Dibenzothiophene Benzothiophene 4,6-Dimethyl dibenzothiophene	β-CD:citric acid/carbon quantum dots	Model oil based on n-octane	Liquid–liquid extraction: 3 h; 30 °C $V_{SUPRADES}$:V_{oil} = 1:3 C_{IN} = 500 ppm Regeneration method: Water-washing Cycle: 3	Electron spin resonance signal	– – –	98.50% 89.23% 93.01%	[16]
Biologically active compounds	Polyphenols	56.45% (w/v) of L-lactic acid:ammonium acetate (7:1) + β-CD	Olive leaves	Liquid–solid extraction: 150 min, 80 °C Stir rate = 300 rpm $R_{L/S}$ = 100 mL/g C_{CD} = 0.7%	Liquid chromatography-diode array-mass spectrometry; Folin-Ciocalteu reagent	113.66 mg/g	–	[13]
		80% (w/v) of glycine: gallic acid: water (7:1:3) + methyl-β-CD	Olea europaea leaves	Liquid–solid extraction: 180 min, 51 °C $R_{L/S}$ = 40 mL/g C_{CD} = 9%	Liquid chromatography-diode array-mass spectrometry; Folin-Ciocalteu reagent	116.65 mg/g	–	[8]
		HP-β-CD:glycerol	Moringa oleifera leaves	Liquid–solid extraction: 180 min, 40 °C Stir rate = 600 rpm $R_{L/S}$ = 40 mL/g C_{CD} = 1%	Liquid chromatography-diode array-mass spectrometry; Folin-Ciocalteu reagent	67.18 mg/g	–	[55]
		β-CD:lactic acid (1:1)	Bayberry	Ultrasonic-assisted extraction 35 min, C_{DES} = 50% $P_{ultrasonic}$ = 948 W	Liquid chromatography-diode array-mass spectrometry; Folin-Ciocalteu reagent	28.85 mg/g	–	[78]

Table 3 (continued)

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
Biologically active compounds: Anthocyanins	Total anthocyanins	20% H_2O (w/w) in choline chloride: malic acid (1:1) + HP-β-CD	Chokeberry	Ultrasonic-assisted extraction: 90 min, 80 °C C_{CD} = 3% $P_{ultrasonic}$ = 320 W	Spectrophotometrically procedure	7.27 cyanidin-3-O-glucoside equivalents mg/g	–	[53]
	Cyanidin-3-O-glucoside	40% H_2O (w/w) in choline chloride:malic acid (1:1) + HP-β-CD		Ultrasonic-assisted extraction: 60 min, 80 °C C_{CD} = 3% $P_{ultrasonic}$ = 320 W	Liquid chromatography-diode array detection	0.49 mg/g	–	
	Cyanidin-3-O-galactoside	40% H_2O (w/w) in choline chloride:malic acid (1:1) + HP-β-CD		Ultrasonic-assisted extraction: 30 min, 50 °C C_{CD} = 3% $P_{ultrasonic}$ = 320 W		3.19 mg/g	–	
	Cyanidin-3-O-arabinoside	40% H_2O (w/w) in choline chloride:malic acid (1:1) + HP-β-CD		Ultrasonic-assisted extraction: 30 min, 50 °C C_{CD} = 3% $P_{ultrasonic}$ = 320 W		1.50 mg/g	–	
Biologically active compounds: flavonoids	Total flavonoids Baicalin Wogonoside Baicalin	7,12-Dimethylbenz[a] anthracene:octanoic acid + β-CD	*Scutellariae Radix*	Ultrasonic-assisted extraction: 30 min, 50 °C C_{CD} = 3% $P_{ultrasonic}$ = 320 W	Liquid chromatography-diode array detection	157.95 mg/g	–	[100]
Polycyclic aromatic hydrocarbons (PAHs)	Acetophenone	β-CD:lactic acid (1:4)	30% aq (w/v) NaCl C_{PAHs} = 500 µg/L	Headspace single-drop microextraction: 90 min, 40 °C $v_{SUPRADES}$ = 6.5 µL V_{sample} = 10 mL; Stir rate: 1000 rpm	High-performance liquid chromatography-ultraviolet (220 and 254 nm)	–	369.7	[30]
	2-Chloroaniline		30% aq (w/v) NaCl C_{PAHs} = 1200 µg/L			–	961.1	
	Benzophenone		30% aq (w/v) NaCl C_{PAHs} = 600 µg/L			–	338.2	
	2-Nitronaphthalene		30% aq (w/v) NaCl C_{PAHs} = 500 µg/L			–	283.1	
	Biphenyl		30% aq (w/v) NaCl C_{PAHs} = 40 µg/L			–	193.9	

Table 3 (continued)

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
	2-Ethylhexyl salicylate		30% aq (w/v) NaCl C_{PAHs} = 1200 µg/L			–	74.1	
	1-Chloro-4-nitrobenzene		30% aq (w/v) NaCl C_{PAHs} = 600 µg/L			–	435.2	
	2-Bromo-4-fluorobenzaldehyde		30% aq (w/v) NaCl C_{PAHs} = 500 µg/L			–	365.5	
	Naphthalene		30% aq (w/v) NaCl C_{PAHs} = 100 µg/L			–	523.2	
	Fluorene		30% aq (w/v) NaCl C_{PAHs} = 100 µg/L			–	274.1	
	Phenanthrene		30% aq (w/v) NaCl C_{PAHs} = 100 µg/L			–	221.5	
	Anthracene		30% aq (w/v) NaCl C_{PAHs} = 100 µg/L			–	148.4	
	Pyrene		30% aq (w/v) NaCl C_{PAHs} = 1000 µg/L			–	34.7	
	Ethyl benzoate		30% aq (w/v) NaCl C_{PAHs} = 250 µg/L			–	366.2	
	Dipentyl phthalate		30% aq (w/v) NaCl C_{PAHs} = 3000 µg/L			–	2.1	
Alkylphenols	4-Octylphenol	β-CD:lactic acid (1:4)	30% aq (w/v) NaCl C_{PAHs} = 1200 µg/L			–	42.9	
	2-Nitrophenol		30% aq (w/v) NaCl C_{PAHs} = 600 µg/L			–	171.5	
	3-*tert*-Butylphenol		30% aq (w/v) NaCl C_{PAHs} = 2000 µg/L			–	715.0	
Organophosphate compounds	Parathion-methyl	Hexanoic acid:menthol (1:1) + HP-β-CD	Water Juice Tea Vinegar	Dispersive liquid–liquid microextraction: 5 min V_{sample} = 5 mL V_{DES} = 175 µL V_{CD} = 500 µL	Isotropic illumination RGB	96.3% 105.7% 94.5% 97.2%	– – – –	[43]

Table 3 (continued)

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
Antibiotic: tetracyclines	Oxytetracycline	Thymol:octanoic acid (1:1) + β-CD	Well water (Noshahr—north of Iran)	Dispersive liquid–liquid microextraction: 5 min V_{sample} = 10 mL V_{DES} = 175 µL m_{CD} = 5 mg pH = 5 Concentration = 300 µg/L	High-performance liquid chromatography with diode array detection	114%	–	[77]
	Doxycycline					84%	–	
	Tetracycline					98%	–	
	Oxytetracycline		Well water (Natanz—middle of Iran)			96%	–	
	Doxycycline					74%	–	
	Tetracycline					84%	–	
	Oxytetracycline		Rainforest water (Noshahr)			104%	–	
	Doxycycline					86%	–	
	Tetracycline					102%	–	
	Oxytetracycline		Coastal sea Water (Caspian Sea - North of Iran)			111%	–	
	Doxycycline					91%	–	
	Tetracycline					105%	–	
	Oxytetracycline		Gardening water (University of Tehran's campus -Tehran, Iran)			101%	–	
	Doxycycline					87%	–	
	Tetracycline					89%	–	
	Oxytetracycline		Mineral water (supermarket in Tehran, Iran)			92%	–	
	Doxycycline					88%	–	
	Tetracycline					82%	–	
Antibiotic: sulfonamide	Sulfapyridine	Thymol:fatty acids + (5%) RAMEB	Livestock farming wastewater	Homogeneous liquid–liquid microextraction: 90 s, 30 °C V_{sample} = 10 mL $V_{SUPRADES}$ = 100 µL $V_{NAOH\ 5\ mol/L}$ = 650 µL $V_{citric\ acid\ 5\%\ aq}$ = 750 µL Stir rate: 7000 rpm/ 5 min	Ultra-performance liquid chromatography-tandem mass spectrometry	86.7%	–	[97]
	Sulfamerazine					96.9%	–	
	Sulfamoxole					99.8%	–	
	Sulfameter					99.8%	–	
	Sulfamethizole					86.5%	–	
	Sulfamethazine					92.3%	–	
	Sulfamethoxypyridazine					105.8%	–	

Table 3 (continued)

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
	Sulfachloropyridazine					96.8%	–	
	Sulfamethoxazole					94.8%	–	
	Sulfamonomethoxine					111.5%	–	
	Sulfadoxine					99.7%	–	
	Sulfisoxazole					97.0%	–	
	Sulfabenzamide					104.3%	–	
	Sulfaclozine					91.0%	–	
	Sulfadimethoxypyrimidine					112.4%	–	
Antibiotic: quinolone	Marbofloxacin					93.9%	–	
	Fleroxacin					91.6%	–	
	Ofloxacin					98.8%	–	
	Pefloxacin					91.4%	–	
	Enoxacin					101.4%	–	
	Norfloxacin					86.3%	–	
	Ciprofloxacin					82.9%	–	
	Danofloxacin					95.5%	–	
	Lomefloxacin					97.2%	–	
	Orbifloxacin					97.1%	–	
	Difloxacin					91.1%	–	
	Sarafloxacin					84.1%	–	
	Sparfloxacin					97.5%	–	
Trace metals	Cu (II)	HP-β-CD:lactic acid (1:4)	Edible oil	Vortex-assisted dispersive liquid–liquid microextraction: 20 min, 75 °C V_{sample} = 10 mL $V_{SUPRADER}$ = 800 µL $V_{DISPERSANT}$ = 80 µL Stir rate: 8000 rpm/ 5 min	Inductively coupled plasma-optical emission spectrometry	99.6%	–	[81]
	Zn (II)					105.2%	–	
	Mn (II)					101.5%	–	

Table 3 (continued)

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
Drugs	Ofloxacin	Decanoic acid:dodecanoic acid (2:1) + CM-β-CD	Water	Single-step liquid–liquid extraction: 12 h/ 50 rpm, 25 °C pH = 3.5 $C_{Ofloxacin}$ = 2 mg/mL a molar excess of chiral selector = 77 ratio $_{DES\text{-}water}$ = 1:2 (v/v) Stir rate: 10 000 rpm/ 10 min	^{19}F NMR spectroscopic method	3.8	–	[66]
Proteins	Trypsin	Trifluoroacetamide and benzyltrimethylammonium chloride-modified β-CD-grafted magnetic beads ($MB\text{-}NH_2$@CD@DES)	Model proteins solution Bovine pancreas crude	Solid-phase extraction: 1 h, 200 rpm, 30 °C pH = 6.0 V_{sample} = 1.0 mL m $_{MB\text{-}NH2@CD@DES}$ = 5.0 mg regeneration cycle: 10	UV–Vis spectrophotometer 280 nm	540.56 mg/g		[92]
	Bovine hemoglobin					549.87 mg/g	–	
	Lysozyme					27.84 mg/g	–	
	Chymotrypsin					14.29 mg/g	–	
	Bovine serum albumin					740.47 mg/g	–	
						447.45 mg/g	–	
Lipids	Total lipid	Ethylene glycol:citric acid (5:1) + β-CD	Wheat straw	Hydrolysis: Time: 12 h Temperature: 50 °C Shaker: 150 rpm Fermentation: Time: 72 h Temperature: 28 °C Shaker: 180 rpm pH = 6.0 batch medium: yeast extract 1.0 g/L, $MgSO_4 \cdot 7H_2O$ 0.5 g/L, KH_2PO_4 1.0 g/L, $(NH_4)_2SO_4$ 2.2 g/L, culture medium: 10% (v/v) inoculum Trichosporon cutaneum	National renewable energy laboratory procedure	8.8 g/100 g	–	[84]

Table 3 (continued)

Type of analytes	Analytes	SUPRADES	Matrix	Pretreatment conditions	Analytical instrumentation	Extraction capacity [mg/g]/ Recovery [%]/Selectivity (α) [-]	EF [-]/Removal [%]	References
Bioactive polyphenolic	Total polyphenols	Lactic acid:ammonium acetate (7:1) + β-CD	Olive leaves	Solid-phase extraction: 150 min, 80 °C V_{sample} = 10 mL $R_{L/S}$ = 100 mL/g Stir rate: 300 rpm	Liquid chromatography-diode array-mass spectrometry	–	2.35	[47]
Polyphenols	Total polyphenols	Octanoic acid:linalool (1:1) + β-CD	Millet powder	Grinding-assisted extraction: 80 s, 50 °C $R_{L/S}$ = 10:1 mL/g m_{sample} = 0.1 g $V_{SUPRADES}$ = 1 mL DES + 16 mg β-CD	UV–Vis spectrophotometer 760 nm	5.85 mg/g	–	[96]

The table describes the target analyte, the matrix, pretreatment condition, analytical instrumentation used in the study as well as the extraction capacity [mg/g], recovery [%], or selectivity (α) [-] obtained in the studies

^{19}*F NMR* fluorine-19 nuclear magnetic resonance spectroscopy, *CD* cyclodextrin, C_{IN} initial concentration of analytes/extracted substances, *CM-β-CD* carboxymethyl-*β*-cyclodextrin, *DES* deep eutectic solvent, *m*: mass, *EF* enrichment factor, *HP-β-CD* hydroxypropyl-*β*-cyclodextrin, *MB-NH_2@CD@DES* trifluoroacetamide and benzyltrimethylammonium chloride-modified *β*-cyclodextrin-grafted magnetic beads, *Methyl-β-CD* methyl-*β*-cyclodextrin, *PAHs* polycyclic aromatic hydrocarbons, *RAMEB* randomly methylated-*β*-CD, *RGB* red–green–blue, $R_{L/S}$ liquid–solid ratio, *UV–Vis* ultraviolet–visible spectroscopy

of cyclodextrin as the dispersant. Cyclodextrin increased the contact area between the promoter and analyte, resulting in improved recovery rates ranging from 80.4% to 105.7%. After hydrolysis under alkaline conditions, the extracted sample was analyzed using a smartphone digital chromatogram, transforming it into a yellow substance [43]. In another study, hydrophobic SUPRADES were developed and utilized as disperser/extraction solvent mixtures in dispersive liquid–liquid microextraction of tetracyclines from water samples. The extraction efficiency of thymol:octanoic acid in 1:1 molar ratio was compared with that of SUPRADES thymol:octanoic acid (1:1)-β-CD, and it was found that the extraction efficiency was enhanced by a factor of two. A limit of detection (LOD) lower than 4.38 µg/L was obtained. In this study, the addition of β-CD to the extraction phase led to enhanced extraction efficiencies through the selective supramolecular host/guest inclusion of tetracyclines. Cyclodextrin improved the dispersibility of the extraction solvent and contributed to the formation of a highly stable, cloudy solution. This contributed to the high efficiency of dispersive liquid–liquid microextraction extraction [77].

Wu et al. investigated the application of SUPRADES as an extraction solvent for the enrichment of six sulfonamides in environmental waters using vortex-assisted dispersive liquid–liquid microextraction. Sulfonylamines were determined using high-performance liquid chromatography equipped with photodiode array detector (HPLC–PDA). This research project entailed the development of a hydrophobic deep eutectic solvents by combining two precursors (benzyltriethylammonium chloride and thymol) and incorporating HP-β-CD, which resulted in a substantial improvement in the enrichment factor for sulfonylamines, reaching 21.6%. The newly developed method exhibited a wide linear range of 1.1–500 µg/L and a low detection limit of 0.3–1.1 µg/L [91]. The same extraction technique was employed to separate and concentrate trace metals (Cu, Zn, and Mn) from the edible oil samples. This study is the first to apply SUPRADES to trace metal extraction. Inductively coupled plasma-optical emission spectrometry was used to measure metal concentrations. HP-β-CD:lactic acid (1:4) was used as an extraction solvent. The authors demonstrated that by increasing the solubility of metal ions through host–guest interactions and mixing with an aqueous solution, water molecules are released within the cavities, creating a driving force for the target to enter the cavities. At the microscopic level, hydrophilic interactions mediated by hydrogen bonds and hydrophobic mitigation of complex interactions between cyclodextrin and the solute components lead to energy-favorable cyclodextrin solvation. The optimal conditions yielded 99.6%, 105.2%, and 101.5% extraction rates for Cu, Zn, and Mn, respectively [81].

Recently, Zhang et al. reported using hydrophobic switchable deep eutectic solvents based on cyclodextrin to extract antibiotics from livestock farming wastewater at trace levels. These solvents undergo a pH-responsive reversible phase transition in an aqueous phase and can extract 13 quinolones and 15 sulfonamides. Homogeneous liquid–liquid microextraction was used as the microextraction technique, and liquid chromatography-triple quadrupole tandem mass spectrometry was used for final determination. They constructed non-covalent interaction-dominated pH-responsive ternary SUPRADES by doping DM-β-CD, RAMEB, and HP-β-CD with thymol:fatty acids switchable deep eutectic solvents. The method had a low limit of detection in the range of 0.0021–0.0334 ng/mL limits of quantification of 0.0073–0.1114 ng/mL and an overall enrichment factor of 157–201 [97].

Lignocellulose valorization

Lignocellulose is the primary component of plant biomass and is a valuable raw material for producing various bioproducts. Converting lignocellulose into useful products, known as lignocellulose valorization, is increasingly essential for sustainable development and environmental protection. This process allows for the efficient utilization of agricultural and forestry waste. Lignocellulose valorization enables the production of biofuels, such as bioethanol and biogas, which can serve as alternatives to traditional fossil fuels [4]. Additionally, lignocellulose can be transformed into biochemicals, like lactic acid or furfural, used in the chemical and pharmaceutical industries [51]. Products derived from lignocellulose valorization, such as biocomposites and nanocellulose, are utilized in construction, automotive, and packaging production, providing ecological alternatives to traditional materials [24, 48, 49, 89]. Lignocellulose can be processed using different methods, such as chemical, thermal, biological, or mechanical extraction [87].

Tan et al. carried out the delignification process of wheat straw using SUPRADES, which was created by combining 3.5% β-CD with ethylene glycol:citric acid (5:1) deep eutectic solvent [84]. The study showed that the proposed ethylene glycol:citric acid + β-CD significantly increased the delignification rate, cellulose saccharification, and hemicellulose removal by 90.45%, 97.3%, and 87.24%, respectively. High efficiency of lignocellulose pretreatment was achieved due to the unique intrinsic hydrophobicity of β-CD, which enabled high extraction capacity/adsorption of degraded lignin/lignin monomers. It was also observed that ethylene glycol prevented condensation and excessive lignin degradation. As a result of the synergistic action of β-CD, citric acid and ethylene glycol resulted in high efficiency of lignin fractionation and in situ protection. The proposed method of wheat straw treatment with ethylene glycol:citric acid + β-CD enabled the practical growing of *Trichosporon*

cutaneum, which produced 8.8 g of total lipids per 100 g of wheat straw.

In another study, a deep eutectic solvent based on lactic acid combined with ammonium acetate in a molar ratio of 7:1 in addition to 0.7% (w/v) β-CD was used to extract polyphenols from olive leaves (*Olea europaea L.*) [47]. Due to their ability to form inclusion complexes, cyclodextrins were used as metabolite stabilizers. In this study, the extraction efficiency was assessed based on the content of polyphenols in the extracts. The highest extraction efficiency of 2.35 was obtained using new green extractants containing cyclodextrins in their structure, which indicates the effectiveness of the proposed new solutions. Zhang et al., proposed the extraction of polyphenols from millet using SUPRADES [96]. In the extraction process, deep eutectic solvent based on octanoic acid combined with linalool and β-CD was used. The highest yield was obtained under optimal conditions, including deep eutectic solvent in a molar ratio 1:1, solid–liquid ratio of 1:10 g/mL, extraction time of 80 s, and β-CD content at 16 mg/mL. The antioxidant efficiency of the extract was always higher by 10–20% compared to the traditional ethanol extract. Additionally, SUPRADES showed up to 5 regeneration cycles a constant polyphenols extraction efficiency of 5.85 mg/g.

These works have shown that SUPRADES are a promising medium for valorizing lignocellulose. This is because SUPRADES can form inclusion complexes with various chemical compounds. Additionally, SUPRADES enable the stability of extracted compounds, protecting them from degradation and oxidation, which is crucial in sustainable biomass processing.

Other applications

Cyclodextrins, particularly β-CD derivatives, are widely used in the pharmaceutical industry due to their availability and non-toxic nature. In a study by Moradi et al., various β-CD derivatives, such as HP-β-CD, CM-β-CD and S-β-CD, were investigated for their potential as chiral selectors [66]. The study aimed to find the most effective chiral selector for separating ofloxacin enantiomers using liquid–liquid extraction based on hydrophobic deep eutectic liquid systems. The highest efficiency in separating R/S-ofloxacin enantiomers was achieved using a deep eutectic solvent based on decanoic and dodecanoic acids in a 2:1 molar ratio coupled with CM-β-CD as the chiral selector. They found that the selectivity of the R/S-ofloxacin separation was most influenced by three variables: pH, an excess of the chiral selector, and the ratio of deep eutectic solvent to water (v/v). Under optimal conditions, which included a 77-fold excess of the chiral selector, a pH of 3.5, and a deep eutectic solvents-water ratio of 1:2 (v/v), the highest selectivity (α) level of 3.8 ± 0.3 was achieved in a single liquid–liquid extraction step. This study offers numerous practical benefits, particularly in the pharmaceutical field. Since enantiomers can have different pharmacological properties, successful separation of ofloxacin enantiomers is essential to produce drugs with increased efficacy and reduced side effects, thus ensuring drug safety and efficacy.

Other research focused on extracting trypsin from protein solutions. Magnetic beads were utilized for extraction, modified using cyclodextrin combined with deep eutectic solvents based on trifluoroacetamide and benzyl trimethylammonium chloride [92]. Modification of the magnetic beads surface with cyclodextrin-deep eutectic solvent allows combining of the advantages of cyclodextrin and deep eutectic solvents, resulting in a significant increase in the extraction capacity of tryptophan through dipole–dipole interaction, hydrophobic interactions, and π-π. When studying trypsin extraction using magnetic beds-NH_2@CD@DES, the following process parameters were optimized: time, temperature, solution pH, ionic strength, initial trypsin concentration, sample volume, type of buffer, and eluent. Under optimal conditions, solid-phase extraction was carried out for both model samples and actual bovine pancreas crude. Trypsin extraction results were 540.56 mg/g and 549.87 mg/g from the model protein solution and bovine pancreas crude sample, respectively. The new extractant maintained a high capacity for up to 10 cycles, which confirmed that magnetic beds-NH_2@CD@DES is an effective and selective trypsin extraction material.

Conclusion

SUPRADES represent a new class of organic solvents with immense potential for diverse extraction techniques, although their practical use presents certain challenges. These solvents have garnered considerable attention due to their distinctive properties, including their ability to form non-covalent interactions with analytes and their inclusion capabilities. However, understanding their physicochemical properties is limited, with parameters such as viscosity, density, water content, and melting and degradation temperatures not routinely measured. This makes it challenging to accurately compare and predict their properties. Future research is needed to address several critical parameters, including vapor pressure, surface tension, toxicity, and biodegradability, as well as to improve their high viscosity and hydrophilicity, which currently reduce extraction efficiency.

Despite these challenges, SUPRADES demonstrate considerable potential as effective extractants, and it is anticipated that there will be an increase in research efforts to elucidate their full capabilities. Many SUPRADES are formulated using non-toxic, biodegradable, and renewable raw materials, aligning perfectly with sustainability goals.

Ongoing research plays a vital role in enhancing their utility by improving analyte solubility and reducing viscosity. The innovative use of cyclodextrin in preparing SUPRADES shows the potential to increase the value of biomass by-products, positively impacting the circular economy. Future investigations are key to addressing the industrial scalability of SUPRADES and ensuring cost-effective large-scale production and utilization. Obtaining regulatory approval for their use in industrial processes will be a significant milestone, given that most cyclodextrins used in SUPRADES production are already approved for use in the food and pharmaceutical industries, making a favorable outcome likely. The future of SUPRADES is bright, with numerous opportunities for groundbreaking research and innovative applications.

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Declarations

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References

1. Abbott AP, Capper G, Davies DL et al (2003) Novel solvent properties of choline chloride/urea mixtures. Chem Commun 1:70–71. https://doi.org/10.1039/b210714g
2. Abbott AP, Capper G, Gray S (2006) Design of improved deep eutectic solvents using hole theory. ChemPhysChem 7:803–806. https://doi.org/10.1002/cphc.200500489
3. Abro R, Kiran N, Ahmed S et al (2022) Extractive desulfurization of fuel oils using deep eutectic solvents—a comprehensive review. J Environ Chem Eng 10:107369. https://doi.org/10.1016/J.JECE.2022.107369
4. Alvira P, Tomás-Pejó E, Ballesteros M, Negro MJ (2010) Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Bioresour Technol 101:4851–4861. https://doi.org/10.1016/j.biortech.2009.11.093
5. Amesho KTT, Lin Y-C, Mohan SV et al (2023) Deep eutectic solvents in the transformation of biomass into biofuels and fine chemicals: a review. Environ Chem Lett 21:183–230. https://doi.org/10.1007/s10311-022-01521-x
6. Arora D, Saneja A, Jaglan S (2019) Cyclodextrin-based delivery systems for dietary pharmaceuticals. Environ Chem Lett 17:1263–1270. https://doi.org/10.1007/s10311-019-00878-w
7. Aroso IM, Silva JC, Mano F et al (2016) Dissolution enhancement of active pharmaceutical ingredients by therapeutic deep eutectic systems. Eur J Pharm Biopharm 98:57–66. https://doi.org/10.1016/j.ejpb.2015.11.002
8. Athanasiadis V, Grigorakis S, Lalas S, Makris DP (2018) Methyl *β*-cyclodextrin as a booster for the extraction for *Olea europaea* leaf polyphenols with a bio-based deep eutectic solvent. Biomass Convers Biorefinery 8:345–355. https://doi.org/10.1007/s13399-017-0283-5
9. Baker EL (1988) Organic solvent neurotoxicity. Annu Rev Public Health 9:223–232. https://doi.org/10.1146/annurev.pu.09.050188.001255
10. Balenzano G, Racaniello GF, Arduino I et al (2023) Cyclodextrin-based supramolecular deep eutectic solvent (CycloDES): a vehicle for the delivery of poorly soluble drugs. Int J Pharm 647:123553. https://doi.org/10.1016/j.ijpharm.2023.123553
11. Brewster ME, Loftsson T (2007) Cyclodextrins as pharmaceutical solubilizers. Adv Drug Deliv Rev 59:645–666. https://doi.org/10.1016/J.ADDR.2007.05.012
12. Bystrzanowska M, Tobiszewski M (2021) Assessment and design of greener deep eutectic solvents—a multicriteria decision analysis. J Mol Liq 321:1–14. https://doi.org/10.1016/j.molliq.2020.114878
13. Chakroun D, Grigorakis S, Loupassaki S, Makris DP (2021) Enhanced-performance extraction of olive (*Olea europaea*) leaf polyphenols using L-lactic acid/ammonium acetate deep eutectic solvent combined with *β*-cyclodextrin: screening, optimisation, temperature effects and stability. Biomass Convers Biorefinery 11:1125–1136. https://doi.org/10.1007/s13399-019-00521-2
14. Chandran D, Khalid M, Walvekar R et al (2019) Deep eutectic solvents for extraction-desulphurization: a review. J Mol Liq 275:312–322. https://doi.org/10.1016/J.MOLLIQ.2018.11.051
15. Chemat F, Anjum H, Shariff AM et al (2016) Thermal and physical properties of (Choline chloride + urea + l-arginine) deep eutectic solvents. J Mol Liq 218:301–308. https://doi.org/10.1016/J.MOLLIQ.2016.02.062
16. Chen M, Zou C, Tang W, Cao Y (2023) Stable hydrogen bonding interactions in supramolecular deep eutectic solvents based on carbon quantum dots: for extraction and oxidative desulfurization. Sep Purif Technol 323:124491. https://doi.org/10.1016/J.SEPPUR.2023.124491

17. Choi YH, van Spronsen J, Dai Y et al (2011) Are natural deep eutectic solvents the missing link in understanding cellular metabolism and physiology? Plant Physiol 156:1701–1705. https://doi.org/10.1104/pp.111.178426
18. Crini G (2014) Review: a history of cyclodextrins. Chem Rev 114:10940–10975. https://doi.org/10.1021/cr500081p
19. Crini G, Fourmentin S, Fenyvesi É et al (2018) Cyclodextrins, from molecules to applications. Environ Chem Lett 16:1361–1375. https://doi.org/10.1007/s10311-018-0763-2
20. Dai Y, van Spronsen J, Witkamp GJ et al (2013) Natural deep eutectic solvents as new potential media for green technology. Anal Chim Acta 766:61–68. https://doi.org/10.1016/J.ACA.2012.12.019
21. Del Valle EMM (2004) Cyclodextrins and their uses: a review. Process Biochem 39:1033–1046. https://doi.org/10.1016/S0032-9592(03)00258-9
22. Di Pietro ME, Colombo Dugoni G, Ferro M et al (2019) Do cyclodextrins encapsulate volatiles in deep eutectic systems? ACS Sustain Chem Eng 7:17397–17405. https://doi.org/10.1021/acssuschemeng.9b04526
23. Di Pietro ME, Ferro M, Mele A (2020) Drug encapsulation and chiral recognition in deep eutectic solvents/β-cyclodextrin mixtures. J Mol Liq 311:113279. https://doi.org/10.1016/j.molliq.2020.113279
24. Dong H, Zheng L, Yu P et al (2020) Characterization and application of lignin-carbohydrate complexes from lignocellulosic materials as antioxidants for scavenging in vitro and in vivo reactive oxygen species. ACS Sustain Chem Eng 8:256–266. https://doi.org/10.1021/acssuschemeng.9b05290
25. Duan Z, Bian H, Gao Z et al (2019) Green fuel desulfurization with β-cyclodextrin aqueous solution for thiophenic sulfides by molecular inclusion. Energy Fuels 33:9690–9701. https://doi.org/10.1021/acs.energyfuels.9b02349
26. Dugoni GC, Di Pietro ME, Ferro M et al (2019) Effect of water on deep eutectic solvent/β-cyclodextrin systems. ACS Sustain Chem Eng 7:7277–7285. https://doi.org/10.1021/acssuschemeng.9b00315
27. El Achkar T, Greige-Gerges H, Fourmentin S (2021) Basics and properties of deep eutectic solvents: a review. Environ Chem Lett 19:3397–3408. https://doi.org/10.1007/s10311-021-01225-8
28. El Achkar T, Moufawad T, Ruellan S et al (2020) Cyclodextrins: from solute to solvent. Chem Commun 56:3385–3388. https://doi.org/10.1039/d0cc00460j
29. El Achkar T, Moura L, Moufawad T et al (2020) New generation of supramolecular mixtures: characterization and solubilization studies. Int J Pharm 584:119443. https://doi.org/10.1016/J.IJPHARM.2020.119443
30. Farooq MQ, Zeger VR, Anderson JL (2021) Comparing the extraction performance of cyclodextrin-containing supramolecular deep eutectic solvents versus conventional deep eutectic solvents by headspace single drop microextraction. J Chromatogr A 1658:462588. https://doi.org/10.1016/j.chroma.2021.462588
31. Ferreira M, Jérôme F, Bricout H et al (2015) Rhodium catalyzed hydroformylation of 1-decene in low melting mixtures based on various cyclodextrins and N, N′-dimethylurea. Catal Commun 63:62–65. https://doi.org/10.1016/j.catcom.2014.11.001
32. Ferro VR, Ruiz E, De Riva J, Palomar J (2012) Introducing process simulation in ionic liquids design/selection for separation processes based on operational and economic criteria through the example of their regeneration. Sep Purif Technol 97:195–204. https://doi.org/10.1016/J.SEPPUR.2012.02.026
33. Foroutani Z, Afshar Mogaddam MR, Ghasempour Z, Ghareaghajlou N (2024) Application of deep eutectic solvents in the extraction of anthocyanins: stability, bioavailability, and antioxidant property. Trends Food Sci Technol 144:104324. https://doi.org/10.1016/J.TIFS.2023.104324
34. Frangopoulos T (2022) A green, efficient approach on extraction of polyphenols from fenugreek seeds (trigonella foenum-graecum): DES and β-cyclodextrin assisted extraction. Waste and Biomass Valorization 13:4403–4415. https://doi.org/10.1007/s12649-022-01785-y
35. Gatiatulin AK, Grishin IA, Buzyurov AV et al (2022) Determination of melting parameters of cyclodextrins using fast scanning calorimetry. Int J Mol Sci. https://doi.org/10.3390/ijms232113120
36. Georgantzi C, Lioliou AE, Paterakis N, Makris DP (2017) Combination of lactic acid-based deep eutectic solvents (DES) with β-cyclodextrin: Performance screening using ultrasound-assisted extraction of polyphenols from selected native Greek medicinal plants. Agronomy. https://doi.org/10.3390/agronomy7030054
37. González-Rivera J, Pelosi C, Pulidori E et al (2022) Guidelines for a correct evaluation of deep eutectic solvents thermal stability. Curr Res Green Sustain Chem 5:1–5. https://doi.org/10.1016/j.crgsc.2022.100333
38. Gonzalez-Diaz A, García-Núñez JA (2023) Hydrophilic deep eutectic solvents: a new generation of green and safe extraction systems for bioactive compounds obtaining from natural oil & fats—a review. Sustain Chem Pharm 36:101278. https://doi.org/10.1016/J.SCP.2023.101278
39. Guan S, Li Z, Xu B et al (2022) Cyclodextrin-based deep eutectic solvents for efficient extractive and oxidative desulfurization under room temperature. Chem Eng J 441:136022. https://doi.org/10.1016/j.cej.2022.136022
40. Guan S, Li Z, Xu B et al (2023) Deep eutectic solvents with excellent catalytic ability for extractive and oxidative desulfurization under room temperature. ACS Sustain Chem Eng 11:6292–6301. https://doi.org/10.1021/acssuschemeng.2c07647
41. Gui C, Villarim P, Lei Z, Fourmentin S (2024) VOC absorption in supramolecular deep eutectic solvents: experiment and molecular dynamic studies. Chem Eng J 481:148708. https://doi.org/10.1016/j.cej.2024.148708
42. Guo H, Li L, Xu X et al (2022) Semi-solid superprotonic supramolecular polymer electrolytes based on deep eutectic solvents and polyoxometalates. Angew Chemie Int Ed. https://doi.org/10.1002/anie.202210695
43. Guo X, Huang X, Jiang H et al (2023) Determination of parathion-methyl in water, juice, tea, and vinegar using cyclodextrin-based dispersive liquid-liquid microextraction combined with smartphone digital image colorimetry. Int J Environ Anal Chem 00:1–12. https://doi.org/10.1080/03067319.2023.2201445
44. Hădărugă NG, Bandur GN, David I, Hădărugă DI (2019) A review on thermal analyses of cyclodextrins and cyclodextrin complexes. Environ Chem Lett 17:349–373. https://doi.org/10.1007/s10311-018-0806-8
45. Haghbakhsh R, Parvaneh K, Raeissi S, Shariati A (2018) A general viscosity model for deep eutectic solvents: the free volume theory coupled with association equations of state. Fluid Phase Equilib 470:193–202. https://doi.org/10.1016/j.fluid.2017.08.024
46. Hansen BB, Spittle S, Chen B et al (2021) Deep eutectic solvents: a review of fundamentals and applications. Chem Rev 121:1232–1285. https://doi.org/10.1021/acs.chemrev.0c00385
47. Houasni A, Grigorakis S, Kellil A, Makris DP (2022) Organosolv treatment/polyphenol extraction from olive leaves (*Olea europaea* L.) using glycerol and glycerol-based deep eutectic solvents: effect on metabolite stability. Biomass (Switzerland) 2:46–61. https://doi.org/10.3390/biomass2010004
48. Huang C, Lin W, Lai C et al (2019) Coupling the post-extraction process to remove residual lignin and alter the recalcitrant structures for improving the enzymatic digestibility of acid-pretreated bamboo residues. Bioresour Technol 285:121355. https://doi.org/10.1016/j.biortech.2019.121355

49. Huang C, Wang X, Liang C et al (2019) A sustainable process for procuring biologically active fractions of high-purity xylo-oligosaccharides and water-soluble lignin from Moso bamboo prehydrolyzate. Biotechnol Biofuels 12:1–13. https://doi.org/10.1186/s13068-019-1527-3
50. Jablonský M, Škulcová A, Ház A et al (2018) Long-term isothermal stability of deep eutectic solvents. BioResources 13:7445–7559. https://doi.org/10.15376/BIORES.13.4.7545-7559
51. Jahangeer M, Rehman MU, Nelofer R et al (2024) Biotransformation of lignocellulosic biomass to value-added bioproducts: insights into bio-saccharification strategies and potential concerns. Top Catal. https://doi.org/10.1007/s11244-024-01941-9
52. Janicka P, Kaykhaii M, Płotka-Wasylka J, Gębicki J (2022) Supramolecular deep eutectic solvents and their applications. Green Chem 24:5035–5045. https://doi.org/10.1039/D2GC00906D
53. Jovanović MS, Krgović N, Radan M et al (2023) Natural deep eutectic solvents combined with cyclodextrins: a novel strategy for chokeberry anthocyanins extraction. Food Chem 405:134816. https://doi.org/10.1016/J.FOODCHEM.2022.134816
54. Kalogiouri NP, Papatheocharidou C, Samanidou VF (2024) Recent advances towards the use of deep eutectic solvents and cyclodextrins in the extraction of food contaminants: from traditional sample pretreatment techniques to green microextraction and beyond. TrAC Trends Anal Chem 173:117649. https://doi.org/10.1016/J.TRAC.2024.117649
55. Karageorgou I, Grigorakis S, Lalas S et al (2018) Incorporation of 2-hydroxypropyl β-cyclodextrin in a biomolecule-based low-transition temperature mixture (LTTM) boosts efficiency of polyphenol extraction from Moringa oleifera Lam leaves. J Appl Res Med Aromat Plants 9:62–69. https://doi.org/10.1016/j.jarmap.2018.02.005
56. Kfoury M, Landy D, Fourmentin S (2022) Combination of DES and macrocyclic host molecules: review and perspectives. Curr Opin Green Sustain Chem 36:100630. https://doi.org/10.1016/j.cogsc.2022.100630
57. Kfoury M, Landy D, Ruellan S et al (2017) Nootkatone encapsulation by cyclodextrins: effect on water solubility and photostability. Food Chem 236:41–48. https://doi.org/10.1016/j.foodchem.2016.12.086
58. Li B, Guo S, Chen Y et al (2024) Net hydrogen bond interaction driven supramolecular deep eutectic solvent formation: the case of cyclodextrins. J Mol Liq 412:125880. https://doi.org/10.1016/j.molliq.2024.125880
59. Liu C, Provatas AA, Parnas RS (2023) Desulfurization of biodiesel produced from waste fats, oils and grease using β-cyclodextrin. Sep Purif Technol 305:122417. https://doi.org/10.1016/j.seppur.2022.122417
60. Makoś-Chełstowska P (2023) VOCs absorption from gas streams using deep eutectic solvents—a review. J Hazard Mater 448:130957. https://doi.org/10.1016/j.jhazmat.2023.130957
61. Makoś-Chełstowska P, Kaykhaii M, Płotka-Wasylka J, de la Guardia M (2022) Magnetic deep eutectic solvents—fundamentals and applications. J Mol Liq 365:120158. https://doi.org/10.1016/J.MOLLIQ.2022.120158
62. Makoś P, Boczkaj G (2019) Deep eutectic solvents based highly efficient extractive desulfurization of fuels—eco-friendly approach. J Mol Liq 296:111916–111927. https://doi.org/10.1016/j.molliq.2019.111916
63. Makoś P, Słupek E, Gębicki J (2020) Hydrophobic deep eutectic solvents in microextraction techniques–a review. Microchem J 152:104384. https://doi.org/10.1016/j.microc.2019.104384
64. Mansour FR, Bedair A, Hamed M et al (2024) Applications of (natural) deep eutectic solvents in liquid phase microextraction: a review. Microchem J 198:110178. https://doi.org/10.1016/J.MICROC.2024.110178
65. Marchel M, Rayaroth MP, Wang C et al (2023) Hydrophobic (deep) eutectic solvents (HDESs) as extractants for removal of pollutants from water and wastewater—a review. Chem Eng J 475:144971. https://doi.org/10.1016/J.CEJ.2023.144971
66. Moradi M, Ferreira AM, Neves CMSS et al (2025) Enantioseparation of ofloxacin using a liquid–liquid extraction system based on hydrophobic eutectic solvents. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2024.128462
67. Morin-Crini N, Fourmentin S, Fenyvesi É et al (2021) 130 years of cyclodextrin discovery for health, food, agriculture, and the industry: a review. Environ Chem Lett 19:2581–2617. https://doi.org/10.1007/s10311-020-01156-w
68. Moufawad T, Moura L, Ferreira M et al (2019) First evidence of cyclodextrin inclusion complexes in a deep eutectic solvent. ACS Sustain Chem Eng 7:6345–6351. https://doi.org/10.1021/acssuschemeng.9b00044
69. Nakhle L, Kfoury M, Mallard I et al (2021) Microextraction of bioactive compounds using deep eutectic solvents: a review. Environ Chem Lett 19:3747–3759. https://doi.org/10.1007/s10311-021-01255-2
70. Nesbitt B (2007) Properties of fluids. Handbook of valves and actuators. Butterworth-Heinemann, Oxford, pp 43–79
71. Osamede Airouyuwa J, Sivapragasam N, Ali Redha A, Maqsood S (2024) Sustainable green extraction of anthocyanins and carotenoids using deep eutectic solvents (DES): a review of recent developments. Food Chem 448:139061. https://doi.org/10.1016/J.FOODCHEM.2024.139061
72. Pacheco-Fernández I, Pino V (2019) Green solvents in analytical chemistry. Curr Opin Green Sustain Chem 18:42–50. https://doi.org/10.1016/j.cogsc.2018.12.010
73. Pena-Pereira F, Kloskowski A, Namieśnik J (2015) Perspectives on the replacement of harmful organic solvents in analytical methodologies: a framework toward the implementation of a generation of eco-friendly alternatives. Green Chem 17:3687–3705. https://doi.org/10.1039/C5GC00611B
74. Rahman MS, Roy R, Jadhav B et al (2021) Formulation, structure, and applications of therapeutic and amino acid-based deep eutectic solvents: an overview. J Mol Liq 321:114745. https://doi.org/10.1016/j.molliq.2020.114745
75. Romero A, Santos A, Tojo J, Rodríguez A (2008) Toxicity and biodegradability of imidazolium ionic liquids. J Hazard Mater 151:268–273. https://doi.org/10.1016/J.JHAZMAT.2007.10.079
76. Santana APR, Mora-Vargas JA, Guimarães TGS et al (2019) Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods. J Mol Liq 293:111452. https://doi.org/10.1016/J.MOLLIQ.2019.111452
77. Sereshti H, Karami F, Nouri N (2021) A green dispersive liquid–liquid microextraction based on deep eutectic solvents doped with β-cyclodextrin: application for determination of tetracyclines in water samples. Microchem J 163:105914. https://doi.org/10.1016/j.microc.2020.105914
78. Shi F, Hai X, Zhu Y et al (2023) Ultrasonic assisted extraction of polyphenols from bayberry by deep eutectic supramolecular polymer and its application in bio-active film. Ultrason Sonochem 92:106283. https://doi.org/10.1016/j.ultsonch.2022.106283
79. Smith EL, Abbott AP, Ryder KS (2014) Deep eutectic solvents (DESs) and their applications. Chem Rev 114:11060–11082. https://doi.org/10.1021/cr300162p
80. Stott PW, Williams AC, Barry BW (1998) Transdermal delivery from eutectic systems: enhanced permeation of a model drug, ibuprofen. J Control Release 50:297–308. https://doi.org/10.1016/S0168-3659(97)00153-3
81. Sun P, Wang C, Li S et al (2024) Supramolecular deep eutectic solvent: a powerful tool for pre-concentration of trace metals in edible oil. Anal Bioanal Chem 416:3533–3542. https://doi.org/10.1007/s00216-024-05304-x

82. Szejtli J (1998) Introduction and general overview of cyclodextrin chemistry. Chem Rev 98:1743–1753. https://doi.org/10.1021/cr970022c
83. Tahir S, Qazi UY, Naseem Z et al (2021) Deep eutectic solvents as alternative green solvents for the efficient desulfurization of liquid fuel: a comprehensive review. Fuel 305:121502. https://doi.org/10.1016/J.FUEL.2021.121502
84. Tan J, Huang J, Yuan J et al (2023) Novel supramolecular deep eutectic solvent-enabled in-situ lignin protection for full valorization of all components of wheat straw. Bioresour Technol. https://doi.org/10.1016/j.biortech.2023.129722
85. Van Osch DJGP, Zubeir LF, Van Den Bruinhorst A et al (2015) Hydrophobic deep eutectic solvents as water-immiscible extractants. Green Chem 17:4518–4521. https://doi.org/10.1039/c5gc01451d
86. Vanda H, Verpoorte R, Klinkhamer PGL, Choi YH (2019) Natural deep eutectic solvents: from their discovery to their applications. Deep Eutectic Solvents. https://doi.org/10.1002/9783527818488.ch4
87. Velvizhi G, Jacqueline PJ, Shetti NP et al (2023) Emerging trends and advances in valorization of lignocellulosic biomass to biofuels. J Environ Manage 345:118527. https://doi.org/10.1016/j.jenvman.2023.118527
88. Vilková M, Płotka-Wasylka J, Andruch V (2020) The role of water in deep eutectic solvent-base extraction. J Mol Liq. https://doi.org/10.1016/j.molliq.2020.112747
89. Wang Y, Liu X, Kraslawski A et al (2019) A novel process design for CO_2 capture and H_2S removal from the syngas using ionic liquid. J Clean Prod 213:480–490. https://doi.org/10.1016/j.jclepro.2018.12.180
90. Wu S, Cai C, Li F et al (2020) Deep Eutectic supramolecular polymers: bulk supramolecular materials. Angew Chemie - Int Ed 59:11871–11875. https://doi.org/10.1002/anie.202004104
91. Wu Y, Zhou M, Yu Q et al (2023) Dispersive liquid-liquid microextraction based on deep eutectic solvent doped with hydroxyethyl-β-cyclodextrin for the determination of sulfonamides in environmental waters. Microchem J 193:109029. https://doi.org/10.1016/J.MICROC.2023.109029
92. Xu F, Wang Y, Liu Z et al (2020) A deep eutectic solvent modified magnetic β-cyclodextrin particle for solid-phase extraction of trypsin. Anal Chim Acta 1137:125–135. https://doi.org/10.1016/J.ACA.2020.09.005
93. Yang Y, Zhao R, Gao H et al (2023) β-Cyclodextrin as a booster for ultrasound-assisted extraction of secoiridoids from Gentiana rigescens using a biobased deep eutectic solvent. Ind Crops Prod 204:117410. https://doi.org/10.1016/J.INDCROP.2023.117410
94. Yue D, Jing Y, Sun J et al (2011) Structure and ion transport behavior analysis of ionic liquid analogues based on magnesium chloride. J Mol Liq 158:124–130. https://doi.org/10.1016/J.MOLLIQ.2010.11.005
95. Zhang C, Wu J, Wang R et al (2021) Study of the toluene absorption capacity and mechanism of ionic liquids using COSMO-RS prediction and experimental verification. Green Energy Environ 6:339–349. https://doi.org/10.1016/J.GEE.2020.08.001
96. Zhang H, Zhao W, Bai T et al (2022) Sustainable extraction of polyphenols from millet using switchable deep eutectic solvents. Lwt 170:114082. https://doi.org/10.1016/j.lwt.2022.114082
97. Zhang J, Li S, Yao L et al (2024) Cyclodextrin-based ternary supramolecular deep eutectic solvents for efficient extraction and analysis of trace quinolones and sulfonamides in wastewater by adjusting pH. Anal Chim Acta 1311:342714. https://doi.org/10.1016/j.aca.2024.342714
98. Zhang J, Yao L, Li S et al (2023) Green materials with promising applications: cyclodextrin-based deep eutectic supramolecular polymers. Green Chem 25:4180–4195. https://doi.org/10.1039/D3GC00489A
99. Zhang Q, De Oliveira VK, Royer S, Jérôme F (2012) Deep eutectic solvents: syntheses, properties and applications. Chem Soc Rev 41:7108–7146. https://doi.org/10.1039/c2cs35178a
100. Zhang Y, Li H, Hai X et al (2024) Designing green and recyclable switchable supramolecular deep eutectic solvents for efficient extraction of flavonoids from Scutellariae Radix and mechanism exploration. J Chromatogr A 1730:465084. https://doi.org/10.1016/J.CHROMA.2024.465084
101. Zhao Y, Zhao J, Huang Y et al (2014) Toxicity of ionic liquids: Database and prediction via quantitative structure-activity relationship method. J Hazard Mater 278:320–329. https://doi.org/10.1016/j.jhazmat.2014.06.018