Journal of Molecular Liquids 275 (2019) 312–322

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Review

Deep eutectic solvents for extraction-desulphurization: A review

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ARTICLE INFO

Article history:
Received 27 October 2018
Received in revised form 12 November 2018
Accepted 13 November 2018
Available online 16 November 2018

Keywords:
Sulphur
Hydro-desulphurization
Extraction-desulphurization
Ionic liquids
Deep eutectic solvents
Green solvent

ABSTRACT

At present, greater pressure is continuously applied to the desulphurization process to produce fuel with low sulphur content. Relying on the conventional hydro-desulphurization (HDS) method totally would result in significant increase in the cost due to the required modifications to the HDS unit, as well as increased consumption of hydrogen, electricity and catalyst. Despite extraction-desulphurization method by employing ionic liquids (ILs) as solvent has gathered attention for the past two decades, the toxicity of ILs led to research works to seek alternative green absorbent as a substitute. Deep eutectic solvents (DESs), a less toxic solvent than ILs discovered in 2001 have been actively researched as a substitute solvent since 2013. This review aims to comprehensively discuss DESs for desulphurization application emphasizing on the factors affecting extraction-desulphurization. DESs as a solvent for extraction-desulphurization exhibited high sulphur removal capabilities. Selection of DESs, extraction time, extraction temperature, model oil ratio, multistage extraction and DESs regeneration are deemed to affect the desulphurization yield. Economical raw material and synthesis cost, low solvent to feed treat ratio and beneficial green solvent characteristic exhibit DESs' suitability for desulphurization.

Contents

1. Introduction . . . 313
2. Deep eutectic solvents . . . 314
  2.1. Classifications of deep eutectic solvents . . . 314
  2.2. Preparation of deep eutectic solvents . . . 315
    2.2.1. Selection of deep eutectic solvents . . . 315
    2.2.2. Molar ratio . . . 315
    2.2.3. Extraction time . . . 315
    2.2.4. Extraction temperature . . . 316
    2.2.5. Initial sulphur concentration . . . 317
    2.2.6. Model oil ratio . . . 317
    2.2.7. Multistage extraction . . . 318
    2.2.8. Regeneration of deep eutectic solvents . . . 318
    2.2.9. Oxidative and catalytic assisted extraction-desulphurization using deep eutectic solvents . . . 318
3. Desulphurization mechanisms using deep eutectic solvents . . . 319
4. Conclusion . . . 319
Abbreviations . . . 320
References. . . . 321

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https://doi.org/10.1016/j.molliq.2018.11.051
0167-7322/

1. Introduction

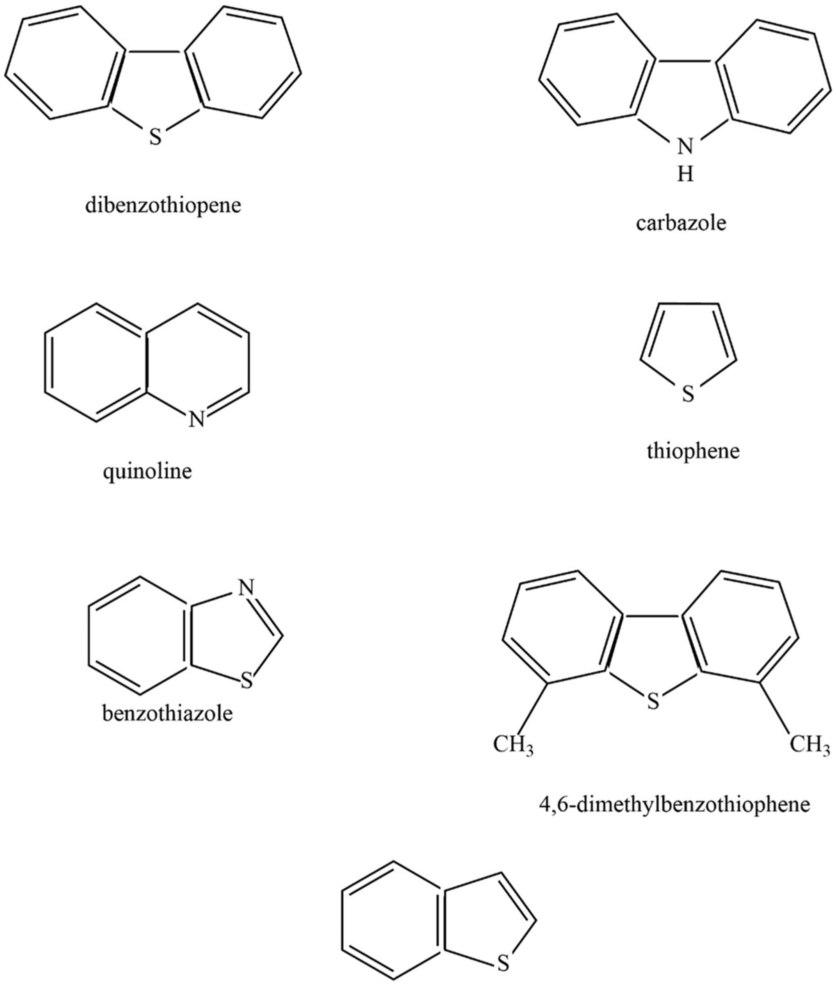
Sulphur dioxide (SO_2), a harmful gas produced during the combustion of fuels such as coal, oil or diesel containing sulphur poses threat to the human health and ecosystem [1–4]. Excessive exposure to SO_2 could lead to respiratory diseases such as asthma, emphysema, chronic bronchitis and can also cause neurological disorders [5–7]. Shortness of breath, wheezing and tightness in the chest during performing physical activities are among the symptoms of an affected respiratory system due to SO_2 exposure. SO_2 also causes irritation to skin and the mucous membranes of the eyes [8]. Besides, SO_2 also reacts with the moisture which results in acidic rain and fogs with low pH value. Acid rain causes erosion of buildings, alters the pH of soil and water (ocean) which adversely affects the aquatic life. This cycle damages the ecosystem.

Among the largest contributors of SO_2 emission are electricity generation by coal general power plants, industrial boilers, crude oil refineries, smelting industries, vehicles and natural volcanic activity. SO_2 emission which peaked in 1980 at 151.51 million tonnes due to rapid industrialization has since then been reduced through regulations enforced to reduce environmental pollution [9]. 90% reduction of SO_2 emission was achieved by the United States between 1980 and 2016 as a result of these regulations [10,11]. Among the regulation imposed on vehicles to reduce environmental pollution is on the allowable sulphur content present in the fuel.

Sulphur, a naturally occurring element in crude oil with undesirable property results in SO_2 due to combustion, inhibit/poison catalyst, as well as causes corrosion to equipment and pipelines. Sulphur in crude oil is majorly present in the form of organo-sulphur compounds such as methyl mercaptan, phenyl mercaptan, cyclohexylthiol, dimethyl sulphide, thiocyclohexane, thiophene and benzothiophene, as well as inorganic sulphur compound such as hydrogen sulphide as shown in Fig. 1. These compounds are either acidic or non-acidic in nature. Crude oil which contains <0.5 wt% of sulphur is considered 'sweet crude oil' while higher is considered 'sour crude oil'.

Realizing the catastrophic effect of SO_2 towards human and ecosystems, policy makers are further imposing more stringent regulation by mandating the use of fuel with reduced sulphur content. In 2009, European Union adopted Euro V fuel standard which stipulated a maximum sulphur content of 10 ppm for both diesel and gasoline [12]. This fuel standard replaced the Euro IV standard that has been in place since 2005 which had an allowable sulphur content of 50 ppm. In the United States, a maximum of 15 ppm of sulphur content has been the norm since 2006 for on-road ultra-low sulphur diesel while for gasoline, an average of 100 ppm of sulphur has been limited since 2017 [12,13]. For China, the sulphur content has been limited to a maximum of 10 ppm for on-road diesel and gasoline as of 2017 [14].

At present, due to the current circumstances of depleting sweet (low sulphur) crude reservoirs, the focus is being shifted towards sour (high sulphur) crudes with up to 14 wt% of sulphur [15,16]. Hence, there is an urge to remove a high amount of sulphur content from sour crudes to meet the ever-stringent permissible sulphur content in fuel. Sulphur removal is divided into three techniques depending on how the compound is removed. These include; catalytic hydro-desulphurization (HDS), solvent extraction and adsorption on molecular sieves. Catalytic



dibenzothiopene

carbazole

quinoline

thiophene

benzothiazole

4,6-dimethylbenzothiophene

benzothiophene

Fig. 1. Organo-sulphur compounds present in the fuel.

HDS applies a reaction of sulphur compounds with hydrogen in the presence of a catalyst. This is a decomposition reaction where hydrogen sulphide (H_2S) is formed while the hydrocarbon liquid is the remnant. Solvent extraction uses the principle of liquid-liquid extraction where the solvent removes sulphur compounds from hydrocarbon stream. It is also used in the removal of H_2S from light gases [17]. Alkanol amines are such solvents used in the process. Mercaptans are also removed by the extraction technique using sodium hydroxide during the sweetening process to remove bad odours and avoid corrosion [18]. Adsorption on molecular sieves is a technique used to remove sulphur from C_3, C_4, C_5 and natural gas. This process is efficient in removing H_2S, sulphides, disulphides and mercaptans [19].

Till present, HDS has been the commonly used method to remove sulphur from crude oil [18]. Despite HDS is efficient to remove aliphatic hydrocarbon sulphur content, however, it is unable to remove polycyclic organic sulphides such as thiophene, benzothiophene, dibenzothiophene and its derivatives which requires deep removal due to their large steric hindrance [18,20]. Even if deep desulphurization could be performed, extremely harsh operating conditions such as high pressure (2 MPa–10 MPa) and temperatures (600 K–700 K) would be required which shall lead to significant increase in the desulphurization cost [21]. Besides, the HDS process is also hindered by the presence of nitrogen compounds in diesel fuel [22,23].

With regard to the above especially on the depleting sweet crude and challenges faced with HDS, research works are actively being carried out worldwide to seek possibilities of removing sulphur from sour crude meeting the stipulated fuel standard [19,24–26]. In response to this, extraction-desulphurization has been widely researched mainly due to the simplicity of desulphurization process, low energy consumption, as well as lower temperature and pressure operating conditions as compared to HDS [27]. Ionic liquids (ILs) have gained momentum for the past 20 years as a solvent for extraction-desulphurization. ILs are generally molten salts. The temperature 373 K is taken as the international agreement as the highest melting temperature for ILs. ILs are majorly formed from one type of discrete anion or cation held together via ionic bonding which contributes to very low vapour pressure. The possibility of tailoring the properties of ILs by altering the combination of the cations and anions [28,29], as well as the non-volatility portrayed made ILs a promising candidate to replace the conventional volatile organic solvents [30]. The use of ILs for extraction-desulphurization has been comprehensively reviewed by Ibrahim et al. [31]. However, recent studies have raised concerns about the toxicity and poor biodegradability of ILs towards environmental damage [24,25,32,33]. This led to research work seeking a suitable alternative to replace ILs.

Deep eutectic solvents (DESs), a new class of ionic liquid formed as a result of eutectic mixture of Lewis/Bronsted acids and bases which may consist of different anionic and/or cationic species emerged as a suitable replacement. This eutectic mixture has a melting temperature far below its constituents [34–39]. Despite DESs and ILs have many characteristics and physical properties in common, they are different types of solvents with different chemical properties. Research on ILs has been carried out since the past two decades while the first paper reported on DESs as a solvent for extraction-desulphurization was reported on 2013 [20]. The aim of this review is to critically analyse DESs for its desulphurization capabilities.

2. Deep eutectic solvents

DESs are a new class of solvents, analogues to ILs that have attracted great attention because of their excellent physical properties which can be easily tuned for specific uses. DESs consist of a mixture of two or more compounds having hydrogen-bond donors (HBD) and hydrogen-bond acceptors (HBA) that form a eutectic mixture [40]. Synthesis of DESs is relatively simple and does not require organic solvents hence, the environmental impacts resulting from toxic organic solvents can be eliminated. The interacting components are green, easily available and cheap raw materials [41]. Typically, they are formed from a mixture of simple quaternary ammonium halide with a metal salt or inorganic HBD such as amide, carboxylic acids or alcohol [42,43].

DESs are liquid mixtures between room temperatures and up to a maximum of 343 K [43]. The decrease in the eutectic temperature of the formed liquid mixture was demonstrated by Abbott et al. in 2001 when several quaternary ammonium salts (QAS) were heated with zinc chloride [44]. From Table 1, the lowest melting point of DESs achieved was in the range 296–298 K formed using $Me_3NCH_2CH_2Cl/ZnCl_2$. This is an advantage for DESs since it can be used at ambient temperature and pressure during extraction-desulphurization as compared to the conventional method of HDS that requires high temperature and pressure [44]. DESs can be described by a general formula representation Cat^+X^-zY; where Cat^+ is a cation from any ammonium, phosphonium or sulphonium, X^- is a halide anion of a Lewis base and z represents the number of Y molecules that interact with the anion.

2.1. Classifications of deep eutectic solvents

The nature of the complexing agents is used to classify the formed eutectics. The common complexing agents are metal halides/imidazolium salts, hydrate metal halides, HBD and a range of transitional metals [44]. In general, eutectics can be classified into 4 types as shown in Table 2.

Type I eutectic are formed from QAS and metal halide. Examples include chloroaluminate/imidazolium salt mixed with various non-hydrated metal halides such as iron chloride ($FeCl_2$). Other metal chlorides that have been proven to be in type I also include silver chloride (AgCl), copper(I) chloride (CuCl), lithium chloride (LiCl), cadmium chloride ($CdCl_2$), copper(II) chloride ($CuCl_2$), tin(II) chloride ($SnCl_2$), zinc chloride ($ZnCl_2$), lanthanum(III) chloride ($LaCl_3$), yttrium(III) chloride (YCl_3) and tin(IV) chloride ($SnCl_4$) [46]. Type II eutectic are formed from QAS and hydrated metal halide. Hydrated metal halides are cheap and are not affected by air or moisture thus makes it applicable for large-scale processing [46].

Type III eutectic are formed from QAS and HBD. This type of eutectic has been most researched. For example, the formed eutectic from choline chloride and HBD has the ability to solvate a wide liquid which includes chlorides, transitional metals as well as oxides make them attracts much of interest. The formed eutectic is non-reactive with water, relatively cheap, mostly biodegradable and easy preparation as well as the adaptability to wide range of HBD. The HBD used to prepare this type of eutectic (type III) influences the physical properties while the combination with choline chloride determines which purpose it serves. Type III eutectic has shown potential in several applications such as nanoparticle synthesis, heat transfer in fluids, electro-deposition of metals, liquid-gas separation and catalysts in reactions [41].

Type IV eutectic are formed from metal halide and HBD. Inorganic cations possess high charge density and are unable to form eutectics. However, mixture of urea with halides forms eutectics. Through this, useful applications due to the metal cationic complexes have been found [43].

Table 1
Melting points of materials produced from quaternary ammonium chloride and $ZnCl_2$ [44].

Quaternary ammonium chloride/$ZnCl_2$ (1:2 molar ratio)	Melting point (K)
$NH_4/ZnCl_2$	>473
$Me_4N/ZnCl_2$	>473
$Et_4N/ZnCl_2$	363-365
$Me_3NEt/ZnCl_2$	326-328
$Me_3NCH_2CH_2Cl/ZnCl_2$	296-298

Table 2
Classification of eutectics [39,45].

Type	Formula	
Type I	$Cat^{+}X^{-}zMCl_x$	(M = Zn, Sn, Fe, Al, Ga, In)
Type II	$Cat^{+}X^{-}zMCl_x \cdot yH_2O$	(M = Cr, Co, Cu, Ni, Fe)
Type III	$Cat^{+}X^{-}zRZ$	(Z = $CONH_2$, COOH, OH)
Type IV	$MCl_x + RZ = MCl_{x-1}^{+} \cdot RZ + MCl_{x+1}^{-}$	(M = Al, Zn and Z = $CONH_2$, OH)

2.2. Preparation of deep eutectic solvents

In 2003, Abbott et al. [47] mixed choline chloride (melting point 575 K) and urea (melting point 406 K) at a molar ratio of 1:2 to form a eutectic mixture with a freezing point of 285 K. According to the authors, the significant depression in the freezing point would have resulted due to the interaction between the urea molecules and the chloride ion. Hydrogen bonding was formed in the DESs observed using NMR spectroscopy. The authors in the same study also prepared several other DESs by mixing amide compounds with choline chloride in a 2:1 mol ratio. Among the amides were 1-methyl urea, 1, 3-dimethyl urea, 1, 1-dimethyl urea, thiourea, acetamide, benzamide and tetramethyl urea. Through these formed DESs, the authors noticed that only those compounds capable of forming hydrogen bonds with chloride ions formed homogenous liquid with a significant decrease in the freezing point as compared to pure amide. Abbott et al. [47] also reported that the formed DESs (2:1 urea:choline chloride) exhibited high solubility, high conductivity (~1100 mS/cm at 373 K) and low viscosity (~100 cP at 323 K). Since these properties are majorly influenced by the amide and QAS, Abbott et al. [48] suggested that the fluid properties can be tailored for specific applications.

In 2013, Li et al. [20] synthesized DESs using QAS as HBA and organic acids/alcohols as HBD for sulphur removal. The DESs preparation process was carried out using a round-bottomed flask which involved heating the mixture followed by vigorous stirring using a magnetic stirrer at a temperature ranging between 353 K and 403 K. The reaction process was reported to take place for about 3 h to 5 h. The purity of the formed DESs was then confirmed using H NMR. In 2015, Tang et al. [49] prepared arenium ion DESs using chlorinated paraffins-52 with six aromatics (benzene, toluene, *p* xylene, *o* xylene, ethyl benzene and chlorobenzene) and $AlCl_3$ at lower temperatures of 283 K for 1 h. The aromatic such as toluene was added to water free $AlCl_3$ then the chlorinated paraffins-52 was introduced in the mixture slowly done in an inert atmosphere of nitrogen. This mixture formed a dark red homogeneous solution. Other DESs based materials were also prepared in 2015 by mixing zinc chloride with urea and tetra *n* butylphosphonium bromide with $FeCl_2$ [50,51].

In 2016, ILs-based DESs were prepared in inert atmosphere argon where 1 methylimidazole 30 mL and propionic acid were loaded in a magnetic stirrer at 323 K for 24 h while cooling done using an ice bath. Propionic acid was added until a colourless solution was formed [52]. Green carboxylic acid-based DESs were synthesized using tetra butyl ammonium bromide (TBAB) as HBA and formic acid (HCOOH) as HBD. TBAB/HCOOH were mixed in a 250 mL flask stirred using a magnetic stirrer at 353 K for 2 h to form a pale-yellow, transparent and homogenous liquid i.e. TBAB/HCOOH DESs which was later used to remove sulphur [53]. Tetra butyl ammonium chloride-based DESs (TBAC-based) was prepared by Shu et al. [54] in 2016 using TBAC as HBA and ethylene glycol, glycerol, malonic acid as HBD. TBAC was mixed together with either HBD in a round bottom flask for a period between 2 h and 4 h until a homogenous clear solution was formed e.g. TBAC/malonic acid. The DESs was vacuum-dried at 393 K for 2 h then used for extraction-desulphurization. In 2018, Zhao et al. [55] synthesized aromatic based DESs in a 100 mL round-bottomed flask, strongly stirred at 363 K for 1 h for sulphur removal.

Generally, DESs are synthesized by mixing HBA and HBD followed by stirring the mixture while heating it. Fig. 2 shows the interaction between HBA and HBD leading to the formation of DESs.

To date, a number of research works have been reported on extraction-desulphurization using DESs (Table 3). The capability of a variety of prepared DESs in removing sulphur which consisted of various organo-sulphur compounds such as thiophene (TS), benzothiophene (BT) and dibenzothiophene (DBT) in prepared model oil such as n-octane, n-heptane and toluene have been reported. Essentially, several factors have been reported which affect the extraction efficiency such as the selection of DESs, molar ratio of DESs, extraction time, extraction temperature, initial sulphur concentration, model oil ratio, multistage extraction effect and regeneration effect of DESs.

2.2.1. Selection of deep eutectic solvents

Selection of suitable DESs is important as it affects the sulphur extraction efficiency. In a study by Wang et al. [66], the authors prepared 3 different DESs by mixing triethylamine (TEtA) and organic acids formic (Fo), acetic (Ac) and propionic (Pr) acids, independently, at a molar ratio of 1:02. The author reported extraction efficiency of 52.3%, 48.9% and 48.1% for [TEtA][Pr], [TEtA][Ac] and [TEtA][Fo], respectively. In another study, Li et al. [20] used choline chloride (ChCl), tetra methyl ammonium chloride (TMAC), and TBAC as HBA and malonic acid (MA), glycerol (Gl), tetra ethylene glycerol (TEG), ethylene glycol (EG), polyethylene glycol (PEG), and propionate (Pr) as HBD to synthesis DESs. The authors reported that HBAs possessed more influence in sulphur removal in the order of TBAC > TMAC > ChCl while for HBDs in the order of PEG > Pr > EG > TEG > Gl > MA. Similar outcome of different desulphurization yield for different DESs were also reported in other studies [30,52,55,63,65,67].

Besides differences in extraction efficiency, the DESs selection also affects the removal efficiency of different component of organo-sulphur compound. In a study Gano et al. [64], the authors utilized hydrated metal halide-based DESs and achieved 69.57% and 47.28% sulphur removal efficiency for DBT and TS, respectively, in one cycle extraction at optimal conditions. The authors in another study [50] used iron chloride ($FeCl_3$)-based DESs for sulphur removal. The authors reported 64% and 44% extraction efficiencies for DBT and TS, respectively, in a single cycle using model oil. Furthermore, metal ions based DESs (MDESs) have also shown improved sulphur extraction efficiency as compared to traditional DESs. Li et al. [68] reported that the MDESs possess higher extraction efficiency in a single cycle as compared to traditional DESs. This insinuates there three components i.e. HBA: HBD: metal ion in MDESs. In one cycle, 89.53% sulphur removal could be achieved when TBAC: PEG: $FeCl_3$ (4:1:0.05) was used. In comparison with traditional DESs, deep desulphurization of the model oil could be achieved in two cycles of extraction with MDESs (almost 100%). The metal ions are suggested to have aided the desulphurization process. Figs. 3 and 4 show the commonly used HBA and HBD, respectively, for extraction-desulphurization.

2.2.2. Molar ratio

For the influence of molar ratio, Wang et al. [66] prepared 3 DESs by mixing TEtA and organic acids (Fo, Ac and Pr, independently) at a different molar ratio such as 1:02, 1:03 and 1:05. The authors reported that for all three prepared DESs, the extraction efficiency reduced with increasing molar ratio of HBA. Similar outcomes were reported in several other studies [20,50]. To explain this outcome, an increase in the HBD results in the increase of carbon atom chains which in turn decreases the hydrogen bond interactions due to steric hindrance [74]. The HBD wraps around anion affecting packing structure and hence provides more active hydrogen which results in higher sulphur removal.

2.2.3. Extraction time

Concerning extraction time, Li et al. [20] reported that the sulphur was removed tremendously in the first 10 min of the extraction. The

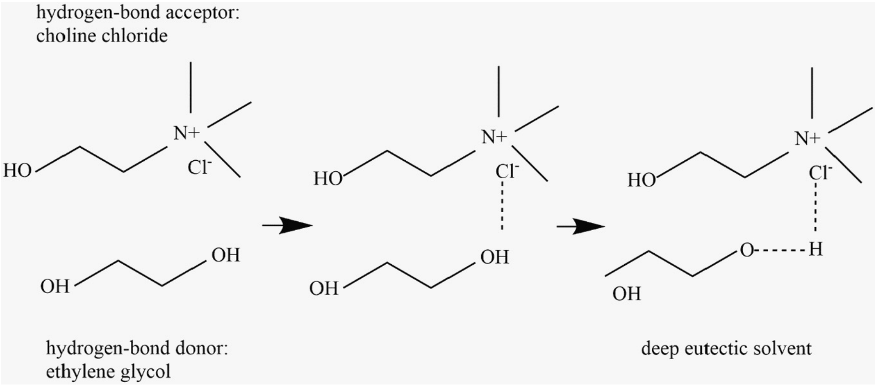


Fig. 2. Interaction of choline chloride (HBA) and ethylene glycol (HBD) forming deep eutectic solvent.

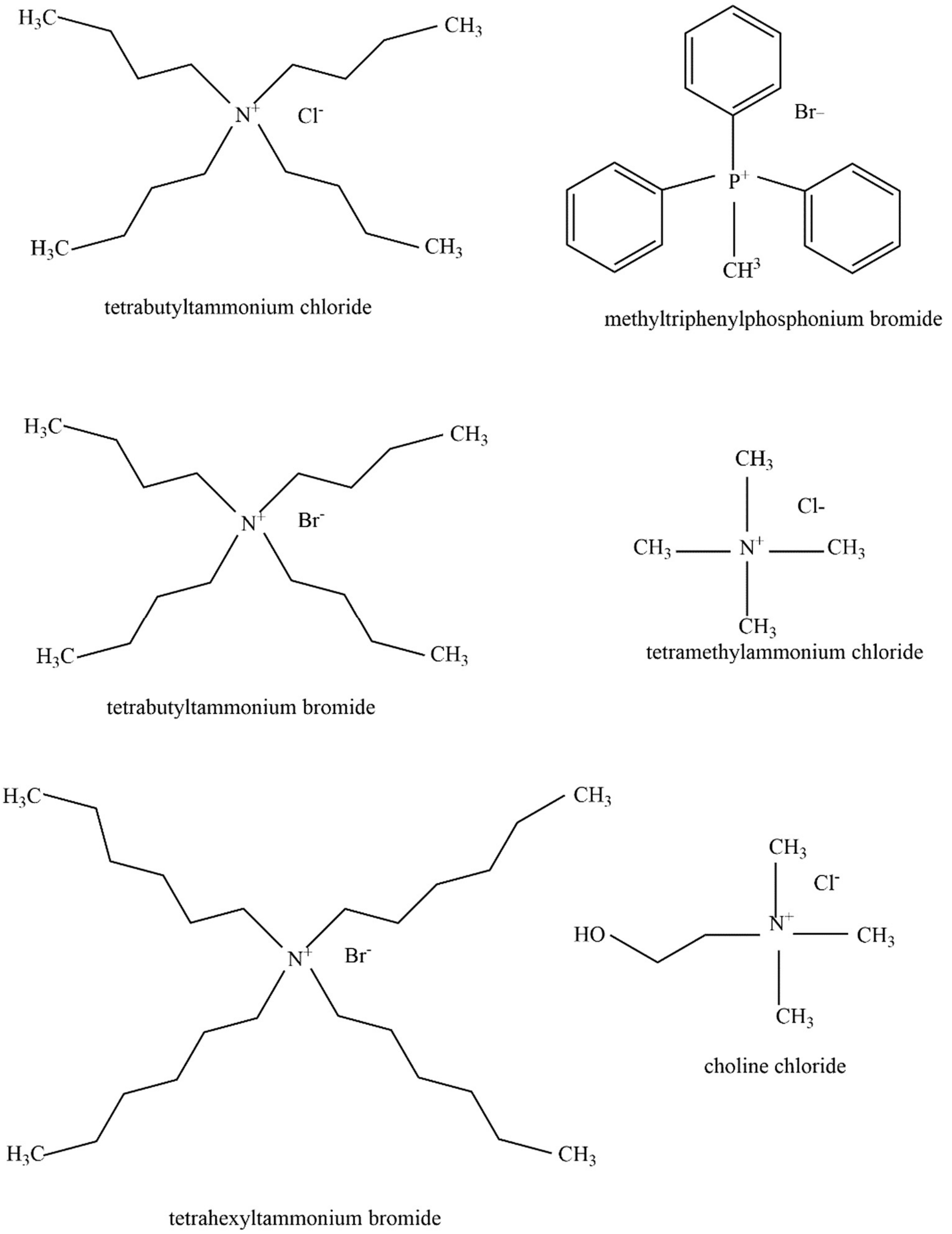
authors suggested that the equilibrium can be attained in 10 min of extraction duration. Agreeing to the above, Tang et al. [49] also reported that the equilibrium can be reached after 10 min of full contact accounting up to 57% of DBT removal using DESs containing toluene. Several other studies also reported similar outcomes of attaining equilibrium within 10 to 20 min of extraction time [68,70,71]. The short equilibrium time can be associated with the low viscosity and high extraction capacity of DESs.

2.2.4. Extraction temperature

With regards to extraction temperature, Tang et al. [49] in a study investigated the effects of temperature on sulphur removal via extraction-desulphurization using DESs. The authors reported that the desulphurization yield reduced by up to 20% at 333 K as compared to at 293 K. Li et al. [20] reported that the sulphur extraction efficiency reduced by 11.5% at 323 K as compared to at 293 K. In another study, Gano et al. [64] reported decreasing extraction efficiency with increasing extraction temperature. Similar outcomes were also reported in other studies [52,66,68,72]. These studies revealed that high temperature is unfavourable for extraction-desulphurization using DESs. The exothermic reaction associated to acid-base complexation suggested to have inhibited the reaction at high temperature [75]. In relation to the exothermic phenomenon, increasing temperature speeds up electrophilic substitution reaction on the DBT aromatic ring [49]. This indicates that the process could be operated at room temperature as compared to the traditional HDS method that requires up to 623 K. To further elaborate on this, DESs viscosity changes linearly with temperature [42,54] as

Table 3
Reported studies on extraction-desulphurization using deep eutectic solvents.

Impurity	DES	Reference
Quinoline, carbazole, dibenzothiophene	Choline chloride/mandelic acid Choline chloride/*p* toluenesulphonic acid	[56]
Dibenzothiophene, 4,6 dimethyl dibenzothiophene, benzothiophene	Metal based deep eutectic solvent Cobalt chloride- based choline chloride/(polyethylene glycol or ethylene glycol or glycerol or propionic acid)	[57]
Thiophene	Tetraethylammonium chloride/ethylene glycol Tetraethylammonium chloride/glycerol Methyltriphenylphosphoniumbromide/glycerol	[58]
Dibenzothiophene, thiophene	Polyethylene glycol/tetrabutylammonium chloride	[59]
Dibenzothiophene	Choline chlorine/propionic acid	[60]
Benzothiophene, dibenzothiophene	Choline chloride/urea Choline chloride/ethylene glycol	[61]
Thiophene, benzothiophene, dibenzothiophene	Triethylamine/*o* hydroxybenzoic acid	[55]
Thiophene	Tetraethylammonium chloride Tetrahexylammonium bromide Methyltriphenylphosphonium bromide/polyol (ethylene glycol &glycerol)	[62]
2-Methylthiopene, 3 methylthiopene	Tetrahexylammonium bromide/ethylene glycol Tetrahexylammoniumbromide/glycerol	[21]
Dibenzothiophene	Tetrabutylphosphonium bromide/dimethylformamide	[63]
3-Methylthiopene, benzothiophene, dibenzothiophene	Toluene/aluminium chloride, chlorinated paraffins 52	[49]
Dibenzothiophene, benzothiophene	Stannous chloride dihydrate/tetra *n* butylphosphonium bromide	[64]
3 Methylthiopene, benzothiophene, dibenzothiophene 4,6 dimethyldibenzothiophene, 4 methyldibenzothiphene	Dimethylethanolamine/irontrichloride	[65]
Dibenzothiophene, thiophene	Irontrichloride/tetrabutylphosphonium bromide	[50]
Dibenzothiophene, benzothiophene, thiophene	Tetrabutylammonium bromide/formic acid	[53]
Dibenzothiophene	1 Methylimidazole/propanoic acid	[52]
Dibenzothiophene	Triethylammonium propionate	[66]
Thiophene	Tetrabutylammonium bromide/sulpholane	[67]
Dibenzothiophene	Tetrabutylammonium chloride/polyethylene glycol/irontrichloride	[68]
Thiophene	Tetra hexylammonium bromide/ethylene glycol Tetra hexylammonium bromide/glycerol	[69]
Thiophene	Choline chloride/phenol	[70]
Dibenzothiophene	Choline chloride/glycerol	[71]
Dibenzothiophene, thiophene	Tetrabutylammonium bromide/polyethylene glycol	[72]
Dibenzothiophene, 4,6 dimethyl dibenzothiophene, benzothiophene	Phenylpropanoicacid/zinc chloride	[73]



tetrabutyltammonium chloride

methyltriphenylphosphonium bromide

tetrabutyltammonium bromide

tetramethylammonium chloride

tetrahexyltammonium bromide

choline chloride

Fig. 3. Commonly used hydrogen-bond acceptor for extraction-desulphurization.

shown in Eq. (1).

$$\ln(\eta) = \ln\eta_o + E_\eta/RT \quad (1)$$

where η is viscosity of DESs; η_o is a constant; T is temperature; E_η is the activation energy for viscous flow.

The decrease in viscosity calls for an increase in temperature hence better mass transfer in the reacting system. These results also correspond to similar trends obtained with ILs and DESs from past published works [20,49,64,76]. Temperatures rise leads to lowering the sulphur partitioning coefficient K_N. This further proves that lower temperatures are sufficient in this process [66].

2.2.5. Initial sulphur concentration

Concerning the initial sulphur concentration, Li et al. [20] reported that the initial sulphur concentration did not influence the partition coefficient. The authors also reported that the extraction-desulphurization via DESs are different compared to via ILs which with increased initial sulphur content, the extraction efficiency increased and then decreased gradually. Similar outcome of the negligible effect of initial sulphur concentration towards extraction efficiency using DESs were also reported by Lima et al. [59], Gano et al. [50], Rahma et al. [72], Gano et al. [64] and Jiang et al. [52].

2.2.6. Model oil ratio

With regard to model oil ratio, it is beneficial to utilize less amount of DESs at an industrial scale. This is to ensure that the cost of adopting DESs for extraction-desulphurization are kept as minimum as possible. The extraction efficiency can be affected due to model oil ratio since the oil and DESs are immiscible which influences the mass transfer. Several studies have reported that an increase in the amount of DESs used for extraction-desulphurization has a direct influence on sulphur removal. These studies revealed that increased DESs to model oil yielded reduced sulphur extraction [20,27,50,53,64,70,76,77]. The ratio of active

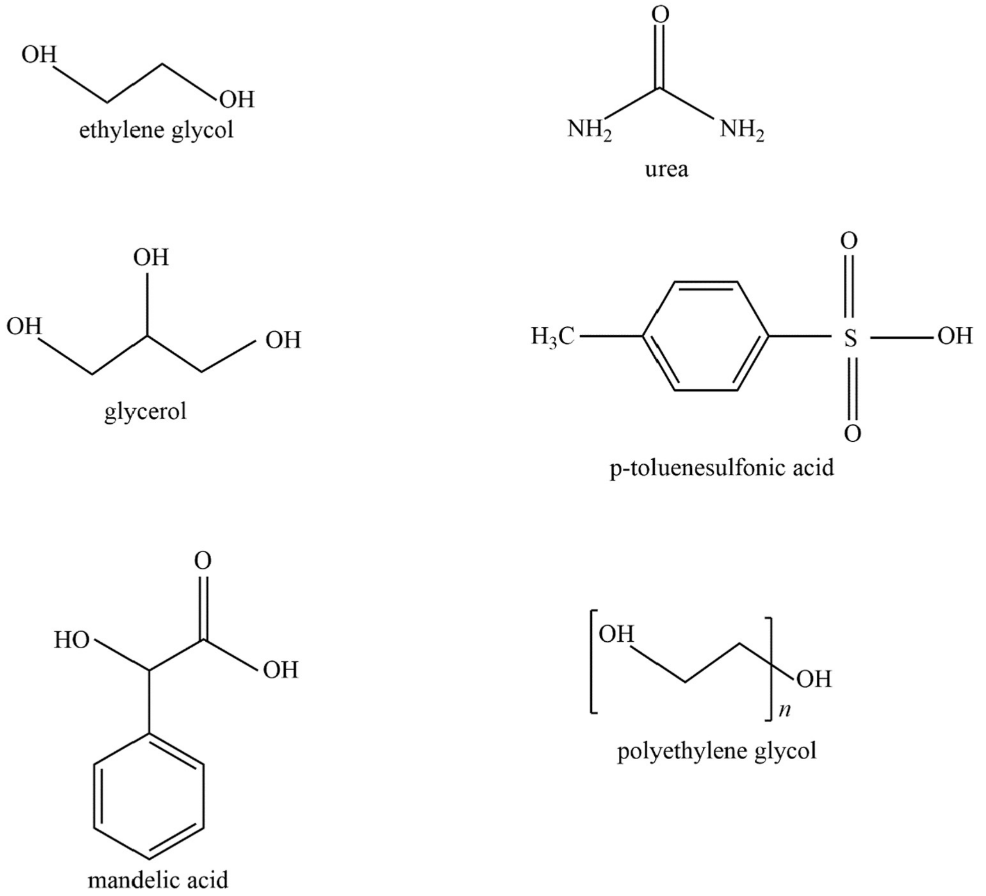


Fig. 4. Commonly used hydrogen-bond donor for extraction-desulphurization.

hydrogen for desulphurization to the amount of model oil is suggested to have influenced the above.

2.2.7. Multistage extraction

For multistage extraction effect, Cheng et al. [63], investigated the effects DBT sulphur extraction under multiple cycles using model fuel tetrabutylphosphonium bromine (TBPB): *N*,*N* dimethulformamide (DMF) (1:3). The authors reported that the desulphurization increased to 98% after 3 cycles as compared to 82% after 1 cycle. The authors also reported that the desulphurization ratio decreased with the reduction in sulphur content in the model oil. The desulphurization ratio reduced from 82.1% from the first cycle to ~71.0% in the second cycle and finally reduced to 61.3% in the third cycle. Hadj-Kali et al. [67] reported sulphur removal reached 98% after 5 cycles of extraction as compared to 35% after 1 cycle. In a study by Li et al. [53], the authors reported that the sulphur removal of BT, DBT and TS increased to 98.32%, 98.24% and 97.6%, respectively, after 3 cycles as compared to 81.75%, 80.47% and 72%, respectively, after a single cycle. The above also agrees with a study reported in 2013 [20] in which reported that the extraction efficiency reached 99.48% after 5 cycles as compared to 82.83% after one cycle. Similar outcome was also reported in which up to 99.5% removal was achieved after 5 cycles depicting deep desulphurization to below 10 ppm as compared to 64% from 1 cycle using TBAC-based DESs [54].

2.2.8. Regeneration of deep eutectic solvents

Concerning the continuous use of DESs without regeneration, Cheng et al. [63] studied the recycling effect of DESs for extraction-desulphurization and observed the extraction capability of the solvent reduced from 82.1% to 5.4% after 5 times of repeated use. Similarly, Li et al. [20] reported that after six times of repeated use, the DESs became saturated and lost its extraction capability. Gano et al. [50] in a study reported that use of DESs without regeneration lost 40% of its extraction ability in the second cycle as compared to the first cycle.

In response to the above, regeneration of DESs such as by washing with organic solvent is required prior to reusing the DESs. Cheng et al. [63] reported that washing of DESs kept the extraction performance constant for 6 times. Similar outcome was reported by Li et al. [20] in which the regenerated DESs was reported effective for 4 extraction cycles. Gano et al. [50] used $FeCl_3$-based DESs for sulphur removal. The authors reported that the DESs can be regenerated and recycled five times without losing its sulphur removal efficiency. Jiang et al. [52] however reported that the extractive capacity of regenerated DESs suffered a mild loss during every regeneration step such as 48.5% after five times as compared to 53.6% during first time usage. Similar marginal decrease in K_N value from 2.14 to 1.96 after recycling five times was reported by Wang et al. [66]. Despite this, the authors did not observe significant reduction in the extraction ability of DESs. In a more recent study, Zhao et al. [55] reported that the extraction efficiency of regenerated DESs was stable for 10 cycles and the loss of DESs could be ignored. The authors also went on to analyse the structure of the regenerated DESs using H NMR and FTIR. The authors reported that the structure of the recycled DESs retained its original structure. The recyclability capability possessed by DESs provided attractive opportunities for large-scale industrial application.

2.2.9. Oxidative and catalytic assisted extraction-desulphurization using deep eutectic solvents

In order to achieve deep desulphurization, there has also been reported works using oxidation or/and catalytic to assist extraction-desulphurization. Concerning oxidation-desulphurization (ODS), there are a variety of oxidants exist with different oxidizing potential and active oxygen. Therefore, it is necessary to select a suitable oxidizing agent based on factors such as cost, eco-friendliness and availability. The most common oxidants employed in ODS include hydrogen peroxide (H_2O_2), superoxide anion (O_2^-), organic peracid and organic hydroperoxide [78].

H_2O_2 is a widely used oxidant which is also stable and environmentally friendly. Several studies have carried out ODS using H_2O_2 in the presence of a catalyst to enhance sulphur removal. The reaction in Eq. (2) shows the oxidation using H_2O_2 [79,80].

$$2H_2O_2 + M \rightarrow MO_2 + 2H_2O \tag{2}$$

Superoxide anion is basically a radical which is free having one electron that is unpaired [64]. These O_2^- are carriers which can exist in gaseous state or solid state such as QAS and alkali metal. However, organic peracids are formed as a result of reaction of H_2O_2 with carboxylic acid such as acetic and formic acid as shown in the reaction Eq. (3).

$$RCOOH + H_2O_2 \rightarrow RCOOOH + H_2O \tag{3}$$

As for the alkyl hydroperoxides, they are reactive compounds generated from nucleophilic displacement of the substrate by H_2O_2 in a basic media or per hydrolysis of alcohols using concentrated hydrogen peroxide as shown in Eq. (4) [78,79].

$$\begin{aligned} &H_2O_2 + OH^- \rightarrow HOO^- + H_2O \text{ (per hydrolysis of alcohols)} \\ &HOO^- + R_2CX \rightarrow R_2CO_2H + X^- \end{aligned} \tag{4}$$

Yin et al. [81] in a study carried out oxidation/extraction desulphurization using acidic DESs in order to achieve higher desulphurization efficiency. Among the HBA used were ChCl and TBAC with HBD *p* toluenesulphonic acid (*p* TsOH). Desulphurization by (ChCl/*p* TsOH) and (TBAC/*p* TsOH) reached up to 99.99%. The authors reported that the stronger the DESs acidity, the higher the desulphurization efficiency. The authors also went on to investigate the effects of oxidant towards the desulphurization. The authors reported the maximum desulphurization efficiency achieved using ChCl/*p* TsOH and TBAC/*p* TsOH without the addition of H_2O_2 as oxidant were 25.2% and 37.8%, respectively, while, up to 99.9% desulphurization could be achieved with the addition of H_2O_2.

Lü et al. [82] in a study reported on the sulphur removal via extractive and catalytic oxidative desulphurization (ECODS) using oxalate-based DESs and H_2O_2 as oxidant. The authors reported that when only oxalate based-DESs was employed, poor desulphurization was observed with hardly any DBT removed. However, with the addition of H_2O_2 to aid desulphurization process, 91% sulphur removal was obtained with TBAC:OXA (1:2) at 323 K for 3 h with $n(H_2O_{2)}/n(DBT) = 5$ meeting environmental standards. Furthermore, at longer duration, the extraction efficiency could reach up to 98%. The authors suggested that this outcome was due to the formation of sulphones compound owing high polarity and high solubility in DESs. In a different study, Lü et al. [83] employed ECODS methods with hybrid Anderson-type Polyoxometalate DESs as a catalyst, H_2O_2 as oxidant and ionic liquid 1 octyl 3 methylimidazolium tetrafluoroborate (OmimBF4) for desulphurization. The authors reported that these combinations yielded up to 100% sulphur extraction carried out at 333 K for 1 h with a negligible decrease in the extraction efficiency up to 20 recycles. Several other studies also reported improved desulphurization via ECODS using DESs [73,84,85].

3. Desulphurization mechanisms using deep eutectic solvents

In order to aid further developments of DESs as an extracting agent, it is essential to understand the extraction-desulphurization mechanism using DESs. In line with this, Li et al. [20] in a study utilized H NMR to study the mechanism of sulphur removal using DESs. Based on it, the authors reported that the peak shape of the active hydrogen changed due to the increased BT ratio. The addition of BT was suggested to destruct the hydrogen bond formed between the DESs chloride anion and active hydrogen [20]. The hydrogen bond interaction led to the reinforcement of the sulphur atom's electron withdrawing ability for the hydrogen atoms in the benzene ring and TS ring from BT. This occurrence culminated in a decrease in the electron density for both the benzene and TS rings, as well as their corresponding hydrogen nucleus electron density.

Li et al. [20] in the same study also observed that the vibrating magnetic field strength decreased and the chemical shift values increased. The authors went on to suggest that the increase in BT caused the hydrogen atoms to move to lower fields. Li et al. [20] also reported that the peak of the carboxyl group gets narrower with increasing concentration of BT. The authors suggested that this could be due to the destruction of the hydrogen bond in DESs that is formed between the chloride ion (Cl^-) and active hydrogen (H^+) as a result of BT addition [20]. Hence, hydrogen bond is highlighted as a major factor which influences the desulphurization. The extractive mechanism described above corroborates with several other studies [20,49,53,67].

The mechanism for ECODS using DESs is shown in Fig. 5. There are two ways for the interaction between DESs and sulphur atom such as the benzene ring from HBA and the ring around the sulphur atom based on similarity-compatibility theory reported by Mao et al. [73] and Nie et al. [86]. Firstly, the aromatic structure of DBT is weakened by the strong interaction between DESs and DBT thus susceptible to oxidation. Secondly, there is π-complexation between sulphur atoms and metal ions. DBT is oxidized to $DBTO_2$ (sulphones) using H_2O_2 by the hydroxyl radicals due to the reaction of metal ion and H_2O_2 in the MDES [87,88]. The reduced acid in the DESs may be oxidized by the peroxide to start the next catalytic cycle which leads to a continuous removal of sulphur in model [82,84]. Furthermore, the acidity of the DESs is also a major factor which influences ECODS since the stronger the acidity in DESs, the higher sulphur extraction. This was justified using electron paramagnetic resonance spin-trap technique with 5,5 dimethyl 1 pyrroline n-oxide [66]. It is also noted that BTO_2 (sulphones) polarity is larger than the non-oxidized sulphur has a higher tendency to dissolve in DES.

4. Conclusion

This review revealed that the interest in DESs as a solvent for extraction-desulphurization has grown significantly in the past 6 years. Both ILs and DESs are capable solvents for extraction-desulphurization, however, DESs is a better choice compared to ILs due its low toxicity and biodegradability. Up to 99% sulphur removal in model oil can be achieved via extraction-desulphurization using DESs. Several factors such as DESs selection, ratio of HBA to HBD, extraction time, extraction temperature, ratio of model oil to DESs and multistage extractions affect the desulphurization yield. Selection of DESs influences both the sulphur removal efficiency and the component of organo-sulphur compounds being extracted. Increased ratio of HBA to HBD reduces the extraction efficiency. Extraction time of 10 to 20 min is sufficient for maximum sulphur removal as equilibrium can be attained within this duration. Increased extraction temperature reduces the desulphurization yield. This is associated to the reduced viscosity and hence the mass transfer as a result of increased temperature. Initial sulphur concentration had a negligible effect on the extraction efficiency. Increased DESs to model oil yielded lower desulphurization. This is beneficial to the industry since less amount of DESs are required for desulphurization. Multistage extraction could produce up to 99.5% sulphur removal depicting deep desulphurization to below 10 ppm of sulphur conforming to Euro V standard. Regeneration of DESs such as by washing with organic solvent is required prior to re-use in order to produce constant extraction performance. Most theoretical and experimental discussions on the extraction mechanisms concluded that the hydrogen bonding between DESs and organo-sulphur compound were

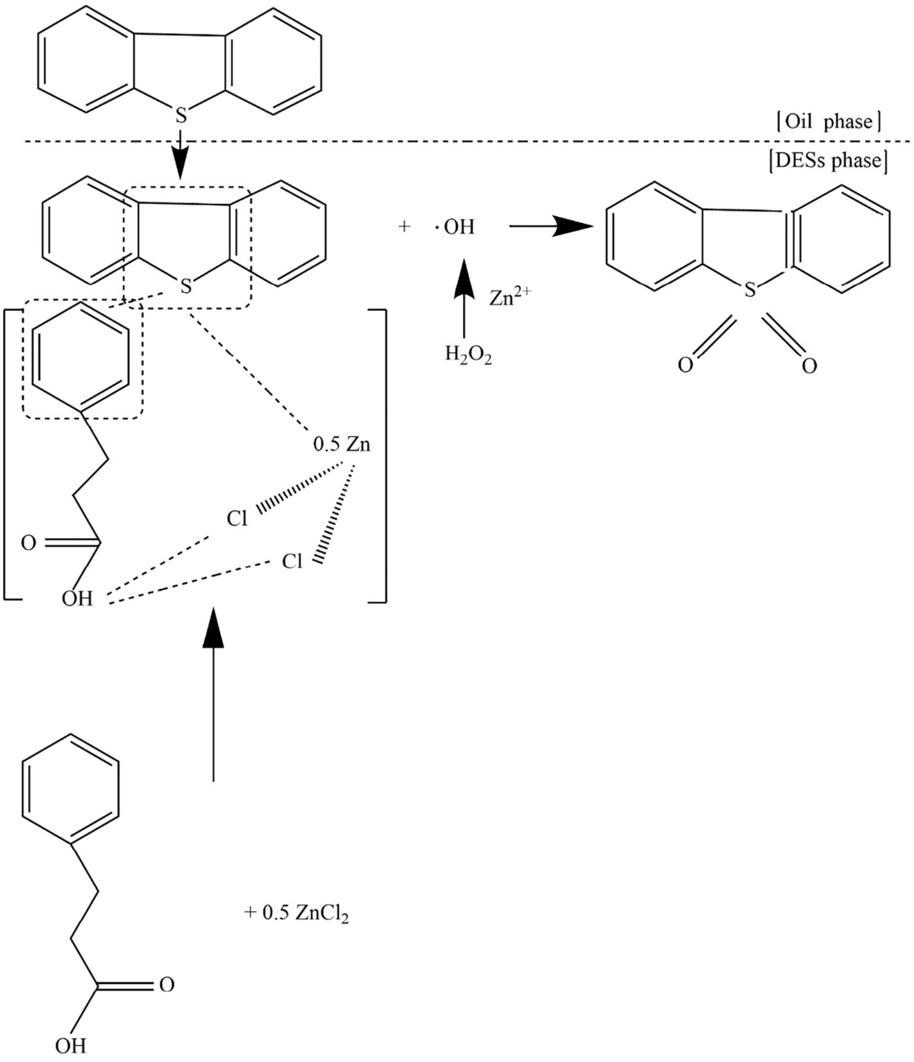


Fig. 5. Extractive and catalytic oxidative desulphurization mechanism.

attributed for the extraction. Assisted extraction-desulphurization with oxidation and catalyst such as ECODS can be incorporated with DESs to produce higher sulphur removal efficiency than DESs alone. DESs as a promising solvent for extraction-desulphurization is expected to attract more research works in the coming years leading to adoption in the industry displacing existing HDS.

Abbreviations

Ac	acetic
AgCl	silver chloride
BT	benzothiophene
$CdCl_2$	cadmium chloride
ChCl	choline chloride
CuCl	copper(I) chloride
$CuCl_2$	copper(II) chloride
DBT	dibenzothiophene
DESs	deep eutectic solvents
DMF	*N,N* dimethulformamide
ECODS	extractive and catalytic oxidative desulphurization
EG	ethylene glycol
$FeCl_2$	iron chloride
Fo	formic
Gl	glycerol
H_2S	hydrogen sulphide
HBA	hydrogen bond acceptors
HBD	hydrogen bond donors
HCOOH	formic acid
HDS	hydro-desulphurization
H_2O_2	hydrogen peroxide
ILs	ionic liquids
$LaCl_3$	lanthanum(III) chloride
LiCl	lithium chloride
MA	malonic acid
MDESs	metal ions based DESs
ODS	oxidation-desulphurization
PEG	polyethylene glycol
Pr	propionic/propionate
p TsOH	*p* toluenesulphonic acid
SO_2	sulphur dioxide
TBAB	tetra butyl ammonium bromide
TBAC	tetra butyl ammonium chloride
TBPB	tetrabutylphosphonium bromine
TEG	tetra ethylene glycerol
TMAC	tetra methyl ammonium chloride
$SnCl_2$	tin(II) chloride
$SnCl_4$	tin(IV) chloride
TS	thiophene
TEtA	trimethylamine
QAS	quaternary ammonium salts

YCl_3	yttrium(III) chloride
$ZnCl_2$	zinc chloride

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