# Desulfurization of diesel oil by selective oxidation and extraction of sulfur compounds by ionic liquids—a contribution to a competitive process design†

**Andreas Seeberger**[*a] **and Andreas Jess**[b]

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Extraction of S-compounds like dibenzothiophenes from diesel oil by ionic liquids (ILs) indicate that such a process could be an attractive alternative to common (deep) desulfurization by hydrotreating. The efficiency of the extraction increases if the S-species are previously oxidized to the corresponding sulfoxides and sulfones as these species have a much higher distribution coefficient compared to the non-oxidized derivatives. The present work combines the extraction of oxidized S-compounds from diesel oil by ILs and the subsequent IL regeneration, *i.e.* the removal of the oxidized S-species from the S-loaded IL by means of water addition which leads to a displacement of the S-compounds from the IL. Thus, water separation by evaporation is needed before the IL can be re-used for extraction. Model oils containing single sulfones as well as real pre-oxidized diesel oils were investigated. Based on the experimental results the energy consumption of the extractive desulfurization process was estimated. The evaporation of water from the IL is the crucial step with regards to the energy consumption of the process. The energy demand is comparable to classical hydrotreating, if a multi-stage evaporation is used.

## Introduction

During the last four decades much attention has been given to the deep desulfurization of transportation fuels like diesel oil and gasoline since the sulfur-limits for these fuels were gradually decreased, *e.g.* in Europe for diesel fuel from about 5000 ppmw in the 1970s to 10 ppmw nowadays (1 ppm = 1 mg kg$^{-1}$). For fuel cells (both for automotive and stationary systems) liquid fuels like gasoline or diesel oil are important as a source for the fuel gas (respectively $H_2$), at least for bringing such systems onto the market. Then a S-content of even less than 10 ppmw S is needed or desirable.

State of the art in desulfurization technology is hydrodesulfurization (HDS). Thereby the organic S-compounds are converted to $H_2S$ and the corresponding hydrocarbons using catalysts mostly based on CoMo or NiMo. Typical reaction conditions are 350 °C and 30 to 100 bar hydrogen pressure. So high pressure reactors are needed, resulting in high investment costs. Hydrogen, which is fed into the HDS-reactor together with preheated oil is only consumed to a small extent in the trickle bed reactor and needs to be separated from the desulfurized oil and recycled into the reactor. Typically, recycle-rates of up to 50 are needed, which results in high (re)compression costs.

The reactivity of sulfur compounds for HDS strongly depends on the molecular structure. While thiols, thioethers and disulfides are readily converted, cyclic and aromatic sulfur compounds like thiophenes or benzothiophenes are much less reactive.[1-3] Particularly refractory are dibenzothiophene (DBT), methyldibenzothiophenes (MDBT) and above all 4,6-dibenzothiophene (4,6-DMDBT).

The rate to convert these species by HDS decreases in the named order by factors of about 2 and 10, respectively.[1-3] Thus, conventional HDS-technology is limited or at least expensive for deep desulfurization, and ultra-low sulfur specifications for diesel and fuel oils with a high content of DBT-derivatives can only be met by severe reaction conditions with respect to pressure and residence time (reactor size), which both lead to a higher $H_2$-consumption. An increase of the HDS-activity of the catalysts by a higher temperature is limited, because undesired side reactions (cracking, coke formation and thus catalyst deactivation) are then accelerated.

The extractive desulfurization of fuels like diesel oil by ionic liquids (ILs) is discussed for several years now as an interesting alternative route to provide ultra clean diesel oils.[4-8] Clear advantages of such an extractive desulfurization are that such a process would work at or around ambient temperature and pressure and without the need for hydrogen. However, two drawbacks have often been identified that prevent an extraction process based on ILs from large scale realization.

Although many ionic liquids show reasonable distribution coefficients for model sulfur compounds present in diesel oil such as for dibenzothiophene (DBT), the distribution coefficients reached for real diesel oils are relatively poor,[5] see Table 1. Pre-desulfurized diesel oils (*e.g.* with 100 ppm S) still have to be desulfurized to less than 10 ppm, and mostly contain

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[a] *SepaPro GmbH, An der Heide 16, 92353, Postbauer-Heng, Germany. E-mail: andreas.seeberger@sepapro.de; Fax: 49 9180 941482; Tel: 49 9180 941442*
[b] *University of Bayreuth, Department of Chemical Engineering, 95447, Bayreuth, Universitaetsstr. 30, Germany. E-mail: jess@uni-bayreuth.de; Fax: 49 921 557435; Tel: 49 921 557430*

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**Table 1** Sulfur partition coefficients $K_N$ (definition see eqn (1)) for extraction of DBT and DBT-derivatives with [BMIM][OcSO$_4$] from n-dodecane (model oils) and from various S-species present in real pre-desulfurized diesel oil (data from Ref. 5)

| S-Compound | $K_N$ in mg S$^{-1}$ kg$^{-1}$(IL)/g S$^{-1}$ kg$^{-1}$(oil) |
|---|---|
| DBT | 1.9 |
| 4-MDBT | 1.3 |
| 4,6-DMDBT | 0.9 |
| Various S-species | 0.3–0.8 |

only multiple alkylated dibenzothiophenes. These compounds show lower distribution coefficients compared to DBT, which results in a reduced extraction efficiency and a higher number of extraction steps, respectively.

An interesting option to increase the distribution coefficients is the selective oxidation of the sulfur compounds to the respective sulfoxides and sulfones.[9–13] By this means the polarity of the sulfur compounds and thus the extractability by ILs increases.

The second problem of an extractive desulfurization process based on ILs is the regeneration of the sulfur loaded IL after extraction. Three methods are mostly considered: (1) The sulfur compounds are directly removed from the IL by distillation, but in case of diesel or heating oil, (high) vacuum would be needed, as the normal boiling point of sulfur compounds such as alkylated dibenzothiophenes is high (about 340 °C for 4,6-DMDBT). Thus, this method is probably only applicable for desulfurization of gasoline where the S-species have a relatively low boiling point. (2) Secondly, the S-compounds may be reextracted by a low-boiling organic solvent, but then an additional separation step is needed, *e.g.* the distillative separation of the S-compounds and the solvent. (3) Thirdly, the S-compounds could be displaced by the addition of water to the S-loaded IL as the distribution coefficient strongly decreases to almost zero if enough water is added.[14,15] The sulfur compounds then form a second liquid phase (mostly together with small amounts of hydrocarbons that are also extracted by the IL) or sometimes even precipitate.[12]

## Experimental

The ionic liquid used in this work is 1-ethyl-3-methylimidazolium diethylphosphate [EMIM][DEP]. The IL was purchased from Merck/Solvent Innovation (Darmstadt) and was used without further purification. The water content was measured by a Karl-Fischer titration (Metrohm 831 KF).

As a model diesel oil n-dodecane from Haltermann (99%) mixed with selected S-compounds such as dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), and the oxidized sulfur compound dibenzothiophene sulfone (DBTO$_2$) were used (all purchased from Sigma Aldrich).

Pre-desulfurized "real" diesel oil (here named conventional diesel oil, Con-DO) with 130 ppmw sulfur was provided by the MiRO refinery (Karlsruhe). Pre-desulfurized diesel oil with completely oxidized sulfur compounds (here named Preox-DO, 100 ppmw sulfur) was provided by Eni R&M Division, R&D Department (formerly EniTecnologie, Milan).

The sulfur concentration in the different oils was measured by an Antek Elemental Analyzer 9000. The identification of single sulfur compounds was done by means of a sulfur specific gas chromatography (Varian CP 3800 with pulsed flame photometric detector). The gas chromatograms can be found in the ESI.†

The extraction experiments were conducted using an IL-to-oil ratio (related to mass) of one, starting for the multistep experiments with 20 g of both oil and IL in the first extraction step (see Fig. 3). For one step extractions (determination of $K_N$ values) 5 g of each, oil and IL, were used. Extraction time was 15 min in a turbulent stirred system. It was assured (by respective experiments with varied mixing time) that the extraction equilibrium was always reached. For a given ratio of the mass of the IL-phase to the mass of oil the sulfur content in the IL after the extraction is calculated based on the measured remaining sulfur content in the oil and a mass balance with respect to sulfur. The corresponding distribution coefficient $K_N$ is defined by

$$K_N = \frac{m_{\text{S,IL-phase}} / m_{\text{IL-phase}}}{m_{\text{S,oil}} / m_{\text{oil}}} \qquad (1)$$

The measurement of the boiling temperatures of IL/water-mixtures with different water content was carried out at atmospheric pressure. The mixture was slowly heated in a well-mixed glass cylinder. As soon as boiling was visible (bubble formation) the respective temperature was noted and the water concentration in the IL-water-mixture was determined by Karl-Fischer-titration.

## Results and discussion

Appropriate ILs with good extraction characteristics, which are mostly discussed in the literature, are imidazolium-, pyridinium- or quinolinium-based ILs with anions such as alkylsulfates, alkylphosphates or halogen-containing anions.[5,8,15,16] An ideal IL should have a high distribution coefficient for S-compounds, a low cross solubility of hydrocarbons, a low viscosity, and a fast phase separation rate after mixing/extraction. Considering the thermal and hydrolytic stability as well as availability and costs, the halogen-free IL 1-ethyl-3-methylimidazolium diethylphosphate [EMIM][DEP] seems to be a good candidate for practical use and was therefore considered in this work.

### 1. Extraction of oxidized sulfur compounds

Usually, dibenzothiophene (DBT) is used as the standard model S-compound in the open literature for experiments on desulfurization by extraction or by other means. However, DBT is not really representative for the remaining S-species present in pre-desulfurized diesel oil. The much more refractory S-species 4,6-dimethyldibenzothiophene (4,6-DMDBT) represents much better the S-species left in pre-desulfurized diesel oil.

Table 2 shows that for the given IL ([EMIM][DEP]) DBT (in n-dodecane) shows a fairly good distribution coefficient of 1.5 whereas 4,6-DMDBT only has a $K_N$-value of 0.3. For real pre-desulfurized diesel oil (Con-DO), an even lower (mean) distribution coefficient of 0.2 is obtained. For an attractive industrial extraction process a distribution coefficient between 1 and 5 would be ideal. (If the $K_N$-value is too high, the regeneration of the S-loaded IL may be problematic). Thus, the

**Table 2** Distribution coefficients of model and real diesel oils if [EMIM][DEP] is used for extraction[a]

| Oil | Sulfur content | Sulfur compound/s | Distribution coefficient $K_N$ (mg S kg$^{-1}$ IL)/(mg S kg$^{-1}$ oil) |
|---|---|---|---|
| Model diesel oil | 170 ppmw in n-dodecane | DBT | 1.5 |
| Model diesel oil | 101 ppmw in n-dodecane | 4,6-DMDBT | 0.3 |
| Pre-desulfurized conventional diesel oil (Con-DO) | 129 ppmw | Various sulfur species | 0.2 |
| Model diesel oil | 243 ppmw in toluene | $DBTO_2$ | 5.4 |
| Pre-desulfurized and pre-oxidized diesel oil (Preox-DO) | 27 ppmw (determined by GC analysis) | 4,6-$DMDBTO_2$ | 3.2 |
| Pre-desulfurized and pre-oxidized diesel oil (Preox-DO) | 100 ppmw | Various oxidized S-species | 2.1 |

[a] Mass ratio oil:IL = 1 : 1, mixing time 15 min, 23 °C. $DBTO_2$ was dissolved in toluene as the solubility in n-$C_{12}$ is poor.

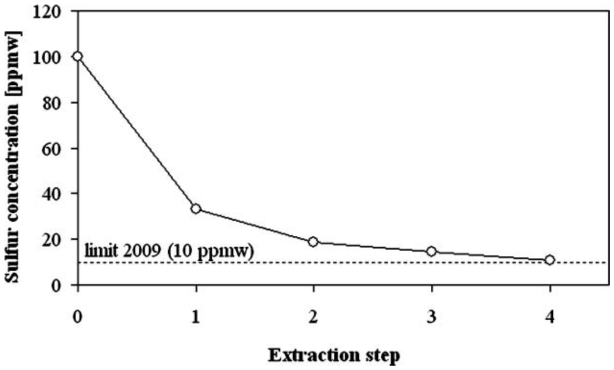

**Fig. 1** Multi-step cross flow extraction of real diesel oil with oxidized sulfur compounds (Preox-DO) with [EMIM][DEP] (mass ratio oil : IL = 1 : 1, 23 °C).

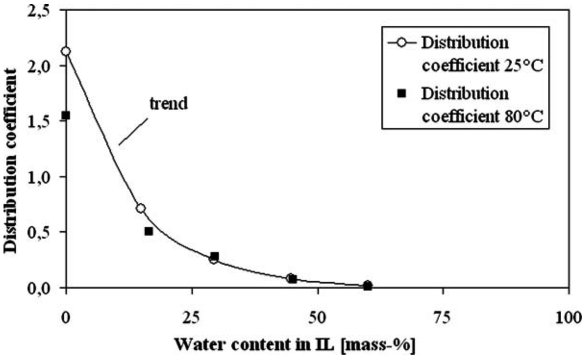

**Fig. 2** Extraction of real diesel oil with oxidized sulfur compounds (Preox-DO) with [EMIM][DEP] at elevated water content and different temperatures (mass ratio oil : IL-phase = 1 : 1).

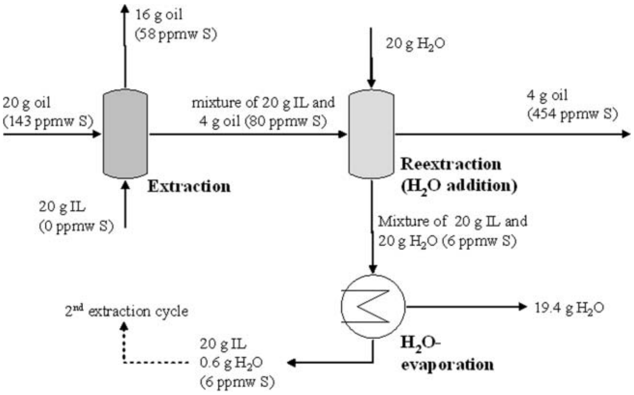

**Fig. 3** Extraction of a model diesel oil (DBT in n-dodecane) with [EMIM][DEP] with IL-regeneration by $H_2O$-addition (143 ppmw S as DBT in n-dodecane, water content used for IL-regeneration: 50 mass-%, extraction temperature: 23 °C, water evaporation: 30 mbar, 85 °C, 5 h).

IL [EMIM][DEP] is (as other ILs also) not an ideal candidate for deep desulfurization of real pre-desulfurized diesel oil.

The extraction is considerably improved if the corresponding sulfones are used. If for example dibenzothiophene sulfone ($DBTO_2$) mixed with toluene is used as model oil, the distribution coefficient increases to 5.4 compared to a value of 1.5 for DBT (Table 2). This effect is also given for real diesel oil if all sulfur compounds are pre-oxidized (Preox-DO, Table 2). Now a value for $K_N$ of 2.1 is reached compared to a value of 0.2 for conventional (non pre-oxidized) pre-desulfurized diesel oil (Con-DO). In the present work no investigations were made on the selective oxidation of sulfur compounds. The diesel oil Preox-DO was provided by an industrial partner (Eni R&M Division) who claims that the $H_2O_2$-based oxidation process is economically feasible on a large scale.[17]

The distribution coefficient which is measured for real diesel oils is in general a mean value and depends on the concentration and structure of all sulfur compounds that are present in the oil. Hence, a multi-step desulfurization of diesel oil (Preox-DO, cross flow extraction) was done (Fig. 1). In this particular case only four extraction steps are necessary to reduce the total sulfur concentration from 100 ppmw to the current European limit of 10 ppmw. At the same time the distribution coefficient decreases from initially 2.1 to 0.3 in the final (4th) extraction step.

The exact identification of single pre-oxidized sulfur compounds by the sulfur specific gas chromatography was only possible for $DMDBTO_2$ (lack of respective standards), but the retention times indicate that only oxidized multiple alkylated DBT derivatives are present if the total residual S-content reaches an order of magnitude of 10 ppmw.[18]

## 2. Regeneration of the ionic liquid by addition of water

By adding water to an ionic liquid (which then should of course be miscible with water as in the case of the investigated IL [EMIM][DEP]) the solubility of sulfur compounds in the IL/water-phase drastically decreases. For the sulfur *extraction* this is certainly counterproductive, but this method could be used for a facile and complete displacement of the S-compounds during the *regeneration* of the S-loaded IL as recently shown by Nie *et al.* and Jiang *et al.* for the removal of model sulfur species such as benzothiophene (BT) or DBT from alkylphosphate-based ILs.[14,15] In the present work this regeneration concept was tested for the displacement of oxidized and conventional non-oxidized S-species from [EMIM][DEP]. As a measure for the influence of the water content on the displacement of S-species from a S-loaded IL, the partition coefficient $K_N$ can be used, which can be regarded as the reverse of displacement, *i.e.* $K_N$ is zero for 100% displacement. Different IL-water mixtures were mixed with model oils or real diesel oils that contain single or various oxidized and non-oxidized S-species, respectively, and the distribution coefficient was measured after phase separation.

A typical experimental result is shown in Fig. 2 for [EMIM][DEP]/water mixtures and pre-oxidized diesel oil. It is obvious, that a water content of about 60 mass-% in the IL/water mixture leads to a distribution coefficient of zero, and thus to a complete displacement of all S-species. The influence of the temperature is rather small, and only for a water content of less than about 20 mass-% an increase of temperature leads to a slight decrease of the distribution coefficient $K_N$. At high water concentrations, $K_N$ is independent of temperature.

Very similar results were obtained for the conventional diesel oil and for model diesel oils that contain DBT or 4,6-DMDBT. In all cases, a water content in a range of 40 to 60 mass-% leads to a distribution coefficient of zero and thus to a complete displacement in the S-loaded IL (see Table 3).

For a further test of the concept to use water addition for IL regeneration, a multi-step extraction experiment with model oil (DBT in n-dodecane) as well as with real (pre-oxidized) diesel oil (Preox-DO) with subsequent IL regeneration was conducted. After the extraction of the diesel oil by the IL, the S-loaded IL and the partly desulfurized oil were separated. A small fraction of the hydrocarbons is also soluble in the IL (cross-solubility, here 10% to 20%). If enough water (here 50 mass-%) is added to the IL, this oil fraction and all S-compounds are displaced from the IL and form a second phase. (In case of an industrial process based on the presented concept of IL-extraction/regeneration, this S-rich oil fraction would then be recycled and fed to the HDS process for pre-desulfurization.)

After each regeneration step, the water was separated from the IL by evaporation (30 mbar, 85 °C, 5 h). The (small) remaining water content was measured by Karl-Fischer-titration and the IL was then re-used in the next extraction step. The results are presented in Fig. 3 for the first extraction/regeneration step of DBT removal from model diesel oil and in Fig. 4 for a five-step extraction/regeneration of model oil (DBT in n-dodecane) as well as of real diesel oil that contains oxidized S-species (Preox-DO).

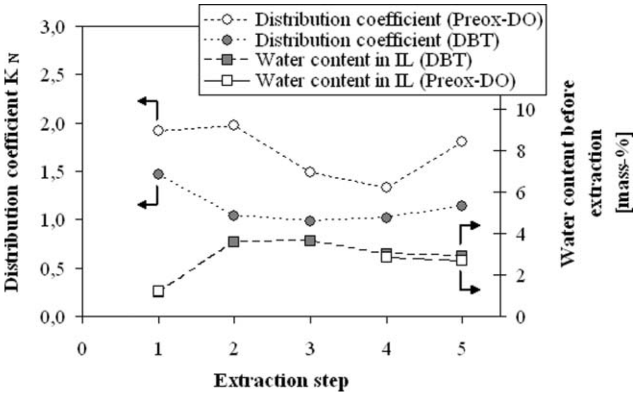

**Fig. 4** Multi-step extraction of model diesel oil (DBT) and of real diesel oil with oxidized sulfur compounds (Preox-DO) with [EMIM][DEP] with IL regeneration by $H_2O$-addition (model diesel oil: 143 ppmw S as DBT in n-dodecane, real diesel oil: Preox-DO with 100 ppmw oxidized sulfur, water content for IL regeneration: 50 mass-%, 23 °C, water evaporation: 30 mbar, 85 °C, 5 h).

For the given rotary evaporator used to separate the water from the IL, a residual water content of the IL in a range of 2 to 3% was reached. Therefore, the distribution coefficient in the second to fifth extraction step (Fig. 4) is slightly lower compared to a complete dry IL used in the first step (Table 2).

The result of the multi-step extraction and regeneration shows that the IL regeneration by $H_2O$ addition is an interesting option for a technical desulfurization process based on ILs but the energy consumption needed for the water evaporation should be not be too high. This aspect was therefore investigated in more detail and is subsequently discussed.

## 3. Energy consumption of IL regeneration

The vaporization of water is an energy-intensive process due to the relatively high enthalpy of vaporization of $H_2O$. In an extractive ionic liquid based desulfurization process combined with water addition for IL regeneration, this step is therefore crucial and has to analysed in more detail.

The following five basic conditions and assumptions were used for this analysis:

- The sulfur content in the diesel oil (Preox-DO) should be decreased from 100 ppmw to 10 ppmw.
- The extraction process is realized in a counter current operated column. Based on the experimental results of the cross flow extraction using [EMIM][DEP] (Fig. 1), the classical

**Table 3** Required water content in [EMIM][DEP] for a complete displacement of S-species from the IL (distribution coefficient $K_N = 0$)

| Oil | Sulfur content | Sulfur compounds | Water content in IL/water mixture needed to reach $K_N = 0$ |
|---|---|---|---|
| Model diesel oil | 170 ppmw in n-$C_{12}$ | DBT | 45 mass-% |
| Model diesel oil | 101 ppmw in n-$C_{12}$ | 4,6-DMDBT | 50 mass-% |
| Con-DO | 129 ppmw | Various S-species | 55 mass-% |
| Preox-DO | 100 ppmw | Various oxidized S-species | 60 mass-% |

McCabe-Thiele approach leads to a ratio of IL to oil of 1.4, if the number of theoretical separation (extraction) stages is limited to five stages which is a reasonable order of magnitude (details in Ref. 18).

- A water content of 50 mass-% in the IL/water mixture is sufficient to regenerate the S-loaded IL almost completely by displacement of the S-species and formation of a S-rich oil phase consisting of all S-species and a small fraction of hydrocarbons also solved in the IL during extraction.
- The separation of water from brines if often done by multi-stage evaporation at different pressure and temperature levels. Here a four-stage evaporation process was assumed.
- The boiling temperature of the water/IL-mixture depends on the IL-content. For a given total pressure, an increasing content of the IL leads to an increase of the boiling temperature of the mixture. For an accurate design of the IL regeneration the respective correlation has to be known which (as shown below) can by far not been simply calculated based on the assumption of an ideal mixture (Raoult's law). As shown in Fig. 5, the measured boiling temperatures of the water/IL-mixture strongly deviates from the values expected for an ideal mixture of water and a second compound with a negligible vapor pressure (here the IL).

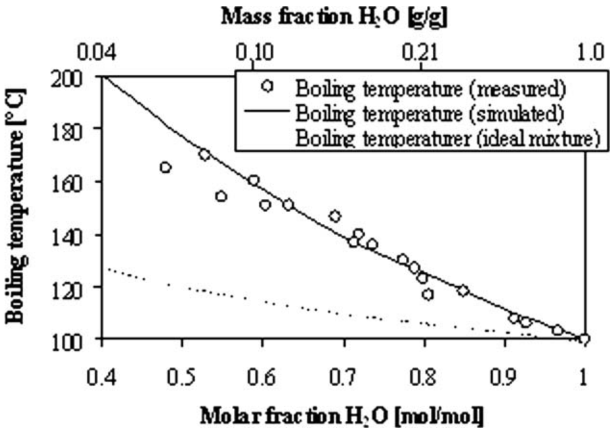

**Fig. 5** Boiling temperature of $H_2O$ at 1 bar depending on the molar fraction of $H_2O$ in [EMIM][DEP] (dashed curve: expected boiling temperature (Raoult's law) for an ideal solution, *i.e.* $\gamma_{H_2O} = 1$).

The partial pressure of water in an aqueous salt solution is given by:

$$p_{H_2O} = \gamma_{H_2O}\, \tilde{x}_{H_2O,IL}\, p_{H_2O,0}(T) \tag{2}$$

with

$p_{H_2O}$ being the partial pressure of water in the gas phase,

$\gamma_{H_2O}$ being the activity coefficient of water (= 1 for an ideal solution, *i.e.* if Raoult's law is valid),

$\tilde{x}_{H_2O,IL}$ being the molar fraction of $H_2O$ in the IL-$H_2O$-phase,

$p_{H_2O,0}$ being the vapor pressure of $H_2O$ (calculated by the Antoine-Equation).

The molar fraction of $H_2O$ ($\tilde{x}_{H_2O,IL}$) can be derived from the mass fraction $x_{H_2O,IL}$ if we assume that the IL mainly consists of ion pairs as reported in the literature:[19]

$$\tilde{x}_{H_2O,IL} = \frac{n_{H_2O}}{n_{H_2O} + n_{IL}} = \frac{m_{H_2O}}{m_{H_2O} + \frac{\tilde{M}_{H_2O}}{\tilde{M}_{IL}} m_{IL}} = \frac{x_{H_2O,IL}}{\left(x_{H_2O,IL} + \frac{\tilde{M}_{H_2O}}{\tilde{M}_{IL}}\left(1 - x_{H_2O,IL}\right)\right)} \tag{3}$$

where $x$ is the mass fraction [–], $\tilde{x}$ is the molar fraction [–], $\tilde{M}$ is the molar mass $\tilde{M}_{[EMIM][DEP]} = 264.26$ g mol$^{-1}$ [kg mol$^{-1}$], $m$ is the mass [kg], $n$ is the substance quantity [mol]

For a given molar fraction of $H_2O$ ($\tilde{x}_{H_2O,IL}$, eqn (3)), the activity coefficient is calculated by eqn (2) based on the measured boiling points at total = 1 bar ( = $p_{H_2O}$) and the values of the vapor pressure of pure water at that temperature ($p_{H_2O,0}$). Fig. 6 shows that in a range of $0.04 < x_{H_2O,IL} < 1$ ($0.4 < \tilde{x}_{H_2O,IL} < 1$) the influence of water on the activity coefficient can be estimated by the following correlation:

$$\gamma_{H_2O} = 0.1 + 0.9 \cdot \tilde{x}_{H_2O,IL}^{\ 3} \text{ (for } \tilde{x}_{H_2O,IL} > 0.4) \tag{4}$$

where $\gamma$ is the activity coefficient [–].

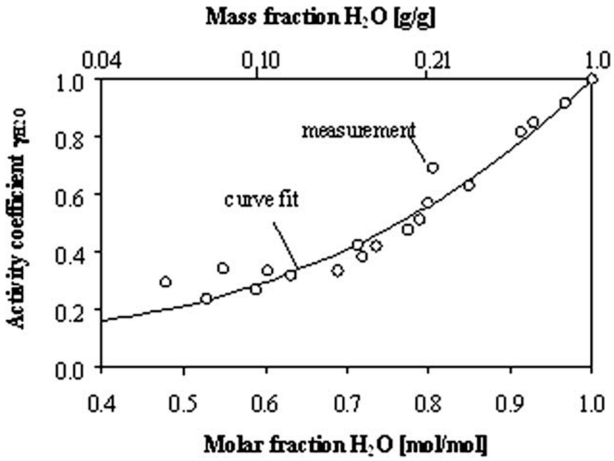

**Fig. 6** Experimental determination and curve fit of the activity coefficient $\gamma_{H_2O}$.

Insertion of eqn (4) into eqn (2) leads to the simulated boiling temperatures already shown in Fig. 5.

By eqn (2) the total pressure and the corresponding boiling temperatures in the different stages of a multi-stage evaporation process were calculated, which leads to the regeneration scheme of a water/IL-mixture as shown in Fig. 7 (data in Table 4). Thereby, the following assumptions were made:

- The temperatures and pressures of the four evaporation steps are determined by the water concentration which has to be reached. The starting values of stage 1 (V-1) are ambient pressure (1 bar), an initial mass content of 50% water, and thus a boiling temperature of 109 °C (see Fig. 5).
- The temperatures and pressures of the four evaporation steps are determined by the water concentration which has to be reached. The starting values of stage 1 (V-1) are ambient pressure (1 bar), an initial mass content of 50% water, and thus a boiling temperature of 109 °C (see Fig. 5).
- The evaporation process consists of four stages, and the water content is reduced to 5 mass-%, which corresponds to a final molar content $\tilde{x}_{H_2O,IL}$ of 0.44.

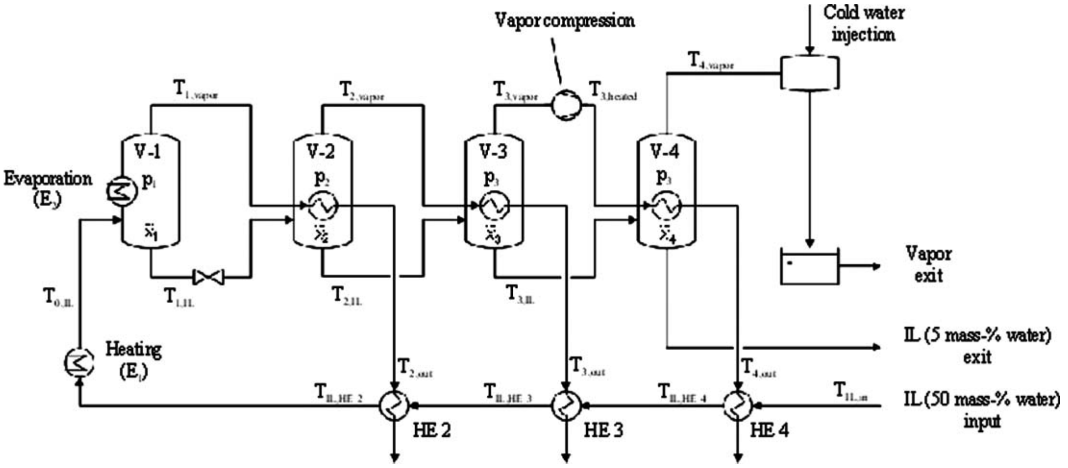

**Fig. 7** Multi-stage evaporation process of IL regeneration for the estimation of the energy demand.

**Table 4** Data of the multi-stage evaporation process of IL regeneration as shown in Fig. 7

| Parameter | Symbol | Value | Unit |
|---|---|---|---|
| Mass fraction of $H_2O$ in IL | $x_1$ | 0.433 | — |
| | $x_2$ | 0.345 | — |
| | $x_3$ | 0.224 | — |
| | $x_4$ | 0.050 | — |
| Molar fraction of $H_2O$ in IL | $\tilde{x}_1$ | 0.92 | — |
| | $\tilde{x}_2$ | 0.89 | — |
| | $\tilde{x}_3$ | 0.81 | — |
| | $\tilde{x}_4$ | 0.44 | — |
| Pressure in evaporators | $p_1$ | 1.00 | bar |
| | $p_2$ | 0.50 | bar |
| | $p_3$ | 0.17 | bar |
| | $p_{3,\text{heated}}$ | 0.59 | bar |
| | $p_4$ | 0.035 | bar |
| Temperature of vapor | $T_{1,\text{vapor}}$ | 109 | °C |
| | $T_{2,\text{vapor}}$ | 93 | °C |
| | $T_{3,\text{vapor}}$ | 74 | °C |
| | $T_{3,\text{heated}}$ | 86 | °C |
| | $T_{4,\text{vapor}}$ | 86 | °C |
| Temperature of IL- $H_2O$-phase | $T_{\text{IL,in}}$ | 25 | °C |
| | $T_{\text{IL,HE 4}}$ | 33 | °C |
| | $T_{\text{IL,HE 3}}$ | 39 | °C |
| | $T_{\text{IL,HE 2}}$ | 46 | °C |
| Temperature of condensate | $T_{2,\text{out}}$ | 100 | °C |
| | $T_{3,\text{out}}$ | 81 | °C |
| | $T_{4,\text{out}}$ | 86 | °C |

- In each stage, the same amount of water is separated. This assumption leads to the molar and mass fractions as listed in Table 4.
- The condensation enthalpy of the vapor that leaves each stage is re-used by heat exchange in the next stage by evaporation at a lower pressure and lower temperature.
- Between the condensing vapor and the boiling IL/water–mixture a minimum temperature difference of 7 °C is assumed to ensure an efficient heat transfer and an acceptable size of the heat transfer area.
- The condensed vapor streams are further used to pre-heat the IL-water-feed (HE 2 to HE 4).
- In the second and third stage (V-2 and V-3) vacuum is applied to enable water evaporation (0.5 bar in V-2 and 0.17 bar in stage 3).
- In the evaporator V-4 a pressure of 35 mbar is assumed as this is the value that can be typically reached by cold water injection. Then the condensation temperature of the vapor leaving the third stage (V-3) is not sufficiently high for evaporation at 35 mbar in stage four (V-4). Thus, the saturated vapor is compressed from 0.17 bar to 0.59 bar to reach a respective increase of temperature (here from 74 °C to 86 °C).

The following energy demands are needed according to Fig. 7 and Table 4:

### Pre-heating of feed and vaporization in the first stage (IL/water-mixtrue with 50 mass% water)

The sensible heat of the condensed vapors (with $T_{2,\text{out}}$ to $T_{4,\text{out}}$) is used to pre-heat the IL-water-mixture in the heat exchangers HE 2 to HE 4. The temperatures of the IL-water mixture and of the water at the in- and outlet of the heat exchangers are determined under the assumption of ideal co-current heat exchangers and a minimum temperature difference between the hot and cold fluid of not less than 7 °C. For the heat capacity of water and of the IL values of 1.8 and 4.16 kJ $\text{kg}^{-1}$ $\text{K}^{-1}$ were used. This calculation leads to a temperature of the pre-heated IL/water-feed of 46 °C when leaving the last heat exchanger HE 2 (Fig. 7). Thus, energy is needed for further heating to the boiling temperature of stage 1 (109 °C, $E_{\text{preheating}}$), and to evaporate the respective amount of water (12 mass-% of the feed, $E_{\text{evaporation}}$). The specific energy demand is given by:

$$E_{\text{preheating}} + E_{\text{evaporation}} = c_{\text{p,IL,in}}\Delta T + 0.237\Delta h_{\text{evaporation,H}_2\text{O}} = 723\frac{\text{kJ}}{\text{kg H}_2\text{O}} \tag{5}$$

where $E$ is the specific energy demand [J $\text{kg}^{-1}$], $c_\text{p}$ is the heat capacity [J $\text{kg}^{-1}$ $\text{K}^{-1}$], $T$ is the temperature [K] and $h$ is the specific enthalpy [J $\text{kg}^{-1}$].

### Vapor compression

The specific energy demand for the vapor compression between stage 3 and 4 (see Fig. 7) is calculated by the isentropic enthalpy difference $\Delta h_{\text{isentropic}}$ and the effectiveness factor $\eta$:

$$E_{\text{compression}} = \frac{\Delta h_{\text{isentropic}}}{\eta} = \frac{\kappa}{\kappa - 1}\frac{RT_1}{\tilde{M}_{\text{H}_2\text{O}}\,\eta}\left[\left(\frac{p_{3,\text{heated}}}{p_3}\right)^{\frac{\kappa-1}{\kappa}} - 1\right] = 278\frac{\text{kJ}}{\text{kg H}_2\text{O}} \quad (6)$$

where $\kappa$ is the adiabatic exponent [–].

Here, a value of the adiabatic exponent of water vapor $\kappa$ of 1.33 was used (value at mean temperature 70 °C). As the compression will not be isentropic an effectiveness factor ($\eta$) of 0.8 was assumed.

### Total energy requirements

In the extraction column, an IL-to-oil ratio according to the McCabe-Thiele approach of 1.4 is needed. Thus for the desulfurization of one kg of diesel oil, 1.4 kg of ionic liquid is regenerated by the addition of 1.4 kg of water. This leads to the overall energy consumption related to the mass of oil:

$$E_{\text{total}} = 1.4\frac{\text{kg H}_2\text{O}}{\text{kg oil}}\left(E_{\text{preheating}} + E_{\text{evaporation}} + E_{\text{compression}}\right) = 1401\frac{\text{kJ}}{\text{kg oil}} \quad (7)$$

This value is about 3.3% of the heating value of diesel oil (42,500 kJ kg$^{-1}$) if we neglect other energy expenses (pumps, pre-oxidation step to produce oxidized S-species). This value is close to the classical hydrotreating process where the energy consumption is in between 1.5% (without $H_2$-production) and 4% (incl. $H_2$-production) of the heating value of the processed diesel oil.[20] Considering the much easier process design of the extraction process (almost ambient pressure and temperature, no need of a catalyst), this leads to the conclusion, that the new process may be competitive or even advantageous for deep desulfurization compared to the HDS-route, above all if not enough hydrogen (as a by-product of reforming of gasoline) is available and has to be produced by steam reforming of natural gas/refinery gas or partial oxidation of heavy oils.

## Conclusions

The extraction of sulfur species from diesel oil by ionic liquids (ILs) is improved by a pre-oxidation of the S-species to the corresponding sulfones and sulfoxides as they have higher partition coefficients compared to the non-oxidized S-species. This is shown here for DBT-derivatives (model oils) and for real pre-oxidized diesel oils, thereby taking the IL 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]) as instructive example.

The regeneration of the sulfur-loaded IL is a crucial step with regard both to the efficiency of the process and the required energy. An efficient regeneration is possible by the addition of water. A water content of 50 mass-% in the IL/water mixture leads to an almost complete displacement of the sulfur species. Thereby, a S-free IL/water–mixture and a S-rich oil phase is formed which consists of all sulfur species and of hydrocarbons which are also solved to a small extent during extraction.

In order to re-use the IL for extraction, the separation of the water by evaporation is needed which can be done by a multi-stage evaporation process in order to save energy. For the design of such a process, the normal boiling points of different water/IL-mixtures were measured and a correlation between the water content and the activity coefficient of water was determined. For the given IL ([EMIM][DEP]), the activity coefficient strongly decreases with increasing IL-content, *i.e.* the boiling point is higher than what is expected according to Raoult's law (ideal mixture with an activity coefficient of one).

The basic design data of a four-stage evaporation process with integrated heat transfer is given. The total energy demand is about 3% of the heating value of the processed diesel oil. This is in the same order of magnitude of the conventional hydrotreating process if the production of hydrogen needed in this case is considered. The new desulfurization process based on pre-oxidation of all S-species, extraction of these species and regeneration of the IL by water addition and subsequent multi-stage evaporation could be an interesting option for deep desulfurization, above all if hydrogen is not available and has to be produced in a separate plant.

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