Shifting desulfurisation equilibria in ionic liquid-oil mixtures

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Abstract

Ionic liquids (ILs) and deep eutectic solvents have been used for the extraction of molecules, particularly natural products. An often studied system is that for thiophene removal from oil. In the current study, ILs have been used for the removal of thiophene (Th), benzothiophene (BT) and dibenzothiophene (DBT) by liquid-liquid extraction. The equilibrium can be shifted by polymerising the thiophenic compounds both electrochemically and chemically. A 1:1 mixture of 1-butyl-3-methylimidazolium chloride (Bmim)Cl and FeCl₃ was used to extract Th and BT from alkane layers using electropolymerisation to shift the position of the equilibrium. While the process could be carried out, the kinetics of polymer formation were too slow to make this a viable process. The final part of the study used a 1:2 (Bmim)Cl: FeCl₃ mixture to chemically remove sulfur containing compounds from alkane layer. It was shown that the rate of the chemical polymerisation reaction of Th is around 1500 times faster than electrochemical polymerisation. Issues associated with the regeneration of the liquid are discussed.

Key words: Thiophene, liquid-liquid extraction, electrochemical polymerisation, desulfurization, imidazolium ionic liquids.

Introduction

Ionic liquids and deep eutectic solvents (DESs) have been proposed as solvents for extraction although one obvious drawback is that the solutes are difficult to remove from the ionic phases as they have low vapour pressures.¹ Liquid-liquid extraction has been extensively studied for the removal of metals from aqueous solutions using hydrophobic ILs and the removal of sulfur containing compounds from oils using hydrophilic ILs.² While numerous solutes have been extracted, relatively little is known about the specificity and thermodynamics of extraction.

A recent study on the extraction of thiophenic compounds from alkane phases into DESs showed that extraction was limited by enthalpic change and driven by entropic change. In most cases the enthalpy of extraction was endothermic limited by the energy required to create a hole in which to put the solute. The highest partition coefficients were found with the liquids with the lowest surface tensions and therefore the lowest cohesive energy densities.³

The extraction of thiophene and its polyaromatic analogues has been studied by several groups in different DESs and while efficient extraction has been observed little is known about the process. Lewis acidic tetrachloroferrate based ILs, particularly those containing imidazolium cations, are very efficient at chemically removing sulfur containing compounds from alkane based liquids. The advantage of using an iron-based catalyst is naturally that it is sustainable and hence has a low cost.

Dharaskar and coworkers used a 1:1(BmimCl): FeCl₃ mixture and found that 59.2% of Th was extracted.⁴ The authors proposed a specific interaction between thiophene and the Fe^{III}-based anion. Li et al.⁵ and Yang et al.,⁶ studied the adsorption of thiophene using a Ag⁺ or Cu⁺-Y zeolite. They found that the metals interacted with the thiophene π orbitals with a donation into the vacant σ orbitals of the metal and a back donation of electron charge to the π^* orbital of thiophene from the d orbitals of metals. The authors believed that the same mechanism occur with the Lewis acidic FeCl₃ based-triethyl ammonium chloride.

In the current study, the extraction and polymerisation of thiophene (Th), benzothiophene (BT) and dibenzothiophene (DBT) was studied from alkanes. Initially, these compounds are extracted and then electropolymerised from decane in an equimolar (Bmim)Cl- FeCl₃ mixture. In the second part, the extraction and chemical polymerisation was carried out in 1:2 (Bmim)Cl: FeCl₃ to compare and determine the rate of their reactions.

Experimental

All materials and reagents employed in this work: ferric chloride, 1-Butyl-3-methylimidazolium chloride, n-decane, thiophene and dibenzothiophene (all Sigma-Aldrich $\geq 99\%$), benzothiophene (Alfa Aesar $> 98\%$), were all used as received. (Bmim)FeCl₄ eutectic mixture has been made according to the literature procedure.⁷

In the extraction experiments, different solutions of Th was prepared in n-decane as a model oil and then stirred and extracted with that of each of the mixture of ILs addition at different conditions of ILs. The same conditions and experiments were repeated with BT and DBT.

The S-content with respect to Th, BT, and DBT in decane was measured by GC-FID with a fused silica capillary column (PE Elite-5, 29.45 m long, 0.25 mm in diameter) connected to gas chromatograph (Perkin Elmer Autosystem XL) using the Totalchrom software. The operational temperature of the FID was 320 °C, and that of the injector was 310 °C. For the first three minutes, the temperature of column was set at 50 °C, increased to 300 °C at a rate of 15 °C min⁻¹, kept at 300 °C for 2 min. Helium was the carrier gas at a flow rate of 1 ml min⁻¹. The quantities of S-compounds in a model fuel were determined from peak areas corresponding to these sulfur species on the gas chromatograph. According to the GC setup, the retention time chromatograms for Th, BT and DBT were around 3.14, 9.88 and 14.70 min respectively. The amount extracted was determined using a calibration plots. Good linear correlations were achieved for analytical technique, with an R² value of more than 0.99 for GC-FID. The error bars for most of the data are within the size of the plot symbols showing that replicate results are accurate.

All electrochemical experiments were carried out using a three electrode set up (Pt working electrode (WE), a Ag wire pseudo-reference electrode (RE) and Pt mesh counter electrode (CE). CVs were carried out at a polished 0.5 mm diameter ($1.963 \times 10^{-3} \text{ cm}^2$) Pt disc working electrode immersed in a (Bmim)Cl FeCl₃ mixture as a function of sweep rate.

Before each experiment, the WE was cleaned and washed with deionised water, polished with alumina paste and after sonicating in deionised water for 5 minutes; it was dried with N₂ gas. The WE acts as a substrate for electro-deposition of polythiophene. Since the polymeric film was deposited by an oxidative process, an inert electrode (Pt) was requested so as not to oxidise concurrently with the aromatic thiophene monomer.⁸

Results and Discussion

Extractive electropolymerisation of Th by 1:1 (Bmim)Cl: FeCl₃

The extraction of Th, BT and DBT has previously been shown to be possible into a range of DESs. Th showed the best extraction efficiency followed by BT and then DBT and this was found to be related to the size of the solute (the latter requiring a larger hole).³ The equilibrium can be driven by making a solid product from the thiophenic compounds by polymerisation of thiophene to form polythiophene (PTh).

Previous work has converted the thiophene to a solid thiophene sulfoxide catalysed by DESs in the presence of H₂O₂ as an oxidising agent.⁹ The issue with this approach is that H₂O is introduced as an aqueous solution as a by-product, contaminating the oil.

In the current study it is proposed that Th could be converted into a solid by polymerising it to polythiophene (PTh). This is an interesting material which has been used in numerous electronic devices as a semiconductor and electrochromic material.^{8, 10} Attempts to drive the equilibrium by electropolymerising the thiophenic molecules in non-metallic DES were unsuccessful. Electropolymerisation of several monomers has successfully been achieved in a variety of ionic liquids although polymer formation can be sensitive to the medium. This topic has been reviewed in more depth by Pringle.¹¹

Csahony et al.,¹² showed that thiophene can be successfully partitioned into an ionic liquid composed of a 1:1 (Bmim)Cl: FeCl₃ mixture from a decane layer. We propose that the efficiency of this partitioning occurs because (C₄mim)FeCl₄ has a relatively low surface tension (46.4 mN m⁻¹) meaning that the enthalpy of hole formation is decreased by adding ferric chloride to the liquid.

In this study, a DES composed of 1:2 molar mixture of choline chloride: ethylene glycol (1:2 ChCl: EG) has been used to extract and electro-polymerise thiophene by cyclic voltammetry (CV). 1:2 ChCl: EG was used with and without FeCl₃, using Pt working and counter electrodes and a Ag wire reference electrode. The cyclic voltammetric response of thiophene in 1:2 ChCl: EG is shown in **Figure 1a**.

Figure 1: CVs for polymerisation of (0.15 mol/L) thiophene in (a) in 1:2 ChCl: EG, (b) 1:2 ChCl: EG with (0.077 mol/L) of FeCl_3 , (c) 0.5 mol/L Th in 1:1 $\text{FeCl}_3/(\text{Bmim})\text{Cl}$ and (d) as (c) but with 0.4 mol/L (0.8mmol) Th in decane. All 40 cycles at 25 °C, scan rate: 50 mV s^{-1} .

Figure 1a shows the clear oxidation and reduction of the thiophene with a half-wave potential of approximately 0.6 V. Scans to 1.2 V do not show the further oxidation to form the polymer growing on the electrode surface. The main reason for this is probably because 1:2 ChCl: EG is a protic solvent containing a hydroxyl group and it could also possibly contains small amounts of water. A large number of studies have shown that the presence of traces of water in the medium precludes the electropolymerisation of thiophene through reaction of the water molecule with thiophene radical cations which make a passivating layer on the working electrode.¹³

The same experiment was repeated using ferric chloride as an electrocatalyst. Ferric chloride is known to be a good chemical catalyst for the polymerisation of thiophene. A redox process is again observed in **Figure 1b**, but this time the redox half wave potential is at a lower over-potential (0.4 V) suggesting that it is the $\text{Fe}^{\text{II/III}}$ redox couple. Again no signal for the polymerisation of Th was observed which again is probably due to the protic nature of 1:2 ChCl: EG.

The 1:1 (Bmim)Cl: FeCl₃ mixture should be sufficiently aprotic to enable electropolymerisation of Th. **Figure 1c** shows a cyclic voltammogram of 0.5 mol/L Th in a 1:1 (Bmim)Cl: FeCl₃ mixture and the characteristic shape is indicative of the polymerisation of Th on the electrode surface. **Figure 1d** shows the same experiment run using Th in decane (0.4 mol/L). A similar voltammogram is obtained to the one where Th was in the ionic liquid phase. This shows that the Th is effectively extracted from the decane layer. The addition of decane should dilute the total concentration of thiophene in the system, so the charge observed should decrease. The observation that the charges with and without decane are similar shows that the partition coefficient must be > 1. The kinetics of polymerisation can be estimated from the charge data. A charge equivalent to 2.25 electrons per molecule will lead to the addition of one molecule of thiophene and 0.25 doping anions (Cl⁻).¹⁴ Consequently, the electropolymerisation charge, Q_{Th} ,¹⁴⁻¹⁵ can be written as:

$$Q_{Th} = nNF \quad (1)$$

where, n is the number of electron reduced or oxidised, N is the number of moles of thiophene formed and F is the Faraday constant.

So as to compare the amount of Th converted to polymer in **Figure 1c** and **d**, the reaction rate has been calculated.¹⁶ The electropolymerisation rates of Th in (Bmim)FeCl₄ were calculated from **Figure 1c** and **d** and are shown in **Table 1**. The rate of the reaction of consumed Th should be equal to the reaction rate of produced PTh. However, owing to the biphasic nature of the system, it was difficult to estimate the amount of Th in the IL phase after 20 cycles from reaction of polymerisation, therefore, reaction rates were calculated in terms of the products.

The data from **Table 1** show that the rate of PTh formation in monophasic system is only marginally higher than that from the biphasic system. Given that an equal volume of decane to (Bmim)FeCl₄ was used the charge should decrease by half, but the observation that it decreases by less than 10% shows that the partition coefficient must be significantly greater than 1.

Table 1: Reaction rate of electropolymerisation of thiophene. Scan rate 50mVs⁻¹, 20 scans, potential window: -0.4 – 1.9V.

Fig.	Q (C)		N of PTh (mmol) from		R (mmol/min)	
	Q_{ox}	Q_{red}	Ox.	Red.	Ox.	Red.
c	0.0183	0.0188	7.6×10^{-4}	8.70×10^{-5}	2.48×10^{-5}	2.84×10^{-6}
d	0.0162	0.0186	6.7×10^{-4}	8.55×10^{-5}	2.2×10^{-5}	2.79×10^{-6}

On the other hand, as can be seen in **Figure 1(c)** and **1(d)**, as the film thickness of the polymer increases, the voltammetric wave for the reduction of the polymer shifts to more negative potentials and for the oxidation peak shifts to more positive values with consecutive scans which is characteristic

of polymer growth. This is possibly due to the polymer conductivity which increases the resistivity of the film on the electrode surface due to slows counter-ion mobility and electron transfer kinetics.¹⁷

The Fe-based ionic liquids cannot chemically polymerise thiophene until the molar ratio of FeCl_3 and (Bmim)Cl is above 1:1. Above this molar ration the liquid becomes more Lewis acidic and coincidentally less viscous. The concentration of free Cl^- is significantly decreased as FeCl_4^- dominates. This also prevents the chloride ion reacting with the radical cation causing polymer termination.

Optimisation of electrocatalytic polymerisation

Equi-volume amounts of IL and oil are clearly impractical and pre-concentration of Th into the IL are clearly required. This was investigated using different rations of decane to IL. **Figure 2** shows the cyclic voltammograms of two different IL: decane ratios. The number of moles of Th converted to polymer in **Figure 2**, was calculated from the charge under the voltammogram using **equation 1** and the data are summarised in **Table 2**.

Figure 2: CVs of a) 1:7 v/v of DES: decane: 0.3 ml includes 1.43 mmoles of FeCl_3 into 1-1 Fe-DES, 2ml of Th -containing decane (0.21 mol/L), b) 1:1 v/v of DES: decane, Th in 2ml of decane is 0.21 mol/L, 25 cycles, mV s^{-1} , 25 °C.

Table 2: Stoichiometry effect on the rate of the electropolymerisation reaction of Th after extraction from decane. Scan rate 50 mV s^{-1} , 25 scans, potential window: $-0.4 - 1.9 \text{ V}$.

IL : Decane (v/v)	Q (C)		N of Th oxidised (mmol)		R (mmol/min)	
	Q_{ox}	Q_{red}	Ox.	Red.	Ox.	Red.
1:7	0.020	0.022	8.09×10^{-4}	1.01×10^{-4}	2.11×10^{-5}	2.62×10^{-6}
1:1	0.023	0.025	9.36×10^{-4}	1.15×10^{-4}	2.44×10^{-5}	3.0×10^{-6}

It is interesting to note that while the current increased in 1:1 volume ratio, there was no significant difference in the amount of PTh deposited when compared with that obtained from 1:7 volume ratio which suggests that polymerisation is rate limiting rather than the solubility of Th in the DES.

The reaction rates shown in **Table 2** are relatively slow which is probably because electropolymerisation is a heterogeneous process.¹⁸ In most homogeneous solution polymerisation reactions, the kinetics of addition reactions are first order in monomer.¹⁹ Assuming the charge is proportional to concentration and the sweep rate can be related to the time of polymerisation then a pseudo first order kinetic plot could be approximated.

$$R = -\frac{dA}{dt} = k[A] \quad (2)$$

where, k is the rate constant of the polymer reaction and $[A]$ is the initial concentration of monomer. It can be seen from **Figure 3** that a plot of $\ln [Th]$ vs t gives an approximately straight line correlation suggesting that the process is pseudo first order with a rate constant of $1.4 \times 10^{-5} \text{ min}^{-1}$.

Figure 3: Plot of a) deposition charge (from reduction peak) against scan rate, b) $\ln(\text{unpolymerised Th})$ vs time for the electrochemical polymerisation of thiophene into 6.87 mmoles of 1:1 (Bmim)Cl: FeCl₃, with 0.25 mmoles Th in 2ml decane, at 30 °C, 15 cycles.

To determine the amount of Th that could be turned over in a given time, the rate of oxidation from **Table 2** (1:7) was used with the initial monomer concentration (0.21M) to calculate the rate constant. This was found to be $1.0 \times 10^{-7} \text{ moles min}^{-1}$. Taking a 1 L sample of decane containing 1wt % of Th and 10 x10 cm WE, the time to remove 75 % of this Th from 1wt % in 1 L fuel using electropolymerisation would be 4.5 hrs. This is clearly far too slow to be practically viable.

Removal of BT from decane into IL mixture followed by electropolymerisation was also attempted and no polymer could be formed with this monomer which was thought to be due to the high reactivity

of radical BT cations, which can undergo fast reaction with the chloride anions or with the imidazolium cation. Electropolymerisation of DBT, was also found to be impossible in this medium.

Extractive chemical polymerisation of Th and its analogues in 1:2 (Bmim)Cl: FeCl₃

For several decades, the lowest sulfur content achieved by HDS of fuels was around 500 mg/kg (around 6 mmol/L).²⁰ To demonstrate the efficacy of the DESs to chemically remove aromatic sulfur compounds mixtures of Th, BT and DBT were prepared in decane. Previously, the process could be estimated to be a dynamic equilibrium between the two phases, however with the Lewis acidic liquids, the Th in the IL phase is constantly being oxidised to form PTh and driving the equilibrium towards to IL phase. By analysing the effect of some factors on the pre-equilibrium, the rate of extraction polymer formation can be determined.

Effect of temperature and stirring

Table 3 shows the ability of 1:2 (Bmim)Cl: FeCl₃ to extract Th, BT and DBT. It can be seen that the amount of each component extracted after 5 min decreases when the temperature is raised. This shows that the extraction must be an exothermic process as the position of the equilibrium is shifted toward the reagents when the temperature is increased as per Le Chateliers's principle. It is not possible to calculate the thermodynamics of phase transfer as the system is not at equilibrium, but it is possible to contrast the data with those for extraction in different DESs where the enthalpy of extraction was endothermic (10 – 70 kJ mol⁻¹).³ Spontaneous polymerisation processes are always strongly exothermic and it could be this driving the extraction of the monomer.

Table 3: Extractive desulfurisation of 35 mmol L⁻¹ of each one of Th, BT and DBT into 1:2 (Bmim)Cl: FeCl₃ mixture, as a function to time, 500 rpm, fuel/IL mass ratio: 2:1.

Temperature (°C)		25		40		
Time (min)		5	10	5	10	20
Extracting (%)	Th	85.7 ± 5	>99.9	76.3 ± 2	95 ± 4	>99.9
	BT	67.5 ± 3	>99.9	75.3 ± 3	92.8 ± 4	>99.9
	DBT	58 ± 6	>99.9	65.8 ± 3.8	90.6 ± 2	>99.9

Transfer of BT and DBT are quite similar once experimental errors are taken into account but either way neither are significantly affected by temperature. This could suggest that the equilibrium is governed by the rate at which the monomer is converted to the polymer (oligomer). After 10 min, the extraction at 25 °C is all but complete whereas those at 40 °C have still not quite gone to completion. This further suggests that the transfer is slightly exothermic. Contrasting these data with

those obtained for the DESs where after 1 h, a significant proportion of Th was still in the alkane phase. It can be seen that converting Th to PTh helps in extracting the Th from the decane phase.

The previous study of thiophene extraction in DESs showed that the surface tension gives a measure of the cohesive energy density in ionic liquids and this in turn controls the viscosity and conductivity of the liquid. The lower the surface tension the larger the void volume and the lower the viscosity.³ Measuring the surface tension of two different molar ratios of the 2:1 and 1:1 FeCl₃: (Bmim)Cl it was found that they were both 46.4 mN m⁻¹. Previously it was found that the best solvent for extracting of Th, BT and DBT was a mixture of pentylene glycol and choline chloride (4:1) which had a surface tension of 46 mN m⁻¹. The ferric chloride decreases the surface tension of BmimCl (71 mN m⁻¹) by delocalising the charge and it also has a stronger interaction with Th than occurs in a non-metallic DES and these two factors are sufficient to change the enthalpy of transfer from endothermic to exothermic which makes the partition coefficient larger.

In the previous studies, the reactivity of organosulfur rings in HDS processes has been reported by some researchers and it was investigated that the reactivity follows the order: Th > BT > DBT.²¹ This could be due to two factors, increasing the size of the solute molecule increase the size of the hole required to accommodate the solute, the interaction between the iron species and the heterocyclic sulfur atom is probably precluded due to steric factors. This also explains why BT and DBT are slower to partition into the ionic liquid since polymerisation of these monomers will be slower due to steric hindrance and deactivation.

The influence of the stirring speed on the sulfur compound extractions is statistically significant as seen in **Figure 4**. Doubling the rotation speed of the stirrer in the ionic liquid phase ensured that all the S-containing species were extracted from the decane at 25 °C within 5 min which took about double the time with a slower stirring rate.

Figure 4: Effect of stirring speed on the extraction of sulfur compounds, IL: fuel mole proportion 1:2. Extraction time was 5 min.

Effect of phase ratio

To investigate the effect of the mass ratio of the organic and DES phases on the extraction efficiency, different mass ratios were employed and the results are shown in **Figure 5**. All were mechanically agitated (500 rpm) with a magnetic stirrer for 5 min and then left to settle for 5 min to ensure complete thermodynamic equilibrium at 25 °C.

Figure 5: Desulfurisation of a mixture of sulfur compounds from decane containing 35 mmol L⁻¹ of Th, BT and DBT into (Bmim)FeCl₄.

It can clearly be seen that the amount of (Bmim)FeCl₄ was an important factor in EDS. Since the iron chloride is still in vast excess to thiophene it is probably a mass transport effect which is still controlling the conversion rate.

Effect of time

A mixtures of Th, BT and DBT were extracted with different oil to IL ratios, all in one mixture tried to elucidate the rate limiting factor. **Figure 6a** shows the efficiency of extracting 35 mmol L⁻¹ of Th, BT and DBT from the decane phase into 2:1 FeCl₃: (Bmim)Cl ionic liquids in an unstirred system. This was done at an IL: oil mass ratio of 1:1.

Figure 6: Extractive desulfurisation of Th and its derivatives as a mixture from decane into 2:1 FeCl₃: (Bmim)Cl at 25 °C, with equimass ratio of IL to fuel: a) extracting S-compound (%), b) plot of ln (monomer) vs time.

After 6 min, 38 % of Th had been extracted and it required about 4 hours to extract all the Th (**Figure 6a**). Comparing this with the stirred system in **Figure 5** it can be seen that mass transport is a very important factor governing extraction and conversion to the polymer. With respect to BT, after 1 h, only 35 % had been extracted and it only reached 100 % after 8 hrs. Removal of DBT was the slowest process with only 34 % removed after 4 hrs. This fits in with the earlier observation that the polymerisation of Th is the fastest followed by BT and DBT. Strong interaction between the Lewis acid and S-species made the extraction easier even when the reaction takes place in the absence of stirring.

The overall removal of the sulfur containing species is given by;

The reaction could either be limited by the transfer of species into the DES or by the activation of the monomer. If it is the latter of these then the reaction could be thought of as a pseudo-first order reaction since the catalyst is present in excess. The rate equation for this type of reaction should therefore approximate to:

$$\frac{[\text{Th}]}{[\text{Th}]_0} = -kt \quad (5)$$

A plot of ln [S-compound] should give a straight line plot. The data in **Figure 6a** were tested in this way and the results are shown in **Figure 6b**. It can be seen that the extraction of all of the sulfur

containing compounds follow this pseudo first order plot. However, it should be stressed that this is by no means proof that this is the definite mechanism for the extraction process. The data do not, however fit well to a second order plot or to a half order plot as may be appropriate if diffusion was the limiting factor. It can therefore only be suggested that a pseudo first order polymerisation may be an appropriate model that fits the observed data relatively well.

Finally, it is important to note the comparative rate constants for the electrochemical and chemical rates of polymer production. Comparing the data for Th from **Figure 6b** with those presented in **Figure 3b**, it can be seen that the rate for the chemical production of PTh is approximately 1500 times faster than the electrochemical process. This would be expected given that the chemical process is a 3-D rather than a 2-D reaction as would be the case for the electrocatalytic process. It should also be noted that the concentration of FeCl_3 is significantly higher for the chemical process.

The main difficulty of using ILs to extract thiophenic compounds from oils is that the polymerisation is a stoichiometric reaction with iron and to make it a catalytic process the Fe(II) produced would have to be reoxidised. If all the Fe(III) is reduced then the IL becomes more viscous and eventually solidifies. It is difficult to extract the polymer from the ionic liquid due to the high viscosity. Regeneration of FeCl_3 were attempted using solvent extraction and an electrochemical set up using a liquid-liquid junction to enable electron transfer.²² Both of these approaches were ultimately unsuccessful and the ionic liquid solidified with extended use. To improve the viability of ionic liquids for preparing ultra-low sulfur fuels it is important to focus on the reoxidation of the ionic liquid. The main issue behind this is maintaining liquid phase behaviour for the ionic liquid and establishing a catalytic method of reoxidation.

Nie and coworkers investigated the EDS process using ILs on commercial diesel samples.²³ The authors suggested that S-removal from commercial fuel is much harder than desulfurisation of model fuel without giving the reasons.²⁴ Similarly, Eßer et al,²⁵ reported the K_p for S-removal of commercial diesel is less than K_p of a model oil. Similarly, Xu et al. and Yu et al. also found that in addition the relatively high moisture content in commercial diesel fuel necessitates additives which have a negative impact on the removal of sulfur compounds.²⁶

For practical applications the other components in fuels need to be taken into account when preparing a sulfur extraction process. Commercial diesel was used but it was spiked with Th, BT, and DBT each at a concentration of 35 mmol L^{-1} . The concentrations of the thiophenic compounds were determined by GC at the same operational reaction conditions as those described above. During the process, the sulfur levels in the upper phase of each one of Th, BT and DBT could be extracted to (27.8, 18.8 and 16.3 mmol L^{-1}) respectively through the optimisation of reaction conditions; which means 79.3, 53.8

and 46.5 % of Th, BT and DBT respectively were removed just after 5 min. This compared with 85.7, 67.5 and 58% respectively for the corresponding extraction from decane. As expected, the extraction data for removing Th, BT and DBT from commercial diesels are lower than from decane. This may be attributed to the coexistence of many aromatics, oxygen and nitrogen additives which compete with the partition of S-compounds in the (C₄mim)FeCl₄ and saturate the ionic liquid phase.²⁷

Conclusion

This study has shown that the main factor controlling the partitioning of species between an oil and an ionic liquid is the enthalpy of solvation of the solute and the enthalpy of hole formation in the DES. These are controlled by the relative solvent-solvent and solvent-solute interactions. Using a mixture of (Bmim)Cl and FeCl₃ causes more thiophene to partition into the ionic phase than when non-metallic DESs are used. This is thought to be due to the low surface tension but also the specific interaction between FeCl₃ and thiophene. It is shown for the first time that electropolymerisation of thiophene can be carried out in the in the 1:1 (Bmim)Cl: FeCl₃ phase by cyclic voltammetry. This can drive the equilibrium to pull the Th from the alkane phase as it is polymerised in the IL phase.

While electrochemical polymerisation of Th is possible it is not practically viable due to the slow reaction kinetics. A 1:2 (Bmim)Cl: FeCl₃ mixture was successfully used to polymerise Th, BT and DBT. The extraction Th into 1:2 (Bmim)Cl: FeCl₃ is exothermic and occurs 1500 times faster than electropolymerisation in 1:1 (Bmim)Cl: FeCl₃.

Regeneration of used IL mixture was difficult because polythiophene does not separate from the ionic liquid (due to similar densities and high viscosity). The polymer causes the ionic liquid to gel which decreases mass transport and stops the polymerisation reaction. To enable ionic liquids to be used for ultra-desulfurisation of fuel the phase behaviour of the catalyst needs to be addressed and a facile method of reoxidation needs to be found.

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