



Application of $V^{IV}O(acac)_2$ type complexes in the desulfurization of fuels with ionic liquids

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ABSTRACT

The acetylacetonate complexes of oxovanadium(IV): $VO(X-acac)_2$ ($X=Cl, CH_3$ and CH_3CH_2) were structurally characterized in several alkyimidazolium ionic liquids by visible absorption and EPR spectroscopies. $VO(Me-acac)_2$ and $VO(Et-acac)_2$ showed solvatochromism in the selected ionic liquids (a λ_1 shift of ca. 120 nm was observed) and most complexes showed two species in the anisotropic EPR spectra in several ionic liquids. It was shown that the ionic liquids anions have coordinating ability and the basicity order found was: $NTf_2^- < OTf^- < BF_4^-$, in agreement with previous findings.

An extraction and catalytic oxidation desulfurization (ECODS) system composed of $VO(X-acac)_2$, H_2O_2 and ionic liquids was tested in the removal of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) from a model oil (*n*-octane) at ambient temperature. The influence of the catalyst, ionic liquid, substrate and the molar ratio of the oxidant (H_2O_2) and the S-containing molecule were examined. The reaction rates of the oxidative desulfurization reaction were found to increase with the molar ratio of H_2O_2 and the S-containing molecule, as expected, however a ratio of 4 was enough to achieve >95% conversion to sulfone. The ionic liquid that showed the best performance with all substrates was bmimNTf₂. In bmimOTf and bmimBF₄ the activity of all catalysts in the ECODS system was low to moderate, which is probably due to the higher coordinating ability of these anions.

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1. Introduction

The use of fossil fuels generates sulfur oxides, which are responsible for smog, acid rain and respiratory problems in humans. Sulfur also hinders the performance of catalytic converters of car exhausts. To limit these effects, it is necessary to reduce the sulfur emissions and thus, the sulfur in the crude oil must be removed at the refining stage. The oil industry is facing increasing pressure to remove organic sulfur compounds from transportation fuels, since governments have been implementing increasingly strict legislation [1].

Currently the removal of sulfur-containing compounds from fuels is achieved by hydrodesulfurization (HDS). This technology can desulfurize aliphatic and acyclic sulfur-containing compounds on the industrial scale. However, to obtain fuels with the low levels of sulfur-containing compounds required nowadays, very harsh conditions have to be applied in HDS, namely high temperatures and pressures, since it is not the best process for the removal of aromatic thiophenes such as benzothiophenes (BTs),

dibenzothiophenes (DBTs), and particularly substituted DBTs. This limitation led to the search for alternative processes, which will operate under moderate conditions and without H_2 and expensive catalysts [2]. Due to short reaction time at ambient conditions, high efficiency and selectivity, oxidation followed by extraction with ionic liquids is regarded to be a promising alternative.

Various ionic liquids have been tested for the extraction of sulfur compounds from *n*-dodecane (model of diesel oil) [3,4], model fuel and commercial gasoline [5,6]. Wasserscheid [3,4] promoted imidazolium alkylsulfates, whereas Nie [7,8] favored imidazolium dialkylphosphates, as candidates for extractive desulfurisation technologies. Holbrey [9] showed that the partition ratio for dibenzothiophene between dodecane and ionic liquids is strongly influenced, and can be controlled, by the selection of the cation (methylpyridinium < pyridinium ~ imidazolium ~ pyrrolidinium) and to a much lesser extent the anion of the ionic liquid. Ionic liquids with ethanoate and thiocyanate anions gave the best extraction performance with each cation. Hansmeier et al. showed recently [10] that the pyridinium-based ionic liquids [3-mebupy]N(CN)₂, [4-mebupy]N(CN)₂ and also [bmim]C(CN)₃ are superior to sulfolane (which is a benchmark extraction solvent for sulfur removal from petrochemical streams) and also outperformed the ionic liquids reported previously in the literature.

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However, and as a general rule, in the absence of an oxidant, ionic liquids have failed to provide high levels of sulfur removal. The introduction of an oxidation step prior to the ionic liquid extraction is a much more appealing approach since the oxidation increases the polarity of the aromatic sulfur compounds, which are then extracted with much higher partition ratios to the ionic liquid phase. This process has been described using p.e. H_2O_2 /ethanoic acid [11]. However, in the absence of a catalyst very high oxidant/sulfur ratios have to be applied, in order to achieve high sulfur removal. Several catalysts have been tested, which can remove high amounts of sulfur with lower oxidant/sulfur ratios: p.e. tungsten and molybdenum complexes [12,13], vanadium oxide [14] and iron complexes [15,16]. These studies have shown the relevance of the topic and the need to develop studies on the application of the oxidation/extraction procedure for the desulfurization of fuels, which is still underdeveloped. Among the different chemical oxidants H_2O_2 is the best option since it has a high content of active oxygen, gives water as the only by-product and is commercially available. When used in conjunction with a transition metal catalyst it forms peroxy species, which oxidize the sulfur compounds. Our approach comes from our previous studies on the behavior of $\text{VO}(\text{acac})_2$ in ionic liquids [17]. This complex and its derivatives are easily obtained, soluble in a huge number of solvents and ionic liquids, and since they are Lewis acids they are able to activate peroxides. So, as a development of previous studies on the structure of vanadium acetylacetonate complexes in ionic liquids [17], we characterized the behavior of $\text{VO}(\text{X-acac})_2$ complexes in alkylimidazolium ILs through spectroscopic techniques and then tested the complexes in the ECODS system with H_2O_2 . Our goal was to use room temperature, short reaction times and low H_2O_2 /sulfur ratios.

2. Experimental

2.1. Materials and reagents

All chemicals used were of analytical reagent grade. 1-Methylimidazole was purchased from Acros Organics and distilled from potassium hydroxide; 1-chlorobutane was purchased from Acros Organics and distilled from phosphorus pentoxide. Lithium bis(trifluoromethylsulfonyl)imide [$\text{Li}(\text{NTf}_2)$] and lithium trifluoromethanesulfonate [$\text{Li}(\text{OTf})$] were purchased from Apollo Scientific and used as received. Bis(acetylacetonate)vanadium(IV) was also obtained from Acros Organics. Dibenzothiophene and 4,6-dimethylbenzothiophene were purchased from Aldrich and 1-benzothiophene from Fluka. Octane and tetradecane were provided from Aldrich and H_2O_2 (30%) was from Panreac.

All syntheses and sample preparations were performed under anaerobic conditions using standard Schlenk techniques. The preparation and spectral data of the ionic liquids have been described elsewhere and are included in SI [18,19].

2.2. Synthesis of the V^{VO} complexes

$\text{VO}(\text{Cl-acac})_2$, $\text{VO}(\text{Me-acac})_2$ and $\text{VO}(\text{Et-acac})_2$ were prepared according to literature procedures [20–22].

Analysis of $\text{VO}(\text{Cl-acac})_2$: found: C 36.0 and H 3.5. Calc. for $\text{C}_{10}\text{H}_{12}\text{O}_5\text{Cl}_2\text{V}$: C 35.96 and H 3.62.

Analysis of $\text{VO}(\text{Me-acac})_2$: found: C 49.1 and H 6.4. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_5\text{V}$: C 49.16 and H 6.19.

Analysis of $\text{VO}(\text{Et-acac})_2$: found: C 52.2 and H 7.1. Calc. for $\text{C}_{14}\text{H}_{22}\text{O}_5\text{V}$: C 52.34 and H 6.90.

2.3. Instruments

^1H NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer. UV–vis spectra were recorded on a Perkin-Elmer

UV–vis Lambda 35 spectrophotometer and the temperature was controlled with a Peltier controller from Perkin-Elmer. The EPR spectra were recorded at 77 K (on glasses made by freezing solutions in liquid nitrogen) and some at room temperature with a Bruker ESP 300E X-band spectrometer. The GC samples were analysed on a GC–MS from Perkin Elmer model Clarus 600 C.

2.4. Vis and EPR spectra

The visible electronic and EPR samples were prepared under nitrogen with schlenk techniques to avoid vanadium oxidation, and exposure of the ionic liquid to water.

2.5. Desulfurization experiments

As a general procedure the desulfurization experiments were carried out in glass vials in which reagents were put together by the following order: the selected catalyst, 0.5 ml of the ionic liquid, 1 ml of the octane solution containing the sulfur compound (the substrate) and tetradecane (the internal standard) in a 1:1 molar ratio. The reactions were initiated with the addition of the oxidant (aqueous H_2O_2). The mixtures were stirred and GC samples were taken from the organic phase (after decantation) at different time intervals: 15 or 30 min and 2 h, to eppendorfs containing a small amount of triphenylphosphine (to deactivate the remaining H_2O_2 and stop the reaction). Stirring was kept constant in all experiments.

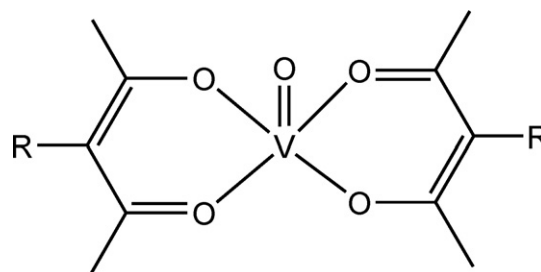
2.6. Analysis

Calibration curves were made with standards containing different molar ratios of the sulfur compound and tetradecane (the internal standard), prepared in octane. The sulfur content of the standards and samples was analyzed using GC with selected programs for temperature ranges of 80–250 °C with a column from “SGE Analytical Science”, type BPX5 (30 m × 0.22 mm).

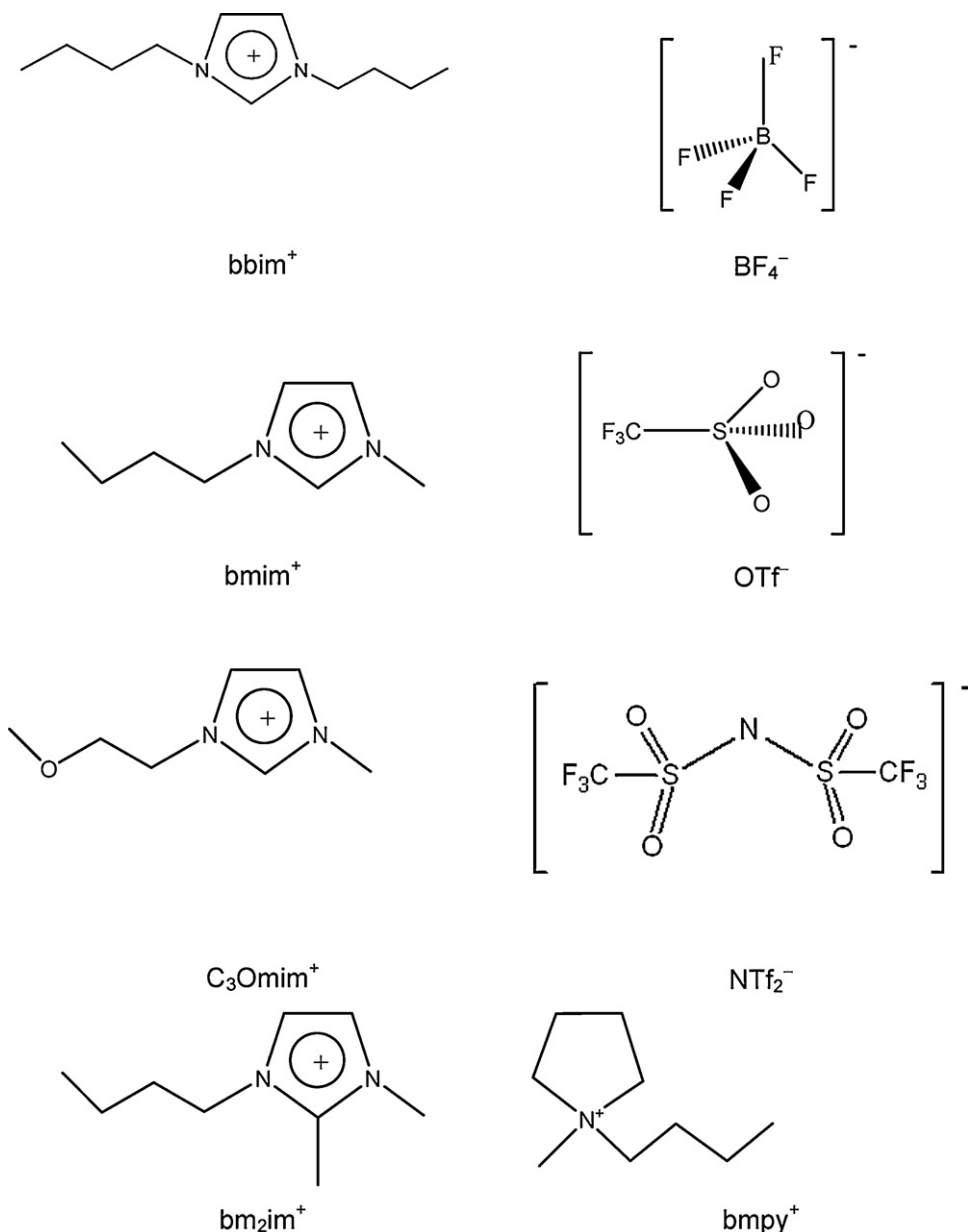
3. Results and discussion

3.1. Characterization the $\text{VO}(\text{X-acac})_2$ complexes in ionic liquids

The complexes studied are shown in Scheme 1. They were synthesised (except **1** that is commercially available) according to published procedures [20–22] and the solid state and solution characterization proved its formulation and purity. The ionic liquid ions chosen for this study are depicted in Scheme 2. The procedure used in its preparation and purification (washing with water, addition of charcoal, and filtration through acidic alumina) afforded colorless liquids, suitable for spectroscopic studies. The



Scheme 1. Formula of the studied complexes. **1**: R = H, $\text{VO}(\text{acac})_2$; **2**: R = Cl, $\text{VO}(\text{Cl-acac})_2$; **3**: R = CH_3 , $\text{VO}(\text{Me-acac})_2$; **4**: R = CH_2CH_3 , $\text{VO}(\text{Et-acac})_2$.



Scheme 2. Molecular formula of the ionic liquid ions used in this study.

analytic characterization showed the absence of impurities, such as residual chloride, which might change enormously their solvation properties.

The complexes were characterized by visible electronic and EPR spectroscopies. The Vis spectra and particularly the position of the lowest energy band give information on the coordinating ability of the ionic liquid anion, which may change the reactivity of the complex. The EPR spectrum is a fingerprint for equatorial coordination since the presence of different complexes in solution is detected due to the different coupling contributions of each equatorial donor group. Thus, the analysis of anisotropic EPR spectra can give detailed information on the number of species present in solution; the symmetry and coordination geometry of the vanadium complex; and the identity of the equatorial ligands through the hyperfine coupling constant A_z (or $A_{||}$).

The characterization by Vis spectroscopy showed that complexes **3** and **4** are solvatochromic, showing a large shift of the lowest energy absorption band: ca. 120 nm for both complexes, in

the ionic liquids used. Complex **2** shows poor solubility in most ionic liquids and therefore low solvatochromism.

Fig. 1 shows the Vis spectra obtained for complex **4** dissolved in the ionic liquids and Table 1 the position of the lowest energy band and the type of anisotropy observed in the EPR spectra. The Vis spectra measured for complexes **2** and **3** are included in the SI.

The d–d absorption spectra of vanadyl complexes are interpreted considering C_{4v} symmetry for the square pyramid, and three transitions are expected, considering the following energy levels [23]:

$$b_2(d_{xy}) < e(d_{xz}, d_{yz}) < b_1(d_{x^2-y^2}) < a_1(d_{z^2})$$

Since it is considered that b_2 is an almost pure vanadium $3d_{xy}$ orbital and $e(d_{xz}, d_{yz})$ is a combination of vanadium and oxygen orbitals, the lowest energy transition (λ_1) – from $b_2(d_{xy})$ to $e(d_{xz}, d_{yz})$ – should be sensitive to axial perturbations from the solvent [24]. Thus, upon dissolution, the five coordinated square pyramidal $\text{VO}(\text{X-acac})_2$ complex may become six coordinated, with the

Table 1
Electronic absorption characterization of the complexes. Low energy absorption band (λ_1), difference in the 1st and 2nd absorption band ($\lambda_{1a} - \lambda_2$), EPR anisotropy and difference in hyperfine coupling constants $A_x - A_y$.

Complex/ionic liquid	bbimNTf ₂	bmimNTf ₂	C ₃ OmimNTf ₂	bm ₂ imNTf ₂	bmimOTf	bmimBF ₄
VO(Cl-acac) ₂ 2						
λ_{1a} (nm)	–	–	–	778.5	763.5	785
Anisotropy	–	–	–	Axial	Axial	Axial
VO(Me-acac) ₂ 3						
λ_{1a} (nm)	675	680.5	689.5	733	780	801
$\lambda_{1a} - \lambda_2$ (nm)	80	81	89	–	–	–
Anisotropy	Rhombic	Rhombic	Rhombic	Axial	Axial	Axial
$ A_x - A_y $ ($\times 10^4$ cm ⁻¹)	6.3	9.4	8.7	–	–	–
VO(Et-acac) ₂ 4						
λ_{1a} (nm)	678	681.5	686.5	757.5	774.5	798.5
$\lambda_{1a} - \lambda_2$ (nm)	80	80	92	–	–	–
Anisotropy	Rhombic	Rhombic	Rhombic	Axial	Axial	Axial
$ A_x - A_y $ ($\times 10^4$ cm ⁻¹)	8.8	9.4	8.8	–	–	–

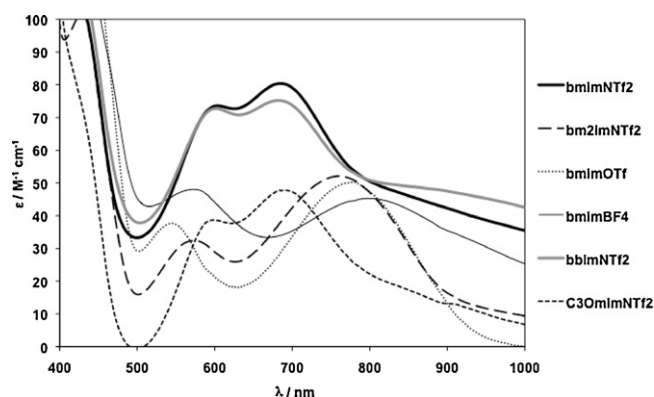


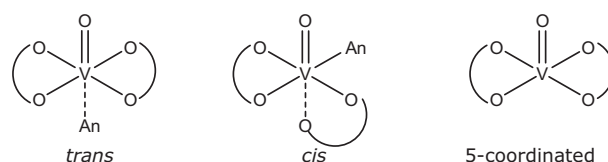
Fig. 1. Electronic absorption spectra of VO(Et-acac)₂ (complex **4**) in the visible region measured in different ionic liquids.

addition of a solvent molecule in the axial position (or an ionic liquid anion) [24–27], and this will affect the position of the low energy band. Hydrogen bonding to the oxo group will also affect this band.

It has also been proposed [28] that a distortion from square pyramid towards a trigonal bipyramide geometry breaks the degeneracy of the $e(d_{xz}, d_{yz})$ orbitals resulting in the appearance of four bands in the Vis absorption spectra (bands *I_a*, *I_b*, *II* and *III*) and rhombicity in the EPR spectra of vanadyl compounds. The distortion of the geometry may be evaluated by analysis of the wavelength difference between the central transitions in the Vis spectrum, $|\lambda_{1b} - \lambda_2|$ and also by the difference between the EPR hyperfine coupling parameters $|A_x - A_y|$. The results suggest that (see Table 1) in bbimNTf₂, bmimNTf₂ and C₃OmimNTf₂ there is a slight distortion of the geometry, towards a trigonal bipyramid in the five-coordinated complexes and in the other group of ILs the complexes are six-coordinated and approach an octahedral geometry. In terms of coordinating ability the following order is proposed: NTf₂⁻ < OTf⁻ < BF₄⁻, which was the same found for VO(acac)₂ [17].

It might seem unexpected, since the anions that are used to make ionic liquids are usually described as non-coordinating, that any difference between the ILs is seen. However, since the anions are in the neighbourhood and there is no other source of potential electron pairs as the solvent is in huge excess, they will interact with the metal centre to some extent. This is essentially a concentration effect.

The EPR spectra of complexes **2–4** were measured at 77 K (in ionic liquid glasses) and Table 2 shows the spin Hamiltonian parameters obtained by simulation [29] for all complexes. In the less coordinating ionic liquids (containing NTf₂⁻ anions) the EPR spectra show asymmetry in the perpendicular region, presenting rhombic



Scheme 3. Structure of the proposed species formed in solution. An = ionic liquid anion. The 5-coordinated complex can be distorted into a trigonal bipyramid.

anisotropy. This suggests a distortion from the square pyramid to a trigonal bipyramid and a 5-coordinated structure (see Scheme 3). In the ILs of the anions with the highest coordinating power (OTf⁻ and BF₄⁻) the EPR spectra are axial, probably due to an octahedral geometry.

In terms of the number of species present in solution, VO(Cl-acac)₂ shows two species in all the measured ionic liquids, in different ratios. In bmimOTf they are ca. 1:1. Moreover, the spin Hamiltonian parameters are roughly the same as the ones obtained for VO(acac)₂ [17]. Complexes **3** and **4** show two species in most of the ionic liquids. Fig. 2 shows the measured spectra at 77 K for complex **3** (the others are included in SI). The parameters for the two species shift slightly in the various ionic liquids, but overall we can say that they correspond to the same type of complexes. Considering the $A_{||}^{\text{est}}$ for the coordination of the 4 equatorial carbonyl groups (168.4×10^{-4} cm⁻¹) we propose the outer species, whose parameters vary between 168.1 and 164.7×10^{-4} cm⁻¹, to be this

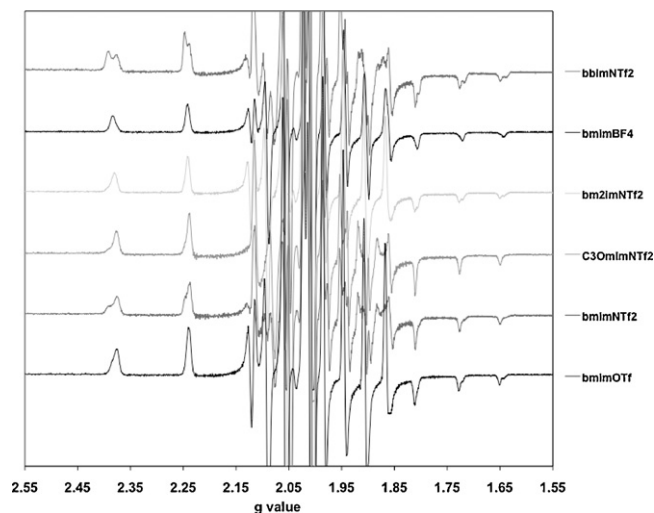


Fig. 2. EPR spectra of VO(Me-acac)₂ measured in different ionic liquids at 77 K.

Table 2
Spin Hamiltonian parameters obtained by simulation of the EPR spectra of the complexes in various ionic liquids.

Complex/ionic liquid	bbimNTf ₂	bmimNTf ₂	C ₃ OmmimNTf ₂	bm ₂ imNTf ₂	bmimOTf	bmimBF ₄
VO(Cl-acac) ₂ 2 g _x , g _y (or g _L) A _x , A _y (or A _L) (× 10 ⁴ cm ⁻¹) g _z or (g _I) A _z (or A _I) (× 10 ⁴ cm ⁻¹)	-	-	-	1.978	1.989	1.980
	-	-	-	59.9	58.6	58.2
	-	-	-	1.946	1.945	1.945
	-	-	-	166.9	167.7	167.7
VO(Me-acac) ₂ 3 g _x , g _y (or g _L) A _x , A _y (or A _L) (× 10 ⁴ cm ⁻¹) g _z or (g _I) A _z (or A _I) (× 10 ⁴ cm ⁻¹)	1.980	1.972, 1.985	a	1.981	1.980	1.981
	58.5	56.8, 50.5	1.973, 1.980	57.0	56.8	58.0
	1.945	1.950	57.8, 49.1	1.946	1.949	1.947
	168.0	162.7	162.4	166.7	162.7	164.7
VO(Et-acac) ₂ 4 g _x , g _y (or g _L) A _x , A _y (or A _L) (× 10 ⁴ cm ⁻¹) g _z or (g _I) A _z (or A _I) (× 10 ⁴ cm ⁻¹)	1.973, 1.975	1.974, 1.980	1.973, 1.980	a	1.981	1.980
	57.8, 52.3	57.3, 48.6	57.0, 49.1	57.9	57.5	57.7
	1.949	1.949	1.949	1.949	1.949	1.945
	167.1	162.9	161.9	162.6	161.8	164.0

^a The second species is observed but in such a low amount that its parameters could not be retrieved by simulation.

Table 3

ECODS experiments with complex **1** (5 mol%) in bmpyNTf₂ with different H₂O₂:DBT ratios.

H ₂ O ₂ /DBT	Conversion (15 min)	Conversion (2 h)
2	52.6	82.3
4	74.3	92.0
6	88.1	94.5
8	53.3	92.2

one. The inner one must therefore correspond to coordination of the ionic liquid anion at the equatorial position since no other type of complex is envisioned.

Overall, the spectroscopic experiments show that all ionic liquid anions have coordinating ability and that three types of species can be formed depending on the basicity of the anion: the *trans* complex containing the anion in the axial position, the *cis* complex with the anion in equatorial position and the 5-coordinated complex (see Scheme 3).

DFT studies with VO(acac)₂ in mmimOTf, presented in a previous report [17], confirmed that the anion OTf⁻ is able to coordinate to VO(acac)₂ with the *trans* isomer being more stable than the *cis* by 4.8 kcal/mol. It also showed the importance of the hydrogen bond donation ability from the cation, showing that the hyperfine coupling constant A_z for the *cis* isomer changes more than 10 × 10⁻⁴ cm⁻¹ upon consideration of the cation association to the VO(acac)₂OTf complex. This explains the observed shift in the Hamiltonian hyperfine parameters in the different ionic liquids.

3.2. Desulfurization of model oil

Since VO(X-acac)₂ complexes show high solubility in a wide range of ionic liquids and are good Lewis acids we tested them in the desulfurization of model fuel with ionic liquids. Among the different chemical oxidants used in oxidative desulfurization (ODS) the best option is hydrogen peroxide. However, in order to make an ODS process competitive with deep HDS we still need to improve the catalytic activity at low H₂O₂/S ratios and the mass transfer in the biphasic system containing the oil fraction and polar phase. Ionic liquids have the ability to act simultaneously as the oxidation solvent and the extraction media (ECODS). As substrates we tested several aromatic thiophenes: benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) and as model oil we used *n*-octane.

Dibenzothiophene was chosen as a sulfur compound representative of the main refractory sulfur-containing compounds in fuel by HDS treatment. Thus, most of the catalytic experiments were performed with this substrate. The experimental conditions and results for this substrate are included in Tables 3 and 4. Depending on the chosen ionic liquid and its miscibility with water, either biphasic (model oil and IL) or tri-phasic (model oil, IL and aqueous H₂O₂) systems were obtained.

By analyzing the data from Table 4 we can see that 30 min are enough, in most cases, to achieve very high conversion values (>90%) in ionic liquids with NTf₂⁻ anions (or PF₆⁻) and with most complexes. These ILs are water immiscible and thus, tri-phasic systems are obtained in the ECODS reaction system.

The screening of the H₂O₂:DBT ratio in bmpyNTf₂ with 5 mol% of VO(acac)₂ (see Table 3) shows that as little as 2:1 ratio was enough to obtain >80% conversion. In the following experiments we used a ratio of 4 to assure that enough peroxide was present to obtain high conversion values. In bmimNTf₂ 1 mol% of complex **1** was enough to get a conversion of 90% (see entries 2 and 3 in Table 4).

In most experiments complexes **3** and **4** showed very similar catalytic activity: high conversions in NTf₂⁻ and PF₆⁻ ionic liquids and moderate in bmimBF₄ and bmimOTf. Complex **2** also showed

Table 4
ECODS experiments with all catalysts with DBT.

Entry	Catalyst	IL	Catalyst (mol%)	H ₂ O ₂ /DBT	Conversion (30 min)	Conversion (2 h)
1	1	bmimNTf ₂	10	9.9	95.9	95.9
2	1	bmimNTf ₂	2.5	4	92.3	95.7
3	1	bmimNTf ₂	1	4	77.2	90.6
4	1	bm ₂ imNTf ₂	10	10	–	95.9
5	1	bmpyNTf ₂	5	4	74.3	92.0
6	2	bmimBF ₄	5	4	48.9	47.8
7	2	bmimOTf	5	4	48.5	50.3
8	3	bmimBF ₄	6	4	45.9	50.0
9	3	bmimOTf	6	4	39.5	52.1
10	3	bmimNTf ₂	5	4	95.7	95.8
11	3	bmimPF ₆	5	4	94.8	96.0
12	3	bbimNTf ₂	6	4	95.0	94.7
13	3	bmpyNTf ₂	5	4	90.0	95.3
14	4	bmimBF ₄	5	4	54.5	56.3
15	4	bmimOTf	6	4	56.8	58.0
16	4	bmimNTf ₂	5	4	95.4	95.7
17	4	bmimPF ₆	6	4	96.0	96.0
18	4	bbimNTf ₂	6	4	94.5	94.8
19	4	bmpyNTf ₂	6	4	64.5	80.0

Table 5
ECODS experiments with several catalysts with 4,6-DMDBT and H₂O₂: 4,6-DMDBT = 4.

Entry	Catalyst	IL	Catalyst (mol%)	Conversion (30 min)	Conversion (2 h)
1	1	bmimNTf ₂	1	27.4	35.1
2	1	bmimNTf ₂	3	–	35.1
3	1	bmimNTf ₂	6	23.8	80.8
4	1	bmimPF ₆	6	46.1	59.1
5	1	bbimNTf ₂	6	33.6	47.4
6	3	bmimNTf ₂	5	92.0	92.4
7	3	bmimBF ₄	5	16.4	16.3
8	3	bmimOTf	5	14.1	36.4
9	4	bmimNTf ₂	5	41.8	60.2
10	4	bmimBF ₄	5	–	14.0
11	4	bmimOTf	5	24.6	33.6

Table 6
ECODS experiments with several catalysts with BT and H₂O₂:BT = 4.

Entry	Catalyst	IL	Catalyst (mol%)	Conversion (30 min)	Conversion (2 h)
1	1	bmimNTf ₂	1	71.6	71.4
2	1	bmimNTf ₂	2	72.9	73.4
3	1	bmimNTf ₂	3	73.2	100.0
4	3	bmimNTf ₂	5	60.4	61.5
5	3	bmimBF ₄	5	61.9	61.8
6	3	bmimOTf	5	59.5	66.4
7	4	bmimNTf ₂	5	64.9	63.6
8	4	bmimBF ₄	5	57.3	57.5
9	4	bmimOTf	5	57.4	56.4

moderate conversions in these two ILs. In general all complexes show very good activity in ionic liquids containing NTF₂[−] and PF₆[−] anions and low reaction times were observed.

3.3. Oxidation of 4,6-dimethyldibenzothiophene (4,6-DMDBT)

This substrate was also tested since it presents high steric hinderance and is the most difficult refractory compound in HDS. Table 5 shows the results obtained in experiments in which a H₂O₂:4,6-DMDBT ratio of 4 was used. In bmimOTf and bmimBF₄ the conversion values obtained are low for all the studied catalysts, and in most other ILs they are only moderate. However complex 3 shows a conversion of 92% in bmimNTf₂ with 5 mol% of catalyst. So, we can conclude that this is the best IL to perform these experiments and that even this difficult substrate can be efficiently oxidized and removed in the ECODS system.

3.4. Oxidation of benzothiophene (BT)

For this substrate complex 1 shows 100% conversion when 3 mol% catalyst were used in bmimNTf₂ (see Table 6). In all other experiments, in which we varied the catalyst, the ionic liquid or the amount of catalyst, the conversions were between 55 and 75%.

4. Conclusions

The spectroscopic studies presented in this paper show that most of the VO(X-acac)₂ complexes have high solubility in ionic liquids and are good solvatochromic probes. The basicity order found was: NTF₂[−] < OTf[−] < BF₄[−], in agreement with our previous findings with VO(acac)₂ [17] and with determinations by others authors with different metal probes [30–32]. Coordination of the ionic liquid anion was observed by both Vis and EPR spectroscopies. Two isomers were found by EPR, which correspond to two types of isomers: *trans* and *cis*. In a previous study with VO(acac)₂ [17] DFT studies showed the higher stability of the *trans* isomers (when compared to the *cis*) and confirmed the importance of the hydrogen bond donation ability from the cation, showing that the hyperfine coupling constant *A*_z for the *cis* isomer changes more than 10 × 10^{−4} cm^{−1} upon consideration of the cation association to the VO(acac)₂OTf complex. This corroborates our spectroscopic studies, which show the presence of both isomers in most of the ionic liquids and a shift in the hyperfine coupling constants, which is probably due to hydrogen bond donation from the ionic liquid cation.

The complexes were used as catalysts in the oxidation of thiophenes from model oil at ambient temperature. Overall, the ECODS studies showed that the VO(X-acac)₂ complexes show very high catalytic activity for the oxidation of the S-containing molecules in the ionic liquids containing the least coordinating anions: NTF₂[−] and PF₆[−].

The best ionic liquid for the process is bmimNTf₂, in which conversions >95% (with BT and DBT) were achieved, when 5 mol% of complexes 1 and 3 were used. Moreover, the use of catalysts allowed the use of low H₂O₂:substrate ratios.

We believe that the use of these catalysts, which are readily available, in other ionic liquids (preferably cheaper) may improve the desulfurization of fuels at ambient temperature with low oxidant:substrate ratios and are an attractive alternative method to current HDS.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2012.03.037>.

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