

On the Nature of V^V Species in Hydrophilic Ionic Liquids: A Spectroscopic Approach

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Heteronuclear NMR experiments, in particular ⁵¹V, were performed with the aim to elucidate the nature of vanadates and peroxovanadates in hydrophilic ionic liquids (i.e., [bmim][BF₄], [bmim][TfO] and [bdmim][BF₄]). The data so far reported clearly indicate that ionic liquids have a strong influence on the solution chemistry of vanadate in water both for the formation of the aggregates (with and without H₂O₂)

and for the rate of peroxide consumption catalyzed by vanadium. In BF₄⁻ containing ionic liquids, formation of vanadate–fluoride adducts is suggested. The obtained results are also discussed in the light of the reactivity data of peroxovanadates in ionic liquids.

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Introduction

The speciation of aqueous V^V at relatively low ionic strengths has been extensively studied, especially by ⁵¹V NMR^[1,2] and by combined ⁵¹V NMR and potentiometric measurements.^[3] It was demonstrated that when metavanadate is dissolved in water, a complex mixture of mono- and oligovanadates is formed, depending on the pH, vanadium total concentration and the ionic strength of the medium. The only cationic hydrolysis product of vanadium(V), VO₂⁺, is the dominating species in the most acidic solutions. By increasing the pH to between 3 and 6, depending on the total concentration, the orange-coloured decavanadates are formed [H_nV₁₀O₂₈⁽⁶⁻ⁿ⁾⁻, n = 0–3].

All the vanadium atoms in decavanadates are octahedrally coordinated and they can be classified according to their position in the structure as capping (4 atoms), corner (4 atoms) and central (2 atoms). They therefore produce three distinct peaks in the ⁵¹V NMR spectra, with intensity ratios of 4:4:2 (or 2:2:1), respectively. At neutral pH, colourless mono-, di- and cyclic oligovanadate species are formed.

These species (H₂VO₄⁻, H₂V₂O₇²⁻, V₄O₁₂⁴⁻, V₅O₁₅⁵⁻, V₆O₁₈⁶⁻) present vanadium nuclei tetrahedrally coordinated to oxygen. Increasing the pH further, at pH > 8, linear tetrameric and/or trimeric (HV₄O₁₃⁵⁻, V₄O₁₃⁶⁻ and

HV₃O₁₀⁴⁻, V₃O₁₀⁵⁻) species are formed, together with the singly deprotonated dimer HV₂O₇³⁻. The main species in alkaline solutions are the monoprotonated monomer HVO₄²⁻ and its dimer V₂O₇⁴⁻. At very alkaline pH (above 12), the only existing species is the vanadate ion, VO₄³⁻.

Many other anions appear when aqueous hydrogen peroxide is added to vanadate solutions.^[4–8] In this case, it was demonstrated that: (i) Diperoxovanadate complexes are present within the pH range 0–11, and the two species [VO(O₂)₂(OH)]²⁻ (–764.5 ppm) and [VO(O₂)₂(H₂O)]⁻ (–691.1 ppm) are predominant in peroxide-rich solutions. (ii) The pK_a value is 7.67 [in 0.150 M Na(Cl) ionic medium] and the large difference in the chemical shift values of the two species (73.4 ppm) makes it possible to detect any change in pH during the recording of the NMR spectra, that is, the peak could be used as an internal pH monitor. (iii) At pH > 6.5, two other species are visible, V(OH)(O₂)₃²⁻ (–732.2 ppm) and V₂(OH)O₂(O₂)₄³⁻ (–754.5 ppm). The triperoxo species is predominant at pH > 8 when the peroxide concentration is in excess (H₂O₂/V = 3:1). As expected, the dimer is favoured at high vanadium concentration and occurs in the pH range 6–9. (iv) On the acidic side, with pH < 3, besides diperoxovanadate complexes, there are two species, [VO(O₂)₂]⁺ (–539.5 ppm) and V₂O₂(O₂)₃ (–669 ppm), the former being the dominant complex at ratio H₂O₂/V = 1 and pH < 2.

⁵¹V NMR is sufficiently advanced that, by using a reference scale, approximate chemical shifts can be predicted for compounds of a known structure^[9] and, vice versa, the approximate coordination environment of unknown compounds can be predicted on the basis of chemical shift values. In general, harder donor atoms, such as oxygen and nitrogen, give peaks further upfield than softer donors, such as sulfur.^[9b] If ligands with conjugated functional groups able of distributing electron density throughout the ligand

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(e.g., phenolates and catecholates) are bound to vanadium, the chemical shift is increased because of low-energy ligand-to-metal charge-transfer (LMCT) transitions. In other words, the chemical shift value of vanadium complexes is inversely proportional to the LMCT energy.^[9c] Conte et al.^[9d] in contrast, studied the correlation between the chemical shift of some peroxovanadium complexes and their reactivity as electrophilic or radical oxidants, and they claimed that ligands that exert a shielding effect on the metal (e.g., picolinic or pyrazinic acids) favour radical reactivity of the peroxo moiety. Unfortunately, the majority of ⁵¹V NMR studies reported in the literature were performed in aqueous solvents, which limits the usefulness of such correlation only to reactions performed in water. Slebođnick and Pecoraro reported^[10] the ⁵¹V NMR spectra of the major species of simple vanadates and peroxovanadates in different mixtures of H₂O/CH₃CN and described the pattern differences by focusing on the absorptions of the major species [VO₂⁺, H_nVO₄ⁿ⁻³, HV₂O₇³⁻, V₄O₁₂⁴⁻, V₅O₁₅⁵⁻, V₁₀O₂₈⁶⁻, VO(O₂)⁺ and VO(O₂)₂⁻]. Generally, they exhibit downfield shifts as the water concentration in the solution decreases, and the magnitude of the shift is dependent on the species. Large vanadate oligomers are subject to small differences in chemical shifts with respect to minor ones and their relative abundance increases with the amount of acetonitrile, as low water concentrations drive equilibria towards aggregation. The behaviour of VO(O₂)₂⁻, instead, is quite particular, because at very low concentrations of water it gradually disappears. Under these latter conditions, two other major peaks (one upfield and the other downfield) emerge, which can be assigned to the diperoxovanadate dimer H_xV₂O₃(O₂)₄^{x-4} (upfield) and to V₂O₂(O₂)₃ (downfield), which is an unsymmetrical dimer that forms at high vanadium concentrations in acidic aqueous solution containing 1.5 or more equivalents of peroxide.^[5,8,11] Almost at the same time^[12] a similar downfield shifting effect of acetonitrile was reported for some peroxovanadium complexes, and they were explained in terms of preferential solvation.

On the basis of these data, the following study was aimed to understand the different reactivity^[13] (in molecular solvents vs. in ionic liquids) observed for peroxovanadium species, trying to identify the nature of the vanadium species in ionic liquids with spectroscopic techniques, especially ⁵¹V NMR spectroscopy.

Results and Discussion

Preliminary UV/Vis analysis performed on diperoxovanadate solutions ([NH₄VO₃] = 1 mM; [H₂O₂] = 2 mM) showed (Figure 1) that when increasing amounts of hydrophilic ionic liquids were added, the absorption of the peroxo complexes became more intense, despite the concomitant dilution.

In order to understand the exact nature of this effect and the reason why it is more pronounced with the tetrafluoroborate anion than with the trifluoromethanesulfonate

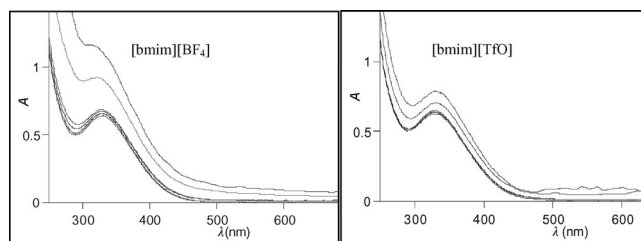


Figure 1. UV/Vis spectra of an aqueous solution containing the diperoxovanadate complexes with an increasing amount of [bmim][BF₄] (left) or [bmim][CF₃SO₃] (right).

(triflate) anion, a ⁵¹V NMR spectroscopic investigation was performed on the vanadium solution both in the absence and in the presence of hydrogen peroxide. In particular, the behaviour of the vanadate salts was studied and three different hydrophilic ionic liquids (Figure 2) were used for this purpose.

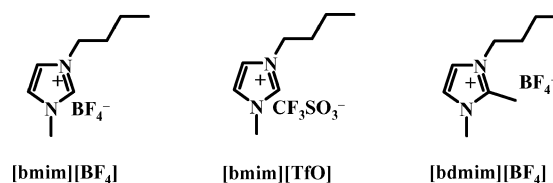


Figure 2. Structure of ionic liquids used in ⁵¹V NMR analysis.

Spectra without H₂O₂

The first step was to study the behaviour of vanadate when the environment was changed from water (well known in the literature) to an almost ionic one. For this purpose, we recorded three series (for each ionic liquid) of ⁵¹V NMR spectra with increasing amounts of ionic liquid. Because the series of [bdmim][BF₄] is quite similar to the [bmim][BF₄] one, only two series of spectra are reported here.

The top spectra in Figures 3 and 4 (no ionic liquid added) show the peaks of the H₂VO₄⁻, H₂V₂O₇²⁻, V₄O₁₂⁴⁻ and V₅O₁₅⁵⁻ species known to be present at neutral pH. These are denoted V₁, V₂, V₄ and V₅ in the spectra. At this 10 mM concentration, V₄O₁₂⁴⁻ is the dominant species.

As it can be seen from the figures, the ionic liquids broaden and cause similar upfield shifts of the peaks originally present in water (mainly the tetramer and the pentamer ones). The pattern of the spectra seems to depend on the nature of the ionic liquid chosen, even when the amount of ionic liquid is as low as 33%. In addition, in the case of [bmim][BF₄] three new and previously unreported peaks appear around -460, -550 and -610 ppm. They become predominant with time and disappear when NaOH is added.

In order to understand this behaviour, mixtures with lower amounts of [bmim][BF₄] were analyzed by ⁵¹V NMR spectroscopy (Figure 5).

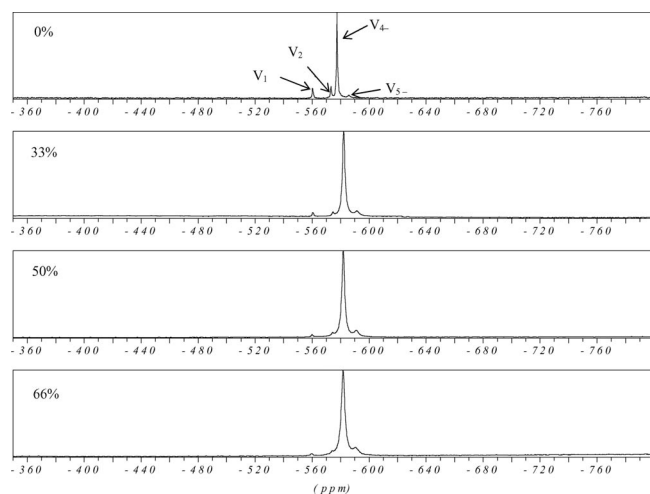


Figure 3. ^{51}V NMR spectra of a 10-mm NH_4VO_3 solution in $\text{D}_2\text{O}/[\text{bmim}][\text{TfO}]$ with increasing percentage of ionic liquid.

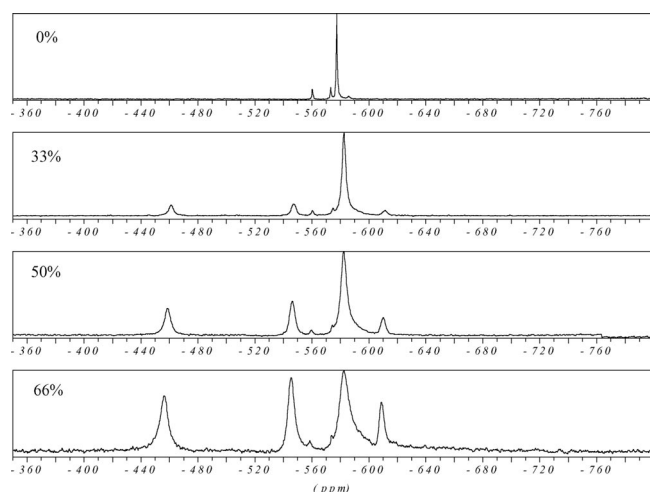


Figure 4. ^{51}V NMR spectra of a 10-mm NH_4VO_3 solution in $\text{D}_2\text{O}/[\text{bmim}][\text{BF}_4]$ with increasing percentage of ionic liquid.

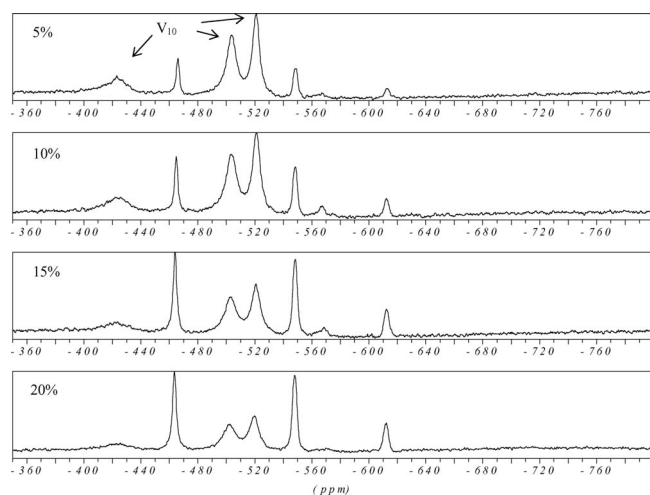


Figure 5. ^{51}V NMR spectra of a 10-mm NH_4VO_3 solutions in $\text{D}_2\text{O}/[\text{bmim}][\text{BF}_4]$ with increasing percentage of ionic liquid.

As it can be seen, the ^{51}V NMR pattern of these solutions is very different from that of the aqueous one even in the case of 5% $[\text{bmim}][\text{BF}_4]$ (see top spectrum in Figure 3 for comparison). The three peaks that are typical in tetrafluoroborate mixtures are present, but three other peaks appear (at -420 , -500 and -520 ppm) due to the formation of V_{10} species.^[1,2,3a,3b,14] These decavanadate peaks become less intense and broadened with the increasing percentage of ionic liquid, whereas the new peaks increase. Indeed, in 33% $[\text{bmim}][\text{BF}_4]$ mixture (see Figure 4) decavanadate peaks are not present. Furthermore, in the spectra with lower amounts of ionic liquid the predominant peak at -580 ppm (V_4) that was visible in Figure 3 does not appear, which thus indicates that the kinetics of the interaction between ionic liquid and vanadate oligomers can be faster for media with lower viscosity. As previously stated in the introduction, decavanadates are formed in water in the 3–6 pH range and, moreover, their chemical shifts are sensitive to pH itself:^[3a,3b,14] so their values can be seen as an approximate pH measurement. By comparing the shifts in these $[\text{bmim}][\text{BF}_4]/\text{water}$ mixtures with those reported in the literature for water solutions, it can be hypothesized that the addition of this ionic liquid to water (at least in small percentages) lowers the pH of the mixtures to values in the range 3–4.

The possibility of chemical exchange between the vanadium nuclei giving the peaks at -460 , -550 and -610 ppm was investigated. Longitudinal relaxation times (T_1) were obtained from nonselective inversion recovery experiments and are reported in Table 1 (see Experimental Section for details).

Table 1. Longitudinal relaxation times (T_1) for the peaks found in $[\text{bmim}][\text{BF}_4]$ spectra.

Peak (ppm)	T_1 (ms)
-460	≈ 0.1
-550	1.3
-610	7.0

Because the first two peaks have very short relaxation times, magnetization transfer can be studied only by the selective inversion of the third peak (-610 ppm). Following this procedure, neither exchange nor a decrease in T_1 of the inverted peak occurred, likely because of the short relaxation times of the other two vanadium species or because the three peaks are due to different vanadium nuclei present in the same molecule. In both cases, vanadium does not exchange in the millisecond timescale. To verify which of these hypothesis holds, 2D ^{51}V NMR COSY spectra were performed, but no significant cross peaks were detected. However, it is difficult to reveal couplings with such broad peaks as these.

Furthermore, kinetic experiments were performed to detect the variation with time of the spectrum of aqueous solutions of NH_4VO_3 after addition of ionic liquid. Two cases were studied: 5% ionic liquid was added in the first case and 20% was added in the second case. The resulting spectra are shown in Figures 6 and 7, respectively.

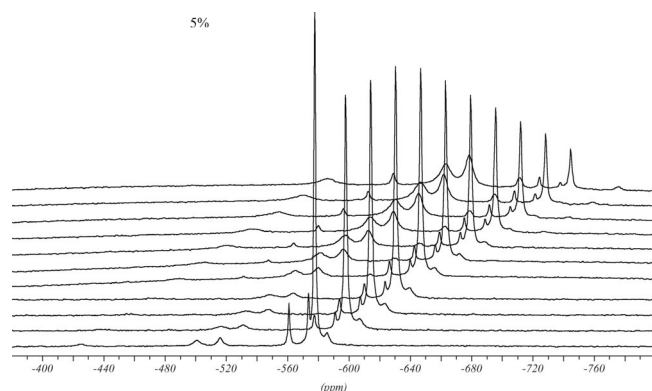


Figure 6. Variation as a function of time for the NH_4VO_3 spectrum in 5% $[\text{bmim}][\text{BF}_4]/\text{D}_2\text{O}$ over a 24-h period.

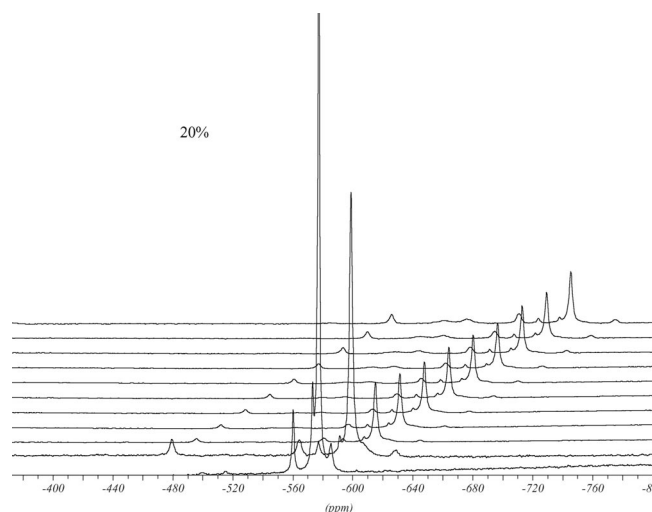


Figure 7. Variation as a function of time for the NH_4VO_3 spectrum in 20% $[\text{bmim}][\text{BF}_4]/\text{D}_2\text{O}$ over a 24-h period.

The behaviour of these two mixtures is quite different. In a 5% mixture (Figure 6), the effect of the ionic liquid is realized as a slow increase in the decavanadates peaks, whereas the other three peaks become detectable only after a long time and with low intensities. In 20% solution (Figure 7), the addition of ionic liquid has an immediate effect, as shown by the formation of the three peaks typical for tetrafluoroborate mixtures. Decavanadate peaks become detectable after a longer time.

In order to understand if this particular behaviour is derived from the organized structure^[15] of ionic liquids, which may produce the existence of ion pairs in such ionic liquid/water mixtures, diffusion experiments (^1H to measure the cation diffusion and ^{19}F to measure the anion one) were performed with 5% solution of $[\text{bmim}][\text{BF}_4]$ in D_2O , without any vanadium. The results from these experiments are reported in Table 2.

Table 2. Diffusion constants for the species present in a 5% mixture of $[\text{bmim}][\text{BF}_4]$ in D_2O ($\delta = 2$ ms; $\Delta = 50$ ms) at room temperature.

Species	Diffusion constants (m^2s^{-1})
bmim cation	0.6×10^{-9}
Tetrafluoroborate anion	1.1×10^{-9}
Water (in 5% $[\text{bmim}][\text{BF}_4]/\text{D}_2\text{O}$)	1.6×10^{-9}
Water in D_2O	1.9×10^{-9}

As it can be seen, the diffusion constants for the bmim cation and the tetrafluoroborate anion are very different, so no inert ion pairs between these two species can be hypothesized. The diffusion constant for water in the 5% ionic liquid mixture is about 15% less than the one in pure D_2O . This reduction can be ascribed to the higher viscosity of the medium, or to an interaction between water and the ions.

Trying to solve this problem from another point of view, it can be observed that the three signals characterizing the tetrafluoroborate mixture always appear together, although the ratio between the integrals is not fixed. The integral ratio between the signal at -460 ppm and the one at -550 ppm seems to be constant (and equal to 1:1), whereas the integral ratio with the signal at -610 ppm is variable. Therefore, it may be hypothesized that in ionic liquid solutions, the scarce presence of water and higher ionic strength favours the formation of highly charged polyanions.^[16] Partial reduction of some V^{V} nuclei to V^{IV} may be invoked to explain the variable value of the ratios of the integrals.

One of the most simple polynuclear vanadium compounds formed in an nonaqueous environment is $[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32})^4]^{[17]}$ an inclusion compound, where an acetonitrile molecule is included in a hemispherical structure of 12 condensed square planar $\{\text{VO}_5\}$ units. It is formed in acetonitrile solutions containing decavanadate, and its ^{51}V NMR spectrum in acetonitrile is characterized by three signals (-590 , -598 and -606 ppm). In order to verify if a dodecavanadate species (or some other species with a similar structure) is responsible for the three peaks in the tetrafluoroborate mixtures, the tetrabutylammonium dodecavanadate was synthesized and its spectrum was recorded in acetonitrile in the presence of increasing amounts of $[\text{bmim}][\text{BF}_4]$. The addition of ionic liquid shifts and broadens the peaks, but no correspondence with the peaks in the tetrafluoroborate mixtures was found.

Because spectra recorded from $[\text{bmim}][\text{TfO}]$ mixtures do not show such peaks, it may be possible that they could originate from the tetrafluoroborate anion itself, independently from the cation. A 30-mm solution of NH_4VO_3 in D_2O was prepared: 0.6 mL of this solution were taken and diluted with 1.2 mL of a saturated NaBF_4 water solution (1 g mL^{-1}), and the spectrum of the resultant 10-mm NH_4VO_3 solution is shown in Figure 8.

This shows that the tetrafluoroborate anion must somehow be the source of the three peaks previously seen at -460 , -550 and -610 ppm. In the NaBF_4 solution, the chemical shifts are -469 , -548 and -613 ppm. Very likely, this behaviour can be ascribed to the hydrolysis of BF_4^- ,

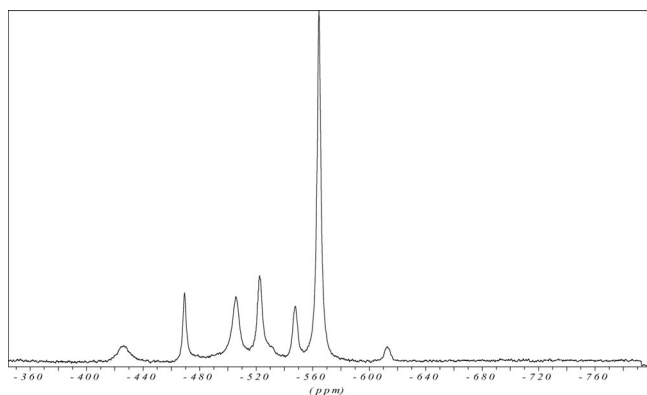


Figure 8. ⁵¹V NMR spectrum of a 10-mm solution of NH₄VO₃ in a mixture of D₂O/saturated NaBF₄ (1:2).

which forms HF.^[18] Because the solution then becomes acidified, the three decavanadate peaks appear as well at -426, -505 and -522 ppm.

Spectra with H₂O₂

From preliminary NMR experiments carried out by adding H₂O₂ in excess to a 10-mm solution of NH₄VO₃ in 90% [bmim][BF₄], two peaks, due to peroxo complexes, were detected. One peak appears at -640 ppm (the most intense) and the other at -690 ppm.

In order to understand which peroxo complexes give rise to these peaks, H₂O₂ was added to all the previous containing vanadate samples to give (peroxide/V) = 2. Under these conditions, diperoxovanadate species are known to be formed in aqueous solution.^[8]

The first spectrum in each series (see Figures 9 and 10) is a comparison spectrum obtained after the addition of hydrogen peroxide to an aqueous vanadate solution. When H₂O₂ is present in twofold excess, the vanadate monomer and oligomers almost disappear and a new signal appears at -690 ppm. This peak is known to arise from a monomeric diperoxovanadate complex [VO(O₂)₂(H₂O)]⁻ (cf. Figures 9 and 10, spectra at the top). In the presence of 50% [bmim][BF₄] (when the vanadate peaks disappear after the addition of hydrogen peroxide), two new peaks appear: one at -674 ppm and the other (a doublet) around -702 ppm. In the cases of [bmim][TfO] and [bdmim][BF₄], two peaks appear as well. In the first ionic liquid at -675 ppm and around -730 ppm, whereas the behaviour of [bdmim][BF₄] resembles that of [bmim][BF₄] (spectra not shown): one peak at -675 ppm and a doublet around -700 ppm.

In the ionic liquid mixtures containing the BF₄⁻ anion, the peak with a higher chemical shift can be attributed to [VO(O₂)₂(H₂O)]⁻. The difference in chemical shift compared with the corresponding one in water is likely due to the presence of the ionic liquid itself, as in the spectra without hydrogen peroxide, or in those of peroxo complexes in acetonitrile.^[10,12]

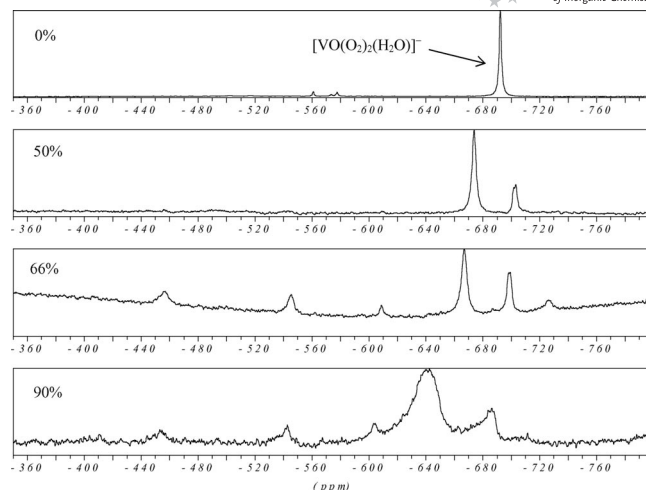


Figure 9. ⁵¹V NMR spectra of 10-mm NH₄VO₃ solutions in D₂O/[bmim][BF₄] with increasing percentage of ionic liquid after addition of H₂O₂ 2:1.

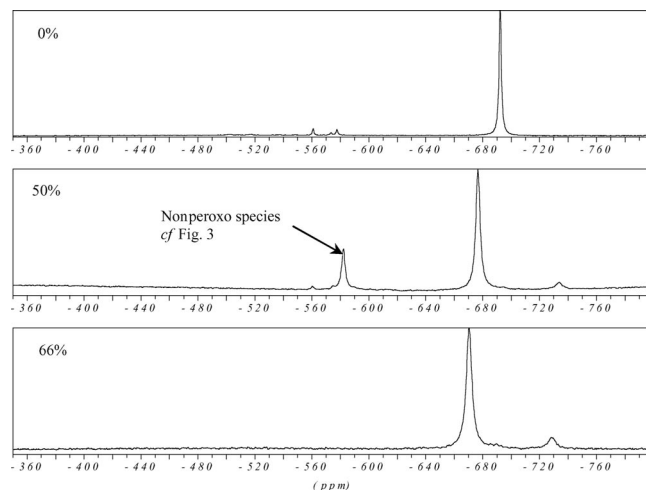


Figure 10. ⁵¹V NMR spectra of a 10-mm NH₄VO₃ start solution after addition of H₂O₂ 2:1 (in D₂O), and with increasing percentage of the ionic liquid [bmim][TfO].

Concerning the other peak, it was observed that the integral ratio with respect to the diperoxovanadate peak increases as the quantity of ionic liquid present in the solution increases, but not with an increase in the vanadium concentration. From these observations it can be hypothesized that the species giving rise to this peak is responsible for the absorbance increase in the UV/Vis spectra of diperoxovanadate by the addition of increasing amounts of ionic liquids (Figure 1).

On the basis of the spectra discussed above and taking into account the hydrolysis of tetrafluoroborate anion, it can be suggested that the absorption at -700 ppm is due to the diperoxofluorovanadate species [VO(O₂)₂F]²⁻,^[19] which is known to be formed by V^V and hydrogen peroxide in the presence of a massive amount of fluoride ions. The structure of this species is shown in Figure 11.

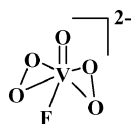


Figure 11. The structure of $[\text{VO}(\text{O}_2)_2\text{F}]^{2-}$.

Its ^{51}V NMR spectrum in water is characterized by a doublet (due to coupling with ^{19}F) around -714 ppm, and it is shifted upfield by substituting water with DMF as solvent. The minor peroxo peak that appears in $[\text{bmim}][\text{TfO}]$ solutions (Figure 10) may be ascribed to an oligomerization process of diperoxovanadate, in analogy to that in acetonitrile.^[10] When H_2O_2 is added to vanadate aqueous solution in a 2:1 ratio and NaBF_4 is present, the ^{51}V NMR spectrum does not show this peak. Thus, without the ionic liquid cation, no peak beside the diperoxovanadate one was detected, which indicates the occurrence of some ionic liquid stabilization effects on the diperoxofluorovanadate.

Kinetics

From a catalysis point of view, the lifetime of H_2O_2 in the system is crucial. In order to get an overview of the H_2O_2 rate of decomposition in ionic liquids, ^{51}V NMR spectra were recorded 24 h after the addition of hydrogen peroxide. Peroxide degradation is faster in ionic liquids than in water. In fact, ^{51}V NMR spectra of diperoxovanadate in “pure” water do not show any consumption of H_2O_2 after 24 h. In contrast, after 24 h in the presence of $[\text{bmim}][\text{BF}_4]$ and $[\text{bdmim}][\text{BF}_4]$, H_2O_2 is completely consumed, whereas in the presence of $[\text{bmim}][\text{TfO}]$ a significant amount of diperoxovanadate is still present.

Degradation of hydrogen peroxide leads to the formation of the peaks that appeared in mixtures before the addition of H_2O_2 itself, which is indicative of the regeneration of vanadate oligomers.

Studies with Added Picolinate

Another peroxovanadate system of synthetic relevance is the one formed by vanadate, hydrogen peroxide and picolinic acid (PicOH), which under feasible conditions leads to efficient aromatic hydroxylation through the formation of the complex $\text{VO}(\text{O}_2)\text{PicO} \cdot 2\text{H}_2\text{O}$.^[20]

Pettersson and coworkers^[21] performed a complete speciation study of the peroxovanadate–picolinate system in aqueous solution (0.150 M NaCl medium). In acidic solution at a 1:1:1 ratio of vanadate/hydrogen peroxide/picolinate, they found a major uncharged species with the same composition as in the above solid compound.

Isolated $\text{VO}(\text{O}_2)\text{PicO} \cdot 2\text{H}_2\text{O}$ is insoluble in ionic liquids, so we tried to form the catalyst directly in the ionic liquid, starting from an ionic liquid soluble vanadate ($[\text{bmim}][\text{VO}_3]$), picolinic acid (in 1:1 ratio) and hydrogen

peroxide. With this strategy and in the presence of benzene, small yields of phenol were detected. Moreover, the yield appeared to depend on the initial amount of hydrogen peroxide that was added to form the catalyst.^[13d]

A 10-mm solution of $[\text{bmim}][\text{VO}_3]$ and PicOH in a mixture of 66% $[\text{bmim}][\text{BF}_4]$ in water was prepared. A ^{51}V NMR spectrum of this solution is reported in Figure 12 (top spectrum). The other spectra in the same Figure were recorded after the addition of hydrogen peroxide in ratios of 1:1 and 2:1 with respect to vanadium.

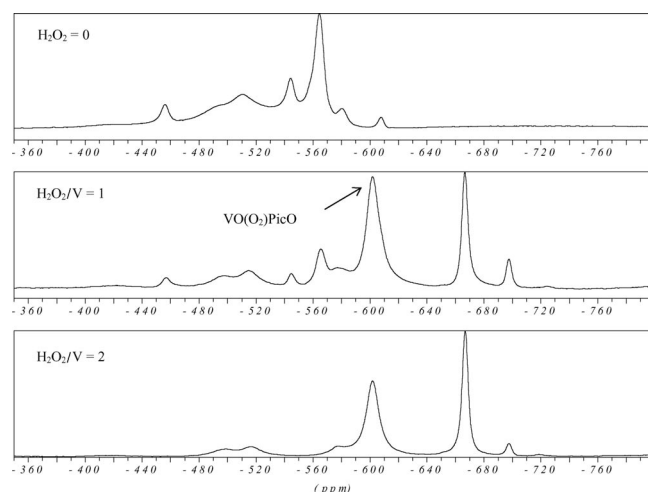


Figure 12. ^{51}V NMR spectra of a 10-mm solution of $[\text{bmim}][\text{VO}_3]$ and 10 mm of picolinic acid in 66% $[\text{bmim}][\text{BF}_4]$ in water before and after addition of H_2O_2 in ratios of 1:1 and 2:1 with respect to vanadium.

The top spectrum (without hydrogen peroxide) is characterized by a broadened pattern in which two new distinct peaks are visible at -565 and -580 ppm. They most likely originate from the interaction between vanadate and picolinate,^[21] and their shift values seem to be influenced by the presence of ionic liquid. The other three distinct peaks (at -455 , -545 and -610 ppm) originate from the interaction between vanadate and tetrafluoroborate anion (cf. the bottom spectrum in Figure 3).

The broad peaks between -470 and -530 ppm are difficult to identify, as in this spectral zone, decavanadate absorptions overlap with those of vanadate–picolinate complexes.^[21] When hydrogen peroxide was added, three additional peaks appeared. The peaks present before the addition of H_2O_2 decreased, and were hardly visible at $\text{H}_2\text{O}_2/\text{V} = 2:1$. The intense and broad peak at -600 ppm most likely arises from the uncharged monoperoxo monopicolinate vanadium complex. Under the present conditions, this species should, from earlier studies,^[21,22] be the dominant one. The other two peaks (at -670 and -700 ppm) were earlier found in 66% ionic liquid mixture containing vanadate and hydrogen peroxide, despite the fact that no picolinic acid had been added (see Figure 9). The more intense peak (-670 ppm) was assigned to the monomeric diperoxovanadate complex and the smaller one (-700 ppm) to

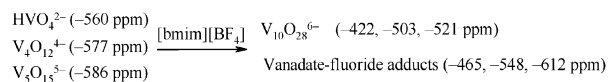
[VO(O₂)₂F]²⁻. It should be noted that these two peaks do not appear in the spectrum of presynthesized catalyst in mixtures of 66% [bmim][BF₄].

We studied also the behaviour of this system by changing the ionic liquid from [bmim][BF₄] to [bdmim][BF₄], but no substantial differences were observed. Increasing the amount of hydrogen peroxide, however, visibly increased the peak at -670 ppm for both ionic liquids.

Conclusions

The data so far reported clearly indicate that ionic liquids have a strong influence on the solution chemistry of vanadate in water both for the formation of aggregates (with and without H₂O₂) and for the rate of peroxide consumption catalyzed by vanadium.

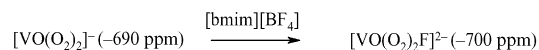
The BF₄⁻ anion is responsible for the formation of the three typical peaks observed in tetrafluoroborate-based ionic liquids (at -465, -548 and -612 ppm). This behaviour may be due to the fact that the anion acts as a fluorinating agent^[23] in the presence of a suitable acceptor, such as vanadium.^[24] As a consequence, formation of vanadium-fluoride adducts can be suggested.



Moreover, it is very well known^[18a] that aqueous sodium tetrafluoroborate solutions are acidic to litmus, as hydrolysis occurs to produce HF. The fact that the solutions become acidic can also explain the appearance of decavanadate peaks (at -420, -505, -523 ppm). Results of selective inversion recovery experiments are congruent with the hypothesis of a multinuclear species (-460, -550 and -610 ppm), whereas NMR diffusion ones, performed on 5% [bmim][BF₄] water solution, in the absence of vanadium, showed that aggregation through ion pairs, that is, an organized matrix effect, is not important. It can be hypothesized that from the tetrafluoroborate anion two parallel processes may originate: (i) It can react with water to produce HF, which consequently favours the formation of decavanadate and vanadium-fluoride adducts. (ii) It may react directly with vanadium to produce vanadium-fluoride adducts only. The observed change with time of a 10-mm aqueous vanadate solution in a 5% [bmim][BF₄] in comparison to the change with time of a 10-mm vanadate solution in a 20% mixture supports the fluoridation hypothesis. In the 5% mixture, decavanadate is initially formed, and then the other three peaks appear. In 20% mixture, the situation is completely reversed and the three peaks appear first. Moreover, decavanadate peaks do not emerge in spectra from moderately to high percentage of ionic liquid (from 33 to 90%). In contrast, solutions with a low percentage of ionic liquid (up to 20%) show peaks that disappear with time.

Even though the literature on vanadium oxyfluorides is quite rich,^[25] ⁵¹V NMR characterization of such species is not available. Thus, a direct comparison with literature data is not possible.

Ionic liquids containing a more stable anion than tetrafluoroborate (viz. triflate) have no particular effect on the spectrum of aqueous vanadate solutions, except for peak broadening. In contrast, ionic liquids seem to have an effect on peroxovanadate species, independently of the anion. In fact, whereas in water the addition of H₂O₂ produces only one peak, that is, the diperoxo complex, in ionic liquids other peaks are present. Taking into account the fluorinating ability of tetrafluoroborate, the most intense among the secondary peaks that form in the presence of BF₄⁻ may be seen as diperoxofluorovanadate [VO(O₂)₂F]²⁻,^[19] as it appears as a doublet and at lower ppm values than other diperoxovanadate species. Time-sequence spectra seem to suggest that this fluoro species is in equilibrium with diperoxovanadate.



For the peroxo peaks appearing in other ionic liquids than [bmim][BF₄] (viz. triflate), different anion interactions may be taken into account, such as coordination or dimerization of peroxovanadate species, in analogy with what was observed in acetonitrile.^[10] The formation and the low stability of these secondary species may be the reason for the enhanced peroxide consumption rate.

The analyses performed on the V/H₂O₂/picolinic acid system confirm that under the conditions adopted to carry out benzene hydroxylation, VO(O₂)PicO·2H₂O forms, as observed by the appearance of an absorption around -600 ppm.^[21,22] The addition of further hydrogen peroxide only seems to enhance absorption of diperoxovanadate.

Different from other peroxo species, the monoperoxo-picolinate absorption is not shifted by the addition of ionic liquid. This behaviour is in contrast to that in acetonitrile.^[12] Indeed, VO(O₂)PicO·2H₂O in acetonitrile reacts with benzene, whereas under similar conditions in [bdmim][BF₄] only a small amount of phenol formed.^[13d]

Experimental Section

General Methods: All the NMR samples were prepared by dissolving ammonium vanadate (Acros Organics) in D₂O and then adding the desired volume of ionic liquid. The amount of ammonium vanadate was calculated in order to have a 10 mM final concentration after the addition of ionic liquid. UV/Vis analyses were performed by starting with a 1-mM solution of ammonium vanadate, successively diluted up to 0.3 mM by addition of ionic liquids. Ionic liquids were prepared by using literature procedures.^[13a] ⁵¹V NMR spectra were recorded with a Bruker AMX 400 spectrometer at "Università degli Studi di Roma Tor Vergata" and with a Bruker DRX 360 spectrometer at "Debreceni Egyetem" (University of Debrecen, HU). An inverse broad-band probe head was used with 5-mm sample tube. The pulse width was 30° with a 100 ms relaxation delay

to ensure complete longitudinal relaxation of all the ^{51}V . The post processing was done by XWinNMR and WinNMR software developed by Bruker Biospin Co.

The diffusion constants (D) of bulk and the ionic liquid components were measured by ^1H and ^{19}F NMR spectroscopy by using a stimulated pulse field gradient program (*ledbpgp2s*) provided with the Bruker spectrometer. Usually 16 gradient steps were employed with full gradient power by applying 2 ms gradient pulse length (δ) and 50 ms diffusion time (Δ). The diffusion coefficients were calculated by nonlinear least-square fitting from the attenuation of signals (I) at increasing gradient powers (G) according to the following equation:

$$I = I_0 \exp[-DG^2\gamma^2\delta^2(\Delta - \delta/3)]$$

where I_0 is the integrated intensity of the NMR signals when $G = 0$ and γ is the magnetogyric ratio of the measured nuclei. The method was calibrated on diffusion constant of D_2O by using a value of $1.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K.

The longitudinal relaxation time T_1 values were measured by means of standard Bruker inversion recovery program by using exponential fitting to the measured intensity versus mixing time curves. The selective excitation was made by using a Dante sequence with 50 elements and 0.5 μs pulse length.

All the spectra in solutions without hydrogen peroxide were recorded at least 24 h after sample preparation. Spectra with hydrogen peroxide were recorded as soon as possible after the addition of peroxide itself to previously prepared samples. Tetrabutylammonium dodecavanadate was synthesized starting from the corresponding decavanadate.^[17]

General Procedure: Tetrabutylammonium hydroxide $[\text{N}(\text{Bu})_4\text{OH}]$ (19.5 mmol) was dissolved in water (50 mL) and V_2O_5 (9.8 mmol) was added. After complete dissolution of the anhydride, water was removed by evaporation, and the obtained solid, corresponding to tetrabutylammonium vanadate $[\text{N}(\text{Bu})_4\text{VO}_3]$, was dried under vacuum. Once this product was isolated, it was dissolved (0.5 mmol) in methanol (90 mL) and glacial acetic acid (5 mL) was added to allow the formation of the decavanadate $[\text{H}_4\text{V}_{10}\text{O}_{28}]^{2-}$ anion.^[26] After a sudden change in colour (from almost colourless to orange), the resulting reaction mixture was heated to reflux for 3 h. Precipitation was induced by partial solvent evaporation and subsequent diethyl ether addition. Crystals were collected by suction filtration and then washed with diethyl ether and dried under vacuum. Once tetrabutylammonium decavanadate was isolated, it was dissolved in acetonitrile, and the resulting mixture was heated to reflux for a short period (some minutes). The resulting $[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32})^{4-}]$ was isolated^[17] by addition of diethyl ether until precipitation occurred. The solid compound was purified by crystallization from a acetonitrile/ethyl acetate (1:2) at very low temperature (-18°C). Yield: 45%. The identity of this compound ($[\text{CH}_3\text{CNC}(\text{V}_{12}\text{O}_{32})^{4-}]$) was confirmed^[17] by ^{51}V NMR analysis in CH_3CN . The expected three peaks were visible at -590 , -598 and -606 ppm.

Supporting Information (see footnote on the first page of this article): Selection of ^{51}V NMR spectra for vanadates and peroxovanadates; graph referring to the magnetization transfer experiments on the three peaks appearing in $[\text{bmim}][\text{BF}_4]/\text{H}_2\text{O}$ (50%) (selective inversion of the -610 ppm peak does not show any effect on the integral of the -450 and -550 ppm peaks).

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