

Vanadium Oxide Complexes in Room-Temperature Chloroaluminate Molten Salts

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The dissolution of vanadium(V) oxide (V_2O_5) in various ionic liquids has been studied to determine the complexes formed with respect to melt composition and V_2O_5 concentration. Vanadium oxide did not dissolve in either 1-*n*-butyl-3-methylimidazolium tetrafluoroborate or 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquids. V_2O_5 was found to dissolve at temperatures greater than 70 °C in 1-ethyl- and 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate ionic liquids. Analyses of vanadium-containing melts by ^{51}V , 1H , and ^{13}C NMR and infrared spectroscopy indicate the emergence of different species as a function of melt acidity. In basic and neutral melts, $VO_2Cl_2^-$ and a metavanadate species of the form $[(VO_3)_n]^{n-}$ are observed. The species $VO_2Cl_2^-$ is the prominent product in basic melts, but as the melt becomes neutral or as the concentration of V_2O_5 is increased, the concentration of the metavanadate species is found to increase. However, V_2O_5 has been found to react in acidic melts to form volatile $VOCl_3$.

Introduction

There has been a growing interest in the study of ambient-temperature ionic liquids as an amiable solvent for the study of transition metal chloro complexes. Ionic liquids represent an ideal nonaqueous environment for studying the reactions of these transition metal complexes free from the effects of solvation and solvolysis phenomena.¹ Many transition metal chloro complexes^{1–4} and their reactivities toward various hydrocarbons^{3,5} have been investigated in this unique media. In addition to metal chlorides, stable oxochloro complexes have been observed in these liquids.^{6–9} Oxygen-containing transition metal compounds have been used extensively in industry as catalysts or as supports for other catalytic materials. For example, vanadium oxides and other related vanadium-containing compounds are widely used as catalysts,¹⁰ especially for oxygen-transfer reactions.¹¹ Vanadium compounds have been studied extensively to determine their catalytic properties and to gain

insight into the mechanisms of these reactions.^{12,13} Room-temperature chloroaluminate molten salts provide an ideal aprotic environment in which vanadium compounds may be used and studied as catalysts or as battery cathodes. Thus, it is necessary that the stability of V_2O_5 or that of the reaction products in these melts be understood. The objective of the present study is to determine the reactions of V_2O_5 in Lewis basic, neutral, and acidic chloroaluminate ionic liquids of varying vanadium(V) oxide content.

Several studies have shown a variety of vanadium species to be stable in Lewis basic 1-ethyl-3-methylimidazolium tetrachloroaluminate ionic liquids, EMIC/ $AlCl_3$.^{14–16} Hanz and Riechel have shown that chloride can be added to VCl_3 to form higher order chloride complexes up to VCl_6^{3-} and that each

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vanadium(III) complex can be reversibly oxidized to a corresponding vanadium(IV) complex.¹⁴ However, not all chloride-containing vanadium compounds are stable in ionic liquids, as many react with the medium to form new species. For example, VOCl_3 and VCl_6^{2-} react in basic chloroaluminate melts to form VOCl_4^{2-} and VCl_6^{3-} , respectively.¹⁵ Welton and co-workers formed the salt 1-ethyl-3-methylimidazolium tetrachlorooxovanadate(IV) to further explore the chemistry of oxygen-transfer reactions of vanadium compounds by studying both the X-ray crystal structure of the salt and conducting a spectroscopic investigation of its structure in a basic EMIC/ AlCl_3 melt.¹⁶ To further understand the nature by which oxychloro vanadium complexes are formed, the dissolution of V_2O_5 in EMIC/ AlCl_3 and 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate, BMIC/ AlCl_3 , ionic liquids was examined in the present study through a spectroscopic investigation. To gain more insight into these processes, an investigation of the effects of melt acidity and vanadium concentration on the types and stability of the products formed was undertaken.

Experimental Section

Instrumentation. ^{51}V NMR spectra were recorded at 105.2 MHz and $25 \pm 1^\circ\text{C}$, using a Varian/NOVA 400 MHz spectrometer equipped with a 10 mm broad band probe. Typically, spectral widths of 150 kHz, pulse widths of 8 μs (90° pulse angle), and line broadening of 50 Hz were used. All ^{51}V NMR spectra were collected using neat samples in 5 mm sample tubes which were placed inside 10 mm tubes containing $\text{CO}(\text{CD}_3)_2$ for deuterium locking. All ^{51}V NMR chemical shift literature values and those for the present experiments are reported relative to neat VOCl_3 (0 ppm).

^1H and ^{13}C NMR spectra were recorded using a Bruker 500 spectrometer. These spectra were collected neat or in CD_3CN solvent with chemical shifts measured in ppm relative to the external reference tetramethylsilane (TMS). Infrared spectra were collected on a Perkin-Elmer 1600 spectrometer using both NaCl salt plates and polypropylene film. The mass spectra were collected using a PerSeptive Biosystems delayed extraction MALDI time-of-flight mass spectrometer. An N_2 laser was used to thermally excite the ionic liquid to expel the ions into the time-of-flight region of the spectrometer for mass analysis.

Reagents and Synthesis. All compounds were synthesized and purified using published methods. The 1-ethyl-3-methyl-1*H*-imidazolium chloride (Aldrich) was dissolved in a minimal amount of acetonitrile and recrystallized from toluene.¹⁷ Residual solvent was driven off by heating the powder to 90°C under reduced pressure. Aluminum(III) chloride (Aldrich) was purified by vacuum sublimation.¹⁸ The reagents 1-chlorobutane, 1-methylimidazole, 99.99% anhydrous vanadium oxide, sodium metavanadate, sodium tetrafluoroborate, and sodium trifluoromethanesulfonate were used as supplied by the Aldrich Chemical Co. VOCl_3 (Aldrich) was distilled in vacuo prior to use. Acetonitrile and toluene (Aldrich) were dried over activated molecular sieves in a nitrogen atmosphere. All other solvents were distilled from appropriate drying agents under nitrogen.

The 1-*n*-butyl-3-methylimidazolium chloride (BMIC) was prepared by refluxing 1-methylimidazole in an excess of 1-chlorobutane for 24 h.¹⁷ The excess chlorobutane was removed by evaporation and the crude product recrystallized from acetonitrile. The 1-*n*-butyl-3-methylimidazolium tetrafluoroborate was prepared by adding equal molar amounts of sodium tetrafluoroborate to a solution of BMIC in acetone at room temperature.¹⁹ The 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate²⁰ was prepared in the same manner using sodium trifluoromethanesulfonate. Both mixtures were stirred for 24 h, filtered, and

evaporated to yield the crude products. All experiments were performed in inert-atmosphere gloveboxes under dry nitrogen or argon. Glassware was oven dried under reduced pressure prior to use.

Results and Discussion

The dissolution of vanadium oxide occurred in acidic, neutral, and basic EMIC/ AlCl_3 and BMIC/ AlCl_3 melts at temperatures above 70°C . At no time did V_2O_5 or the products formed during the dissolution process precipitate out of solution after the ionic liquid reached room temperature. V_2O_5 was found to be rather soluble in the chloroaluminate ionic liquids. For example, 0.15 g of V_2O_5 was found to dissolve in 1.0 g of basic EMIC/ AlCl_3 at a mole ratio of 1.0:0.8 (EMIC: AlCl_3). No formal solubility constants were determined due to the reaction of the vanadium oxide with the solvent. The Lewis acidity of the melts may be expressed in terms of the chloride concentration,²¹ which depends on the molar ratio of the constituent 1-alkyl-3-methylimidazolium chloride salt and AlCl_3 . Neutral melts contain an equal molar ratio of AlCl_3 and EMIC (or BMIC) with AlCl_4^- as the predominant anion, although trace amounts of Cl^- and Al_2Cl_7^- are present.^{1b,22} Acidic melts contain an excess of AlCl_3 , thus increasing the concentration of the acidic species (Al_2Cl_7^-) in the melt, while basic ionic liquids have higher concentrations of Cl^- due to excess EMIC in the melt. Although the dissolution of vanadium oxide occurred in chloroaluminate melts, it did not appear to dissolve in the inherently neutral ionic liquids 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, $[\text{BMI}][\text{BF}_4]$, or 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate, $[\text{BMI}][\text{CF}_3\text{SO}_3]$, at temperatures up to 100°C with constant stirring for 24 h.

The 1-alkyl-3-methylimidazolium cation was not affected by the dissolution process nor did it appear to react with the vanadium compounds formed over the range of compositions examined, as indicated by ^1H and ^{13}C NMR spectra. The ^{51}V NMR results displayed distinctly different products for the dissolution of vanadium oxides in acidic melts as compared to those formed in basic and neutral melts. The dissolution of vanadium oxide was first attempted in open vials within an inert atmosphere drybox. However, the samples prepared in this manner displayed no ^{51}V NMR signals in acidic melts. Therefore, all subsequent samples were prepared in closed containers and transferred to NMR tubes prior to obtaining the spectra. Samples of V_2O_5 dissolved in acidic melts in this manner displayed a single peak at -1 ppm, indicating that V_2O_5 reacts with the chloroaluminate species to form volatile VOCl_3 in acidic melts.

The dissolution of V_2O_5 in acidic melts was further examined in a modified bulb-to-bulb vacuum transfer apparatus, as shown in Figure 1. In the drybox, the vanadium oxide and chloroaluminate melts were placed inside the larger vessel. The apparatus was sealed via a threaded stopcock, removed from the drybox, and evacuated. It was then closed to form a self-contained system. The large vessel was used to heat and stir the V_2O_5 -containing acidic melt while open to the small vessel, which was immersed in liquid N_2 to collect volatile products formed during the dissolution process. The dark red liquid was then

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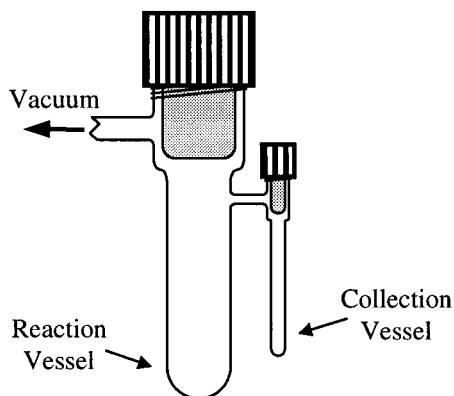


Figure 1. Diagram of the adapted bulb-to-bulb vacuum transfer apparatus. The large vessel is used to heat and stir the sample. The smaller vessel serves as the collection reservoir and is cooled in liquid nitrogen.

transferred to a NMR tube for further analysis. The volatile liquid thus collected displayed a single ^{51}V NMR peak at -3 ppm. It is believed that small amounts of moisture in the system caused partial hydrolysis of VOCl_3 , resulting in the dark red appearance of the liquid.²³ To confirm this, pure VOCl_3 was subjected to a small amount of water vapor and quickly turned dark red in color. The ^{51}V NMR of this sample also displayed a peak at -3 ppm, while pure VOCl_3 in the acidic melts produced a chemical shift at -1 ppm. Infrared studies of the vanadium-containing acidic melts indicate that no other products are formed during the dissolution process.

Neutral and basic chloroaluminate melts form similar species but in varying amounts. The dissolution of vanadium oxide in both neutral and basic melts produces two major ^{51}V NMR signals at -367 and -574 ppm. In addition, a minor peak at -721 ppm is observed in the basic melts, while neutral melts contain minor products indicated by peaks at $+45$ and -398 ppm. The exact chemical shifts for these peaks depend on both the acidity of the melt and on V_2O_5 concentration. For example, chemical shifts from -367 to -365 ppm and from -574 to -570 ppm are observed as the vanadium concentration in a basic melt ($\text{BMIC}:\text{AlCl}_3 = 1:0.60$) is changed from a V_2O_5 :BMIC ratio of 0.010 to 0.362 . A similar $\Delta\delta$ from -367 to -365 is observed for a change in melt composition of $\text{BMIC}:\text{AlCl}_3 = 1:0.38$ to $1:1.00$ with a constant V_2O_5 :BMI ratio of 0.05 . However, a greater $\Delta\delta$ is observed for the signal at ca. -574 ppm. This peak shifts from -577 ppm ($\text{BMIC}:\text{AlCl}_3 = 1:0.38$) to -572 ($1:0.81$) and then back up to -574 in neutral melt ($1:1.00$). The ^{51}V NMR spectra for basic ($\text{BMIC}:\text{AlCl}_3:\text{V}_2\text{O}_5 = 1:0.80:0.190$) and neutral ($1:1.00:0.050$) vanadium oxide-containing melts are shown in Figures 2 and 3, respectively. In addition, the dissolution of sodium metavanadate (NaVO_3) in basic chloroaluminate melts was found to form the same ^{51}V NMR signals as those of V_2O_5 , but was not pursued in any further detail.

The ^{51}V NMR signal at -367 ppm indicates the presence of VO_2Cl_2^- . Similar shifts have been observed for $\text{M}[\text{VO}_2\text{Cl}_2]$ ($\text{M} = \text{AsPh}_4^+$ in $\text{CH}_2\text{Cl}_2/\text{THF}$, PPh_4^+ in CH_2Cl_2 , and NEt_4^+ in THF (THF = tetrahydrofuran)), all of which displayed signals at -359 ppm relative to VOCl_3 .²⁴ VO_2Cl_2^- in acetonitrile²⁵ and

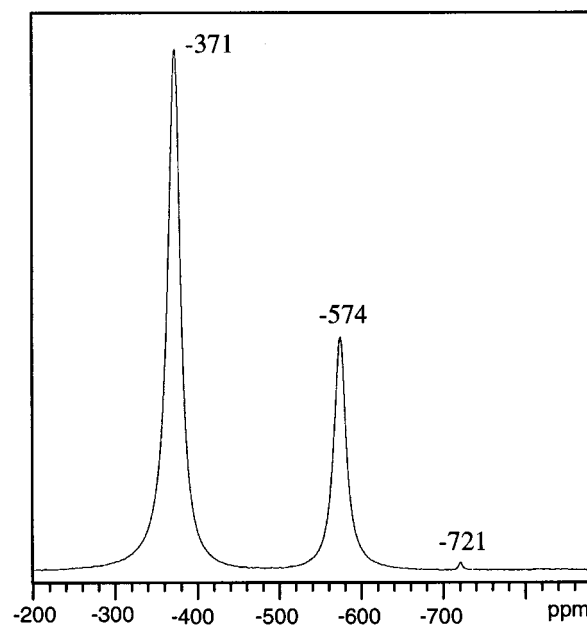


Figure 2. ^{51}V NMR spectrum of EMIC/ AlCl_3 ionic liquid containing V_2O_5 with a mole ratio of $1:0.80:0.190$ (EMIC: AlCl_3 : V_2O_5).

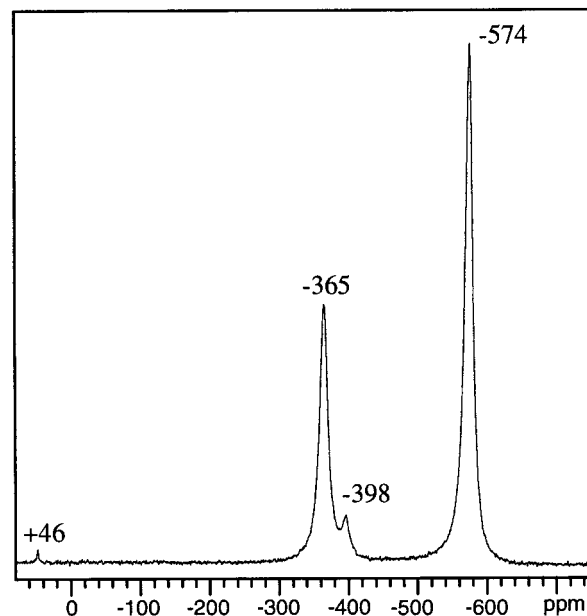


Figure 3. ^{51}V NMR spectrum of BMIC/ AlCl_3 ionic liquid containing V_2O_5 with a mole ratio of $1:1.00:0.050$ (BMIC: AlCl_3 : V_2O_5).

acetonitrile/water²⁶ displayed chemical shifts at -364 and -365 ppm, respectively. Attempts to make $[\text{Et}_4\text{N}][\text{VO}_2\text{Cl}_2]$ by methods suggested in the literature¹⁵ were unsuccessful, and we did not directly compare ^{51}V NMR spectra of independently synthesized VO_2Cl_2^- salts with spectra of V_2O_5 -containing chloroaluminate melts. However, extended X-ray absorption fine structure (EXAFS) of the solid salt $[\text{NEt}_4][\text{VO}_2\text{Cl}_2]$ and a solution formed when this salt is dissolved in a basic EMIC/ AlCl_3 melt are reported in good agreement with one another, indicating that the structure is unchanged upon dissolution in the chloroaluminate ionic liquid.¹⁵ These results provide no evidence for the coordination of the chloroaluminate species at the oxygen atoms nor for any increase in the number of chloride ions in the coordination sphere, which would result in a

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lengthening of all the V–Cl bonds and particularly of the V=O bond. Lengthening of the V=O bond would be expected to appear in the infrared spectra as a decrease in the V=O stretching frequency, but is not seen for VOCl_4^{2-} in the basic melt.¹⁶ Therefore, it is expected that the ^{51}V NMR chemical shift for VO_2Cl_2^- in chloroaluminate melts should not be substantially different from those found in other solvents.

The peak at -574 ppm falls within the regime of iso- and heteropolyvanadates and of $\text{VO}(\text{OR})_3$ species.^{27,28} Slightly basic aqueous solutions of dissolved vanadium oxide produce ^{51}V NMR chemical shifts in the area of -571 to -577 ppm, which have been assigned as the metavanadate species $[(\text{VO}_3)_n]^{n-}$ with n equal to 3 or 4.^{29–32} More recently, the signals at -571 and -574 ppm have been assigned to the $\text{V}_3\text{O}_9^{3-}$ and $\text{V}_4\text{O}_{12}^{4-}$ species, respectively.³³ It is generally accepted that $\text{V}_3\text{O}_9^{3-}$ is the prominent metavanadate ion in dilute solutions,³⁴ and at higher vanadium concentrations the $\text{V}_4\text{O}_{12}^{4-}$ species dominates.^{35–37} The interconversion of these species could be fast and could result in the presence of a single averaged peak, but no chemical shift was observed as the VO_3^- concentration changed from 0.002 to 0.249 M in a slightly basic aqueous solution.³⁸ As stated previously, a shift in chemical shift from -574 to -570 ppm was observed in the chloroaluminate melts as the mole ratio of V_2O_5 increased from 0.01 to 0.36 in a basic melt (1:0.60). A similar shift in chemical shift from -577 to -572 ppm was observed for melts containing a constant mole ratio of V_2O_5 (0.05) as the melt became less basic (1:0.38 to 1:0.81). Both situations should result in a lower concentration of Cl^- ; that is, as the concentration of V_2O_5 is increased, more VO_2Cl_2^- would be formed lowering the Cl^- concentration. Therefore, the shift of the -574 ppm peak is probably due to subtle changes in the local environment at vanadium with changes in chloride concentration rather than a change between vanadate trimer and tetramer.

The neutral melts also display minor peaks at $+46$ and -398 ppm. The peak at $+46$ is most likely due to the presence of a small amount of VOCl_4^- . The ^{51}V NMR chemical shift for VOCl_4^- has been reported as $+50$ in a mixture of dichloromethane and tetrahydrofuran,²⁴ as $+46$ in tetrahydrofuran,^{24,39} and as $+43$ in acetonitrile.²⁵ However, in basic melts, VOCl_4^- reacts with excess Cl^- in the melt to form the reduced species VOCl_4^{2-} .¹⁵ In neutral melts, without excess Cl^- , the persistence of VOCl_4^- in the melt is not surprising. It is possible that VOCl_4^{2-} exists in equilibrium with VOCl_4^- in the neutral melt, but due to its being V^{4+} , it is not detected by ^{51}V NMR. An important characteristic of vanadium is its ability to form polymeric oxoanions.^{40,41} Most iso- and heteropolyvanadates

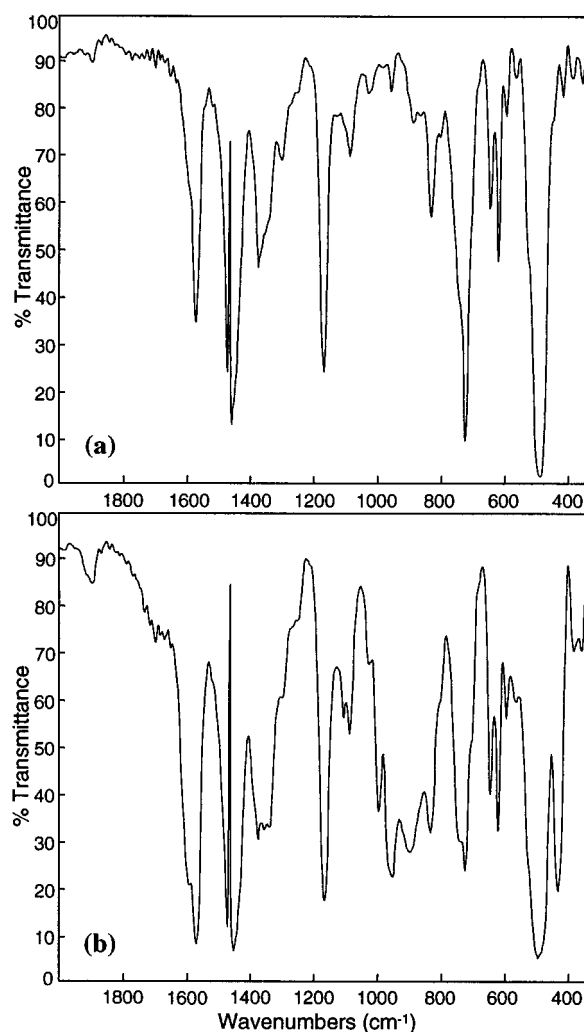


Figure 4. IR spectra ($335\text{--}2000\text{ cm}^{-1}$) of (a) basic EMIC/ AlCl_3 with a mole ratio of 1:0.80 and (b) basic EMIC/ AlCl_3 containing V_2O_5 with a mole ratio of 1:0.80:0.190 (EMIC: AlCl_3 : V_2O_5).

display ^{51}V NMR signals within the δ -range of -409 to -580 ppm.²⁷ The minor signal at -398 ppm in neutral melts and possibly the signal at -721 ppm in basic melts could be due to aluminum heteropolyvanadate species or a chlorine-containing isopolyvanadate.

The infrared spectra of the ionic liquids were recorded neat using both polypropylene film and NaCl salt plates. The IR spectra for neutral and basic vanadium-containing melts display strong absorbances at 997 and 432 cm^{-1} . A small shoulder indicates the presence of a peak in the area of 953 cm^{-1} but is obscured by the N–H and C–H in-plane bending band of the 1-ethyl-3-methylimidazolium cation (EMI^+) at 959 cm^{-1} .⁴² In addition, a strong absorbance occurs in the area of 900 cm^{-1} but is broad and overlaps many of the weaker signals of the imidazole cation. The IR spectra for a basic EMIC/ AlCl_3 melt and one containing V_2O_5 are displayed in Figure 4.

The $\nu(\text{V}=\text{O})$ bond stretch is found in the range of $935\text{--}1035\text{ cm}^{-1}$ as reported for a large set of oxovanadium complexes.^{43,44} The infrared V=O and V–Cl stretching fre-

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Table 1. Infrared V=O and V—Cl Stretching Frequencies for Various Vanadium Compounds

salt	$\nu(\text{V}=\text{O})/\text{cm}^{-1}$	$\nu(\text{V}-\text{Cl})/\text{cm}^{-1}$	ref
[Et ₄ N][VO ₂ Cl ₂]	995 (sym), 946 (asym)	437	15
[Ph ₃ PMe][VO ₂ Cl ₂]	970 (sym), 959 (asym)	438 (sym), 431 (asym)	45
[AsPh ₄][VO ₂ Cl ₂]	971 (sym), 960 (asym)	435	46
[VCl ₂ (15-crown-5)][VOCl ₄] ^a	1021	422 (sym), 366 (asym)	47
[N(PCl ₃) ₂][VOCl ₄]	1023	420, 403, 363	48
[EMI] ₂ [VOCl ₄] in basic EMIC/AlCl ₃	993	obscured by melt	16
[EMI] ₂ [VOCl ₄]	1001	361 (asym), 340 (sym)	16
[Et ₄ N] ₂ [VOCl ₄]	1000	350	49
VOCl ₃	1042	509	50

^a 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane.

quencies for various oxochloro vanadium compounds are shown in Table 1. Infrared spectra are sensitive to both the oxidation state of the vanadium and to the coordination geometry of the complex. The ion VO₂Cl₂[−] has C_{2v} symmetry^{45,46} and would be expected to show two V=O stretches (A₁ and B₁) and two V—Cl stretches (A₁ and B₂).⁴⁵ The absorbances at 997 and the shoulder in the area of 953 cm^{−1} are characteristic of the V=O stretching frequencies, and absorbance at 432 cm^{−1} for the V—Cl stretch of VO₂Cl₂[−] supports the ⁵¹V NMR chemical shift assignment for this species.

The two symmetry-allowed V—Cl stretching modes for VOCl₄^{2−} are expected at 361 and 340 cm^{−1}.^{48,51} The absorbance at 340 cm^{−1} is below the range available to us. The peak at 361 cm^{−1} is obscured by the melt itself, but the IR spectra display a slightly greater absorbance in this area for both neutral and basic vanadium-containing melts, which might indicate the presence of a small amount of VOCl₄^{2−}. The V=O stretch of VOCl₄[−] is expected to occur at a higher wavenumber (~1022 cm^{−1})^{47,48} and is not seen in either basic or neutral vanadium-containing melts.

The strong absorbance that occurs in the area of 900 cm^{−1} is very broad, overlapping many of the weaker signals of the imidazole cation. This cannot be explained by a change in melt acidity and therefore could be due to the presence of another vanadium oxide species. The expected frequency range for M—O—M bonds is in the range of 650–920 cm^{−1}.^{43,52} Therefore, the broad band at 900 cm^{−1} could be an indication of the presence of a metavanadate species.⁵³ The major species found in slightly basic aqueous solutions of V₂O₅ are [(VO₃)_n]^{n−} ions, where *n* is taken as 3 or 4.^{54,55} The infrared spectrum of V₄O₁₂^{4−} in an aqueous solution displays a strong band at 905 and another less intense band at 952 cm^{−1}.⁵⁵ This corresponds well with the broad band at 900 cm^{−1} and the shoulder at 953 cm^{−1}. However, it is not certain if the band at 953 cm^{−1} is due to this species or to VO₂Cl₂[−] or a combination of both.

Table 2. Species Observed for Vanadium Oxide Containing Neutral EMIC/AlCl₃ Ionic Liquids^a

<i>m/z</i>	possible species	rel abundance	<i>m/z</i>	possible species	rel abundance
35	Cl [−]	3	236	V ₂ O ₄ Cl ₂ [−]	11
99	[(VO ₃) _n] ^{n−}	11	245	Al ₂ OCl ₅ [−]	7
118	V ₂ O ₄ Cl ₂ ^{2−}	9	265	V ₃ O ₇ [−]	17
153	VO ₂ Cl ₂ [−]	41	271	V ₂ O ₄ Cl ₃ [−]	21
167	AlCl ₄ [−]	100	281	V ₃ O ₈ [−]	10
172	VOCl ₃ [−]	27	285	AlCl ₃ VO ₂ [−]	21
182	V ₂ O ₅ [−]	19	335	V ₃ O ₇ Cl ₂ [−]	7
217	V ₂ O ₅ Cl [−]	12	364	V ₄ O ₁₀ [−]	9
231	AlCl ₃ VO ₃ [−]	14			

^a The *m/z* ratios are for those species containing ³⁵Cl isotopes exclusively. The relative abundance for each species is given with respect to AlCl₄[−] and represents all isotopic species. Several of these species may arise from the laser desorption process and may not be contained in the ionic liquids as such.

In an attempt to provide further insight into the products formed during the dissolution of vanadium oxide in the ionic liquids, laser desorption (LD) mass spectra of the melts were obtained. The samples were prepared and placed on a gold substrate, which was then transferred from the drybox to the mass spectrometer in a dry argon atmosphere. A large plastic tent was constructed around the sample port, and dry nitrogen was allowed to flow into the tent for approximately 1 h. Although this procedure greatly reduced the contamination of the samples, small amounts of moisture were inevitably present. The positive-ion laser desorption time-of-flight (LD-TOF) mass spectra of the ionic liquids obtained in these studies are in good agreement with those collected by fast atom bombardment (FAB) mass spectrometry.⁵⁶ The LD-TOF mass spectra for both basic and neutral EMIC/AlCl₃ melts display peaks at 83 and 111 *m/z*. These represent the 1-methylimidazole cation and EMI⁺, respectively. The positive ion mass spectra for all melts of varying acidity and vanadium content display similar mass spectra.

Negative-ion LD-TOF mass spectra were more difficult to acquire with the laser power increased to obtain these spectra. However, by increasing the intensity of the laser, desorption of the ionic liquid and vanadium-containing species resulted in fragmentation and recombination reactions in the plume, generating many species not believed to be contained in the melt itself. Therefore, the results presented should be taken at face value due to the pitfalls associated with this technique. Both the neutral and basic vanadium-containing melts display many anionic species. The prominent peaks that appear in the majority of the spectra for vanadium-containing melts are shown in Tables 2 and 3 for the neutral and basic melts, respectively. The peaks at 35, 167, and 245 *m/z* represent the mass-to-charge

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Table 3. Species Observed in Basic EMIC/AlCl₃ Ionic Liquids Containing Vanadium Oxide^a

<i>m/z</i>	possible species	rel abundance	<i>m/z</i>	possible species	rel abundance
35	Cl ⁻	5	231	AlCl ₃ VO ₃ ⁻	14
99	[(VO ₃) _n] ⁿ⁻	3	245	Al ₂ OCl ₅ ⁻	21
153	VO ₂ Cl ₂ ⁻	31	267	AlCl ₄ VO ₃ H ⁻	18
167	AlCl ₄ ⁻	100	285	AlCl ₅ VO ₂ ⁻	17
172	VOCl ₃ ⁻	45			

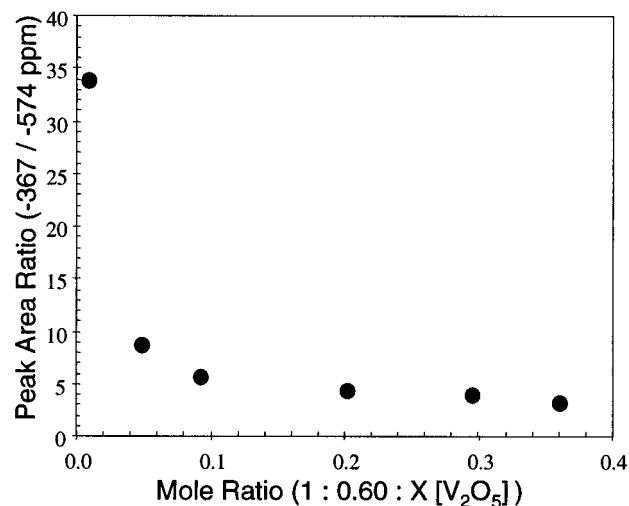
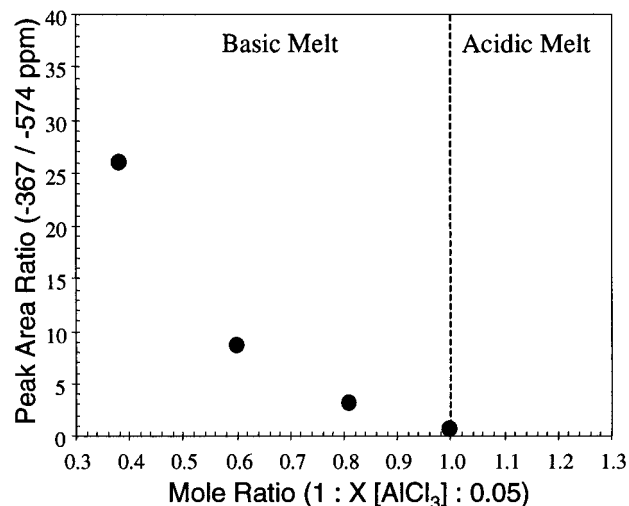
^a The *m/z* ratios are for those species containing ³⁵Cl isotopes exclusively. The relative abundance for each species is given with respect to AlCl₄⁻ and represents all isotopic species. Several of these species may arise from the laser desorption process and may not be contained in the ionic liquids as such.

ratio for compounds containing the ³⁵Cl isotope, which correspond to Cl⁻, AlCl₄⁻, and Al₂OCl₅⁻, respectively. The peaks at 99 and 153 *m/z* represent [(VO₃)_n]ⁿ⁻ and VO₂Cl₂⁻, respectively.

There are two prominent peaks at 231 and 285 *m/z* in these spectra, which represent AlCl₃VO₃⁻ and AlCl₅VO₂⁻, respectively. These species may be better represented as adducts of aluminum chloride and the more prevalent anionic species in the melt to form AlCl₃•VO₃⁻ and AlCl₃•VO₂Cl₂⁻. We speculate that these products are anomalies of the laser desorption process.^{57,58} That is, the pulsed laser creates a dense plume of neutral and ionic species with the neutral aluminum chloride generated by the dissociation of the aluminum tetrachloride anion to form AlCl₃ and Cl⁻ in the plume. As this plume expands, recombination of neutral AlCl₃ with the species VO₃⁻ and VO₂Cl₂⁻ may occur to create these adduct products. The large number of species observed in the mass spectra are due to such processes as fragmentation and recombination reactions, in addition to chloride- and oxygen-transfer reactions that are presumed to have occurred in the plume.^{58,59} This technique has proven to be less reliable for the exact determination of the anionic species in the melt as the desorption laser has obviously created many gas-phase species that are not presumed to be in the melt as indicated by the IR and ⁵¹V NMR studies.

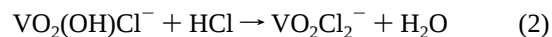
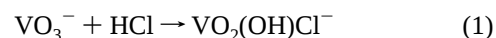
Had these species been present in the ionic liquids they would be expected to appear in the ⁵¹V NMR spectra at these concentrations, but only two major ⁵¹V NMR signals are observed in the neutral and basic melts which have been assigned to [(VO₃)_n]ⁿ⁻ and VO₂Cl₂⁻. Therefore, it is apparent that the laser desorption process has caused many reactions, creating species that are not present in the ionic liquids as such. However, there is a minor ⁵¹V NMR signal at -721 ppm in basic melts and one at -398 ppm in the neutral melts that have not been assigned and could possibly represent one of the species found in these spectra.

There are several possible reaction mechanisms that may account for the formation of the observed species for the dissolution of vanadium oxide in the chloroaluminate melts. At low concentrations of V₂O₅ in a basic melt, there exists an excess of free Cl⁻ and the primary products are VO₂Cl₂⁻ and metavanadates. However, as the concentration of V₂O₅ increases,

**Figure 5.** Plot displaying the ratio of the areas under the ⁵¹V NMR signals at -367 ppm divided by that of -574 as the mole ratio of V₂O₅ increases (BMIC:AlCl₃:V₂O₅).**Figure 6.** Plot of the ratio of ⁵¹V NMR peaks for the area under -367 divided by that of -574 ppm as a function of melt acidity (BMIC: AlCl₃:V₂O₅).

so does the relative amount of metavanadate species. This can be seen in the plot in Figure 5 that shows the ratio for the ⁵¹V NMR peak at -367 (VO₂Cl₂⁻) with respect to that at -574 ppm (metavanadate) in a basic melt (1:0.60) as the mole ratio of V₂O₅ is increased. A similar trend occurs when the mole ratio of V₂O₅ remains constant and the melt composition is changed from basic to acidic (Figure 6). Both of these results are consistent with an increase in the metavanadate species as a decrease in the Cl⁻ concentration in the melt occurs.

Gas-phase reactions of VO₃⁻ and HCl have been examined in a flow tube apparatus.⁶⁰ The reaction between the metavanadate anion and HCl produced VO₂Cl₂⁻ and water as follows:



Upon formation of VO₂Cl₂⁻, no further reaction is observed up to an increased concentration of 50.9 cm³ (STP) min⁻¹ HCl in 0.3 Torr of helium. In contrast, NbO₃⁻ (at 15.1 cm³ (STP)

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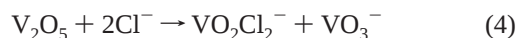
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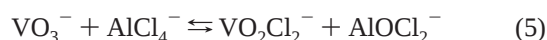
min⁻¹ of HCl) and TaO₃⁻ (at 6.1 cm³ (STP) min⁻¹ of HCl) do not truncate at VO₂Cl₂⁻ but continue to react with HCl in the same manner as shown in reactions 1 and 2 to form NbOCl₄⁻ and TaOCl₄⁻, respectively.⁶⁰ However, in highly acidic environments, the reversible reaction of V₂O₅ with HCl to form vanadyl chloride and water is observed.⁶¹



A possible mechanism for the dissolution of V₂O₅ may involve the reaction with Cl⁻ (as Cl⁻, AlCl₄⁻, or Al₂Cl₇⁻, depending on the melt acidity) to form the major species in these melts.



At low concentrations of vanadium, a single oxygen is lost from V₂O₅ or NaVO₃ to form VO₂Cl₂⁻. This is possibly an oxygen-transfer reaction between VO₃⁻ and AlCl₄⁻ (or Al₂Cl₇⁻):



The oxochloroaluminate species AlOCl₂⁻ has been shown here for convenience as it is still unknown what oxochloroaluminate species are present in these melts.⁸ The VO₂Cl₂⁻ species has been found to be stable in basic chloroaluminate melts¹⁵ and is unlikely to react with a chloroaluminate species to remove any additional oxygen atoms at these melt compositions. In acidic melts, a possible mechanism for the formation of VOCl₃ is the initial dissolution of V₂O₅ in the melt to form VO₂Cl₂⁻ as seen for the reactions of V₂O₅ in basic and neutral melts. However, VO₂Cl₂⁻ may react further with the acidic chloroaluminate species Al₂Cl₇⁻ as follows:



Again, there is no direct experimental evidence that AlOCl₂⁻ is the actual aluminum species generated in reaction 5 or 6 and is considered simply for convenience in balancing the reaction. The VOCl₃ species appears to be stable in acidic melts, for there is no evidence from the IR and NMR studies that would indicate the presence of other species in the ionic liquid.

Conclusion

It has been found that V₂O₅ does not dissolve in the chloroaluminate ionic liquids EMIC/AlCl₃ and BMIC/AlCl₃ to form a stable species. Instead, the dissolution of V₂O₅ at temperatures greater than ~70 °C results in the formation of VO₂Cl₂⁻ and [(VO₃)_n]ⁿ⁻ in basic and neutral melts. The ratio of the species formed depends on both melt acidity and V₂O₅ concentration with VO₂Cl₂⁻ more prominent in basic melts with low concentration of V₂O₅ and [(VO₃)_n]ⁿ⁻ more prevalent in neutral melts or with high concentrations of V₂O₅. Both species appear to be stable in the ionic liquid and do not precipitate out upon cooling to room temperature. It is believed that these species further react with the acidic species Al₂Cl₇⁻ to form volatile VOCl₃ in acidic melts. However, the existence of other low-concentration species with V⁴⁺ such as VOCl₄²⁻ is quite possible. The dissolution of V₂O₅ did not appear to occur in the inherently neutral ionic liquids [BMI][CF₃SO₃] or [BMI][BF₄].

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