

Solvent Exchange

LDRD Final Report

September 2020

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Abstract

This report summarizes the work of evaluating the chemical stability of phosphoramidic acid, N-N-diethyl-, bis(2-ethylhexyl) ester under the Solvent Exchange LDRD project, as a potential solvent exchange chemistry and analog to solvent exchange chemistries used in the TALSPEAK and ALSEP processes as alternatives to the use of tri-butyl phosphate in the PUREX process.

Acknowledgments

We wish to thank Cal Delegard for useful conversations and insights during the execution of this project. This work was carried out under the auspices of the Nuclear Process Science Initiative at PNNL. Funding for the work was provided by PNNL's Laboratory Directed Research and Development Office. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute under DOE contract number DE-AC06-76RLO-1830.

Acronyms and Abbreviations

ALSEP	Actinide/Lanthanide Separation
DBBP	dibutylbutylphosphonate
EI	Electron ionization
GC	Gas chromatograph
HEH[EHP]	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
JIMM	phosphoramidic acid, N-N-diethyl-, bis(2-ethylhexyl) ester
JIMM-OH	phosphoramidic acid, bis(2-ethylhexyl) ester
LDRD	Laboratory Directed Research and Development
MS	Mass Spectrometry
NMR	Nuclear magnetic resonance
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium/Uranium Extraction
TALSPEAK	Trivalent Actinide Lanthanide Separation with Phosphorus-reagent Extraction from Aqueous Komplexes
TBP	tributyl phosphate
TBPO	tributylphosphine oxide
TIC	Total ion chromatography
TPPO	tripentyl phosphine oxide

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1.0 Introduction

This Laboratory Directed Research and Development (LDRD) project was aimed at investigating the radiolytic, chemical, and thermal degradation of the active chemicals of several potential alternative chemistries and analogues to the PUREX liquid-liquid extraction process for uranium and plutonium purification.

The active chemical extractant of the PUREX process is a solution of tributyl phosphate (TBP) in either n-dodecane or kerosene. This solution is contacted with dissolved nuclear fuel in strong concentrations of nitric acid, whereby the uranium and plutonium (depending on the oxidation state) react to form a complex with the TBP which allows them to be selectively dissolved into the organic phase. Similar complexes can be formed with other phosphorus-containing chemicals [Benedict 1981].

In recent years, alternative chemistries to the PUREX process have been investigated for both uranium/plutonium separation and for separation of other fission products. The ALSEP process uses a combination of a diglycolamide and the organophosphorus compound 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) as a primary extractant [Gelis 2014]. Similarly, the TALSPEAK process in its original form uses di-(2-ethylhexyl) phosphoric acid as an extractant to separate the 4f and 5f elements [Nash 2014].

In this work, we evaluate a specific analog of these primary phosphorus-containing chemicals, phosphoramidic acid, N-N-diethyl-, bis(2-ethylhexyl) ester (hereafter, JIMM) to understand its stability to degradation under solvent extraction and storage conditions and its decomposition pathways and degradation products.

2.0 JIMM degradation

Phosphoramidic acid, N,N-diethyl-, bis(2-ethylhexyl) ester (hereafter, JIMM) was synthesized, analyzed and its susceptibility to hydrolysis tested. JIMM was relatively easy to synthesize and distill, and is analogous to ALSEP and TALSPEAK processes.

2.1 JIMM structure and synthesis

The chemical structures of JIMM and four other organo-phosphorus compounds are provided in Figure 2-1.

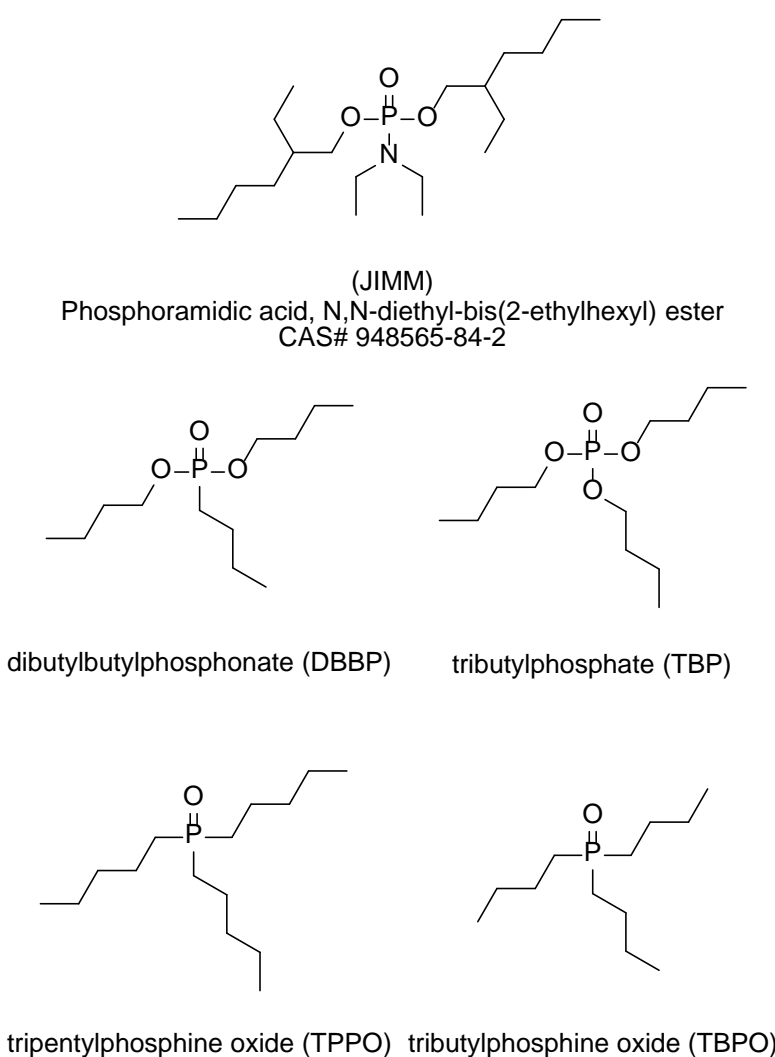


Figure 2-1: JIMM chemical structure, as it relates to four other organophosphorus compounds, including TBP.

JIMM was synthesized by reacting commercially available bis(2-ethylhexyl) hydrogen phosphite and diethylamine as first described by Cherkasov et. al. [Cherkasov 2006]. A yield of 87% was reported by the authors. The reaction scheme is depicted in Figure 2-2.

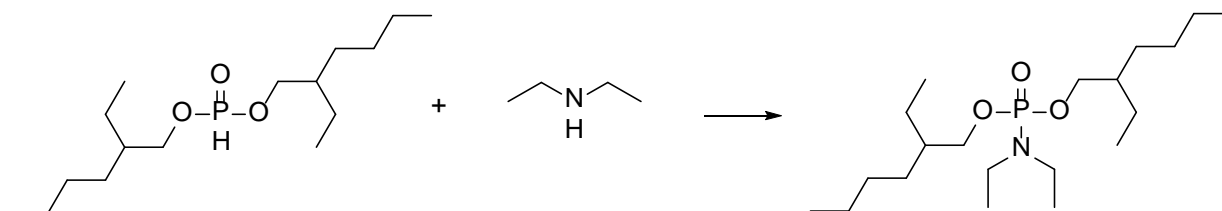


Figure 2-2: Synthetic scheme for JIMM, obtained by reacting bis(2-ethylhexyl) hydrogen phosphite and diethylamine.

The synthesis proceeded as follows. 7.546 g of carbon tetrachloride was added dropwise to a mixture of 15 g of bis(2-ethylhexyl) hydrogen phosphite and 8.96 g of diethylamine at 0-5°C. The reaction mixture was allowed to stand for 30 minutes at 0-5°C and then left for 1 hour at room temperature. The resulting amine hydrochloride was filtered off on a glass frit, and the filtrate was washed with hexane, followed by 5% hydrochloric acid and then twice with deionized water. The filtrate was dried with sodium sulfate, followed by removal of the solvent under vacuum. The remaining residue was distilled in a vacuum to purify the product.

2.2 Gas chromatography analysis

Gas chromatography/mass spectrometry (GC/MS) analysis of the synthesized JIMM revealed it was at least 99% pure based on peak area measurements. Figure 2-3 provides the electron ionization (EI) mass spectrum obtained from MS analysis of JIMM. To our knowledge, this is the first reported mass spectrum of JIMM available.

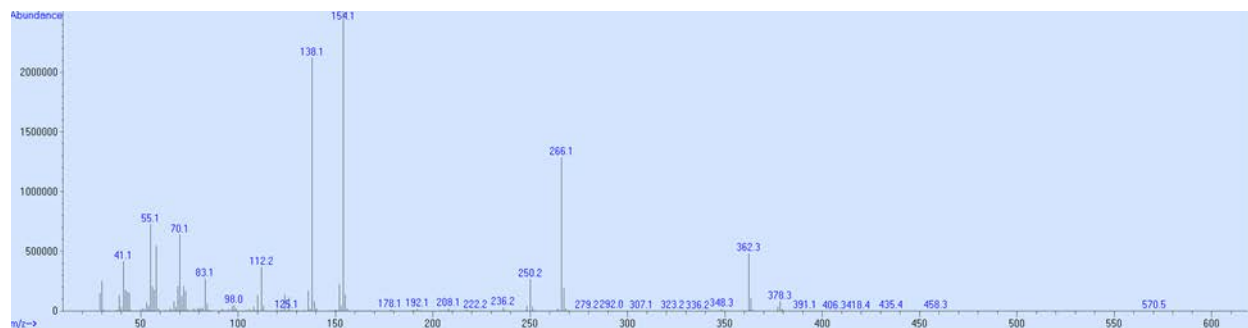


Figure 2-3: EI mass spectrum for JIMM.

JIMM's elution order in GC (for a 5% diphenyl 95% dimethyl polysiloxane GC column) was compared to the other four phosphorus compounds listed in Figure 2-1. Relative to the other molecules, JIMM elutes later because of its overall greater polarity and boiling point. Figure 2-4 depicts the GC/MS chromatogram for JIMM and the other four organophosphorus compounds.

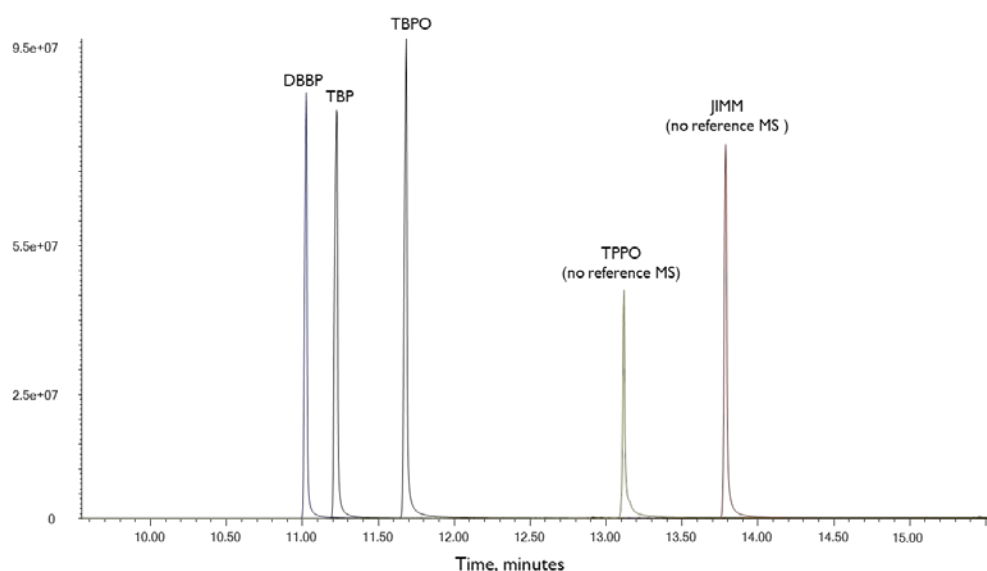


Figure 2-4: GC/MS total-ion current (TIC) chromatogram depicting GC peaks for DBBP, TBP, TBPO, TPPO, and JIMM.

2.3 H-NMR Analysis

H-NMR analysis of the synthesized JIMM revealed it was at least 99% pure. Figure 2-5 depicts the H-NMR spectrum for JIMM. The depicted spectrum was acquired July 2019. The same spectrum was obtained for a sample of JIMM from the same batch in February 2020, demonstrating that JIMM is stable during storage at 22 °C in a closed glass vial with air in the headspace for at least 7 months.

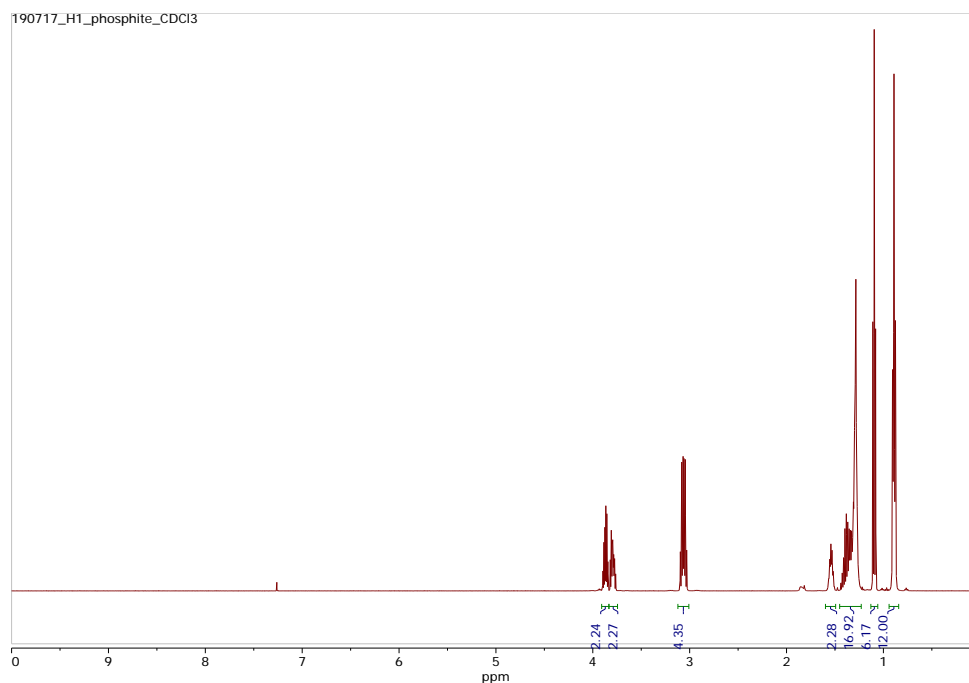


Figure 2-5: $^1\text{H-NMR}$ spectrum for JIMM. The JIMM produced is at least 99% pure.

2.4 Storage and Adsorption to Glass

During storage experiments, it was noticed that JIMM has a strong attraction to glass. The concentration of JIMM dissolved in an organic solvent or aqueous solution decreases very quickly over time and then stabilizes as JIMM adheres to the surfaces of a glass storage container. This drop in JIMM concentration (between a 9-day period) is depicted in Figure 2-6 for JIMM dissolved in decane, hexane, and dichloromethane in glass vials. However, as also shown in Figure 2-6, the JIMM concentration remained constant for JIMM dissolved in TBP because the TBP also adheres to the glass and therefore passivates the glass surface, stopping JIMM from adsorbing to the glass.

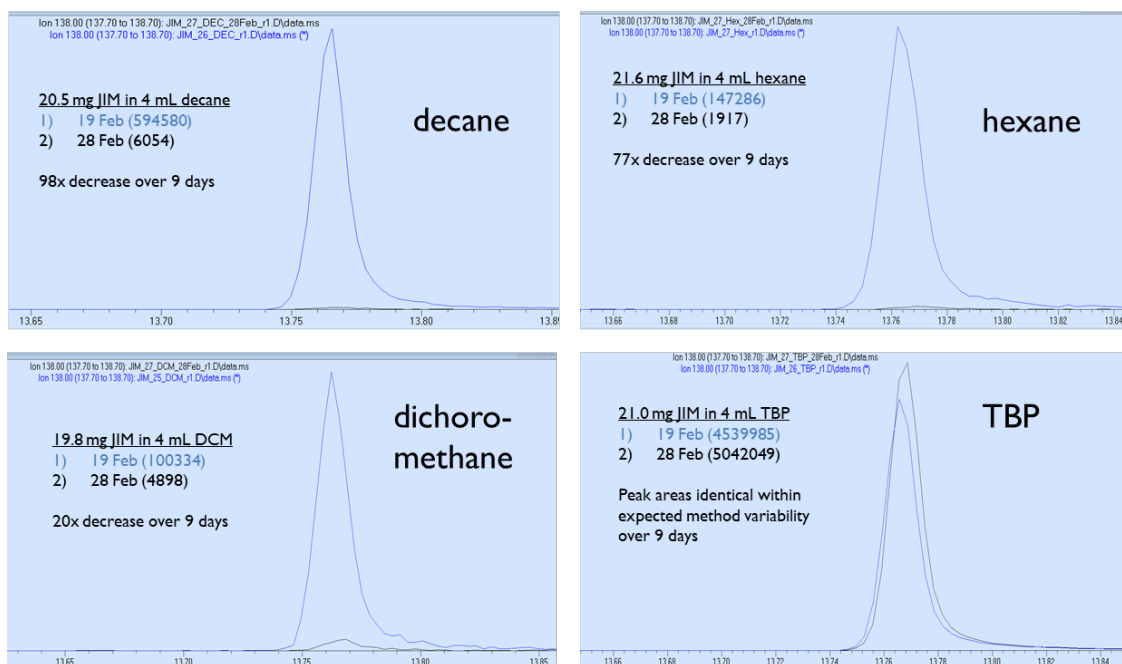


Figure 2-6: Concentrations of JIMM in various solvents presented by the peak intensity (height or area) of the GC/MS peak for JIMM at time zero (blue) and 9 days later (black).

P-NMR analysis of the JIMM in decane solution showed that the only phosphorous compound present was JIMM after several weeks in decane. Figure 2-6 depicts both the P-NMR and H-NMR spectra for the hydrolyzed product of JIMM called JIMM-OH. As shown in Figure 2-6, the P-NMR chemical shift for JIMM-OH is 2.47 ppm. That is quite different from the chemical shift for JIMM at 11.1 ppm (see Figure 2-7), and no JIMM-OH peak was observed after several weeks in the decane solution. P-NMR therefore provided definitive proof that the drop in JIMM concentration was not because of a chemical transformation of JIMM.

H1 and P31 NMR of pure JIMM-OH

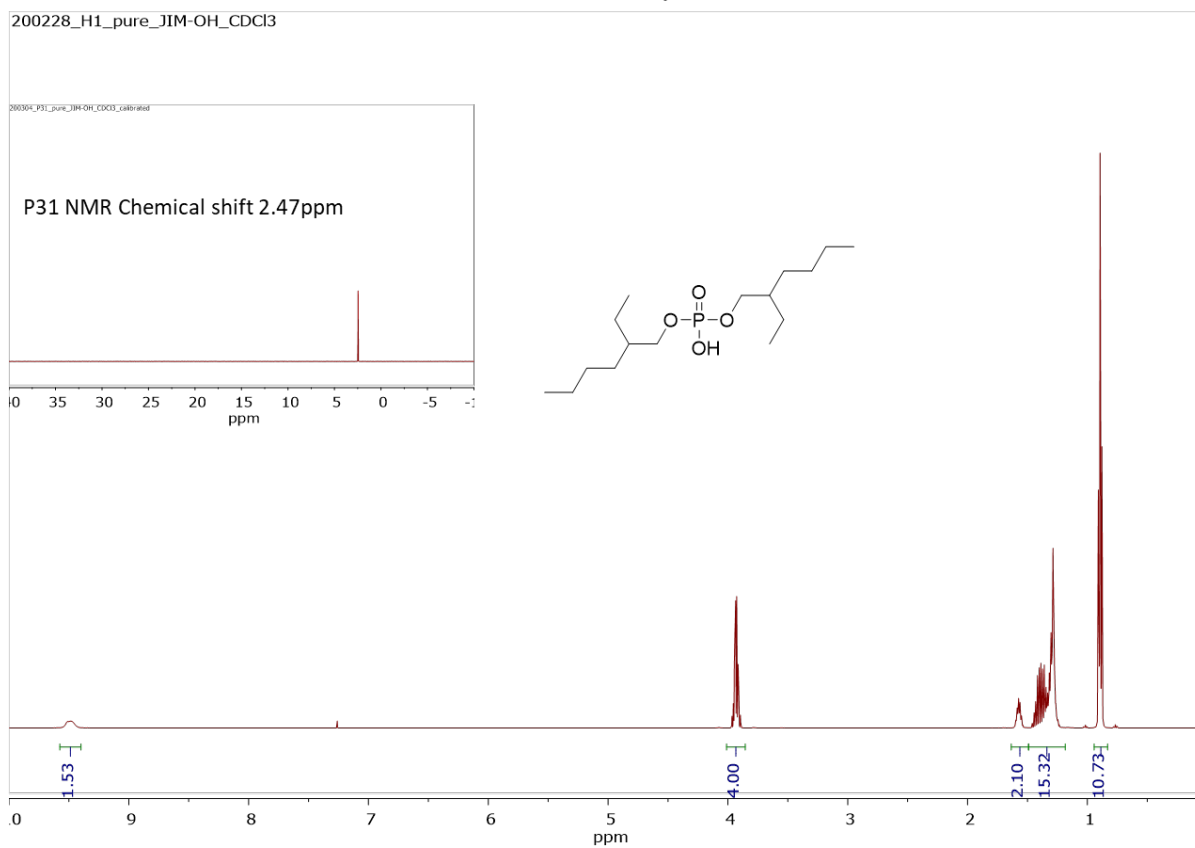


Figure 2-7: H-NMR and P-NMR spectra for JIMM-OH.

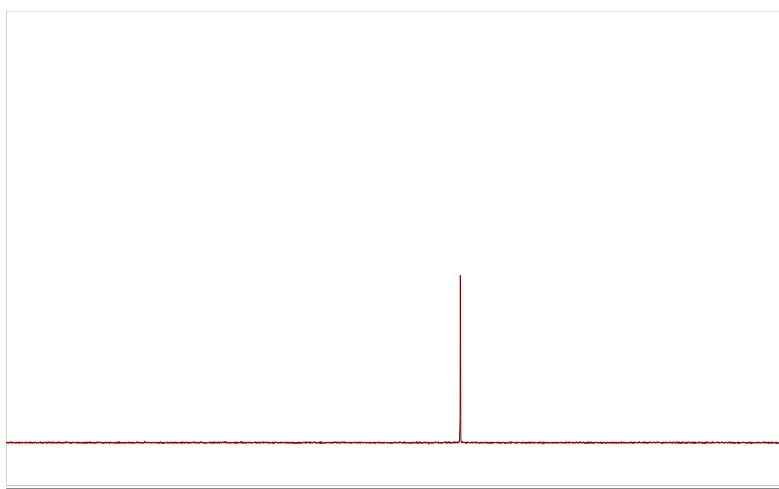


Figure 2-8: P-NMR spectrum for JIMM.

Adsorption of JIMM or TBP to the glass is likely due to the P=O group forming a hydrogen bond to the silanol groups present in untreated glass (i.e., non-silanized glass). Additionally, JIMM can form hydrogen bonds between its tertiary amine group and the silanol groups present in non-silanized glass. Figure 2-9a shows that using silanized glass (silanol OH groups are replaced by a trimethylsilyl groups) keeps the JIMM in hexane from adhering to the container wall compared to untreated glass (i.e., not silanized). Figure 2-9b also shows that by adding TBP to an untreated glass container containing JIMM dissolved in hexane produces a dramatic increase in JIMM concentration as the TBP displaces the adsorbed JIMM from the glass walls. It is important to note that most glass containers used to store neat organic compounds are likely not silanized.

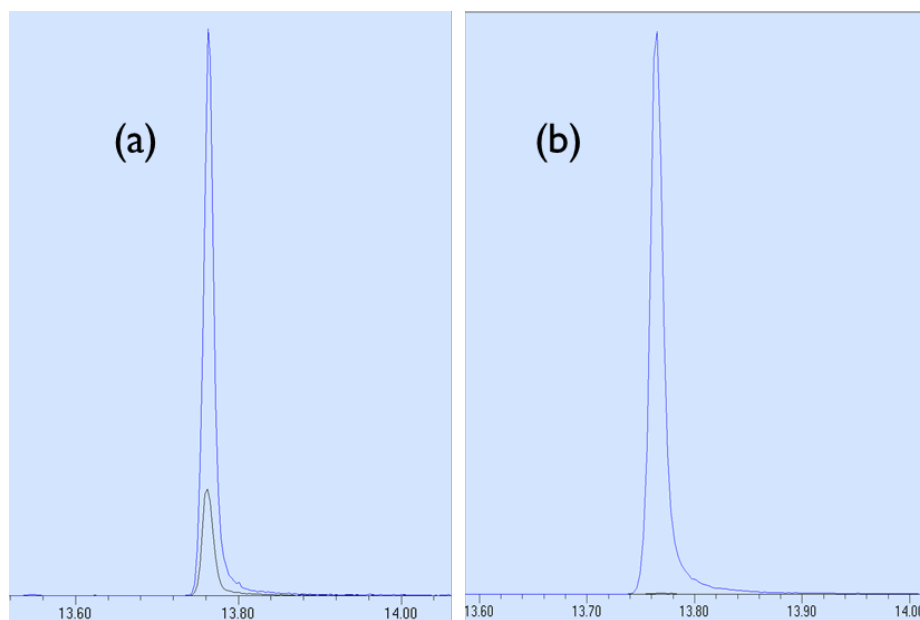


Figure 2-9: (a) Overlaid GC/MS peaks for JIMM samples having the same initial concentration of JIMM in hexane (0.8% w/w JIMM) in a silanized glass vial (blue) and untreated glass vial (black). The drop in JIMM signal is due to the JIMM adsorbing to the untreated glass within 2 hours. (b) Overlaid GC/MS peaks for JIMM before (black) and after (blue) the addition of TBP to an untreated glass vial containing JIMM in hexane.

2.5 Hydrolysis Susceptibility

A solution of 1.3% (w/w) JIMM in 24.8% tributyl phosphate (TBP) and 73.9% decane was made and then vigorously mixed with an equal volume of aqueous 1 M nitric acid (i.e., 5 mL) at 22 °C for 33 days. Mixing was done using a magnetic stirrer in a 20-mL flat bottom non-silanized glass vial. A 5-microliter sample of the JIMM organic layer (top layer) was taken periodically, mixed

with 1.8 mL of hexane and then analyzed by GC/MS to measure any changes in JIMM concentration as a function of time. Changes in the JIMM concentration were measured by changes in the GC/MS peak intensity for JIMM. Figure 2-8 depicts a representative GC/MS chromatogram for the JIMM organic solution used in this hydrolysis study.

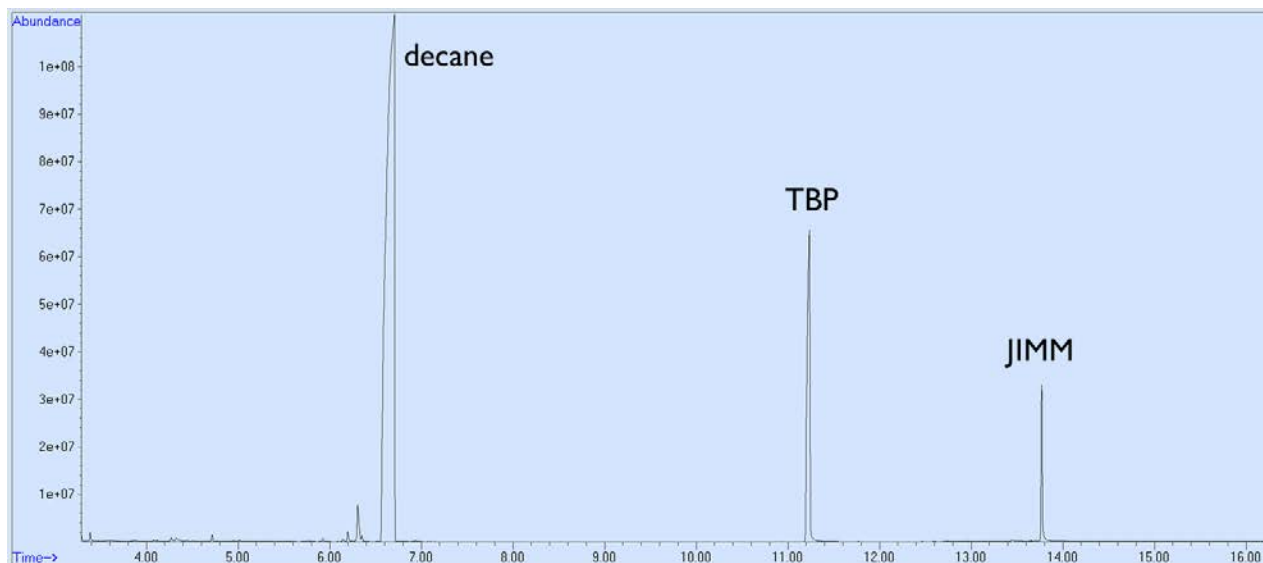


Figure 2-10: GC/MS TIC chromatogram for 1.3% w/w JIMM in 24.8% tributyl phosphate and 73.9% decane solution.

Seven samples of the JIMM organic layer (bottom layer was 1 M HNO₃) were taken and analyzed by GC/MS starting with time zero (13 Feb 2020 / 12:15) and ending 33 days later (17 Mar 2020 / 15:00). The GC/MS chromatograms depicting the JIMM peak for each of the seven samples are depicted in Figure 2-11. While the smallest JIMM peak corresponds to the sample taken at day 33, its peak area is not different enough to rule out sampling and analytical variability. Therefore, no changes in the JIMM concentration were detected; the hydrolysis of JIMM is deemed negligible over a 33-day period.

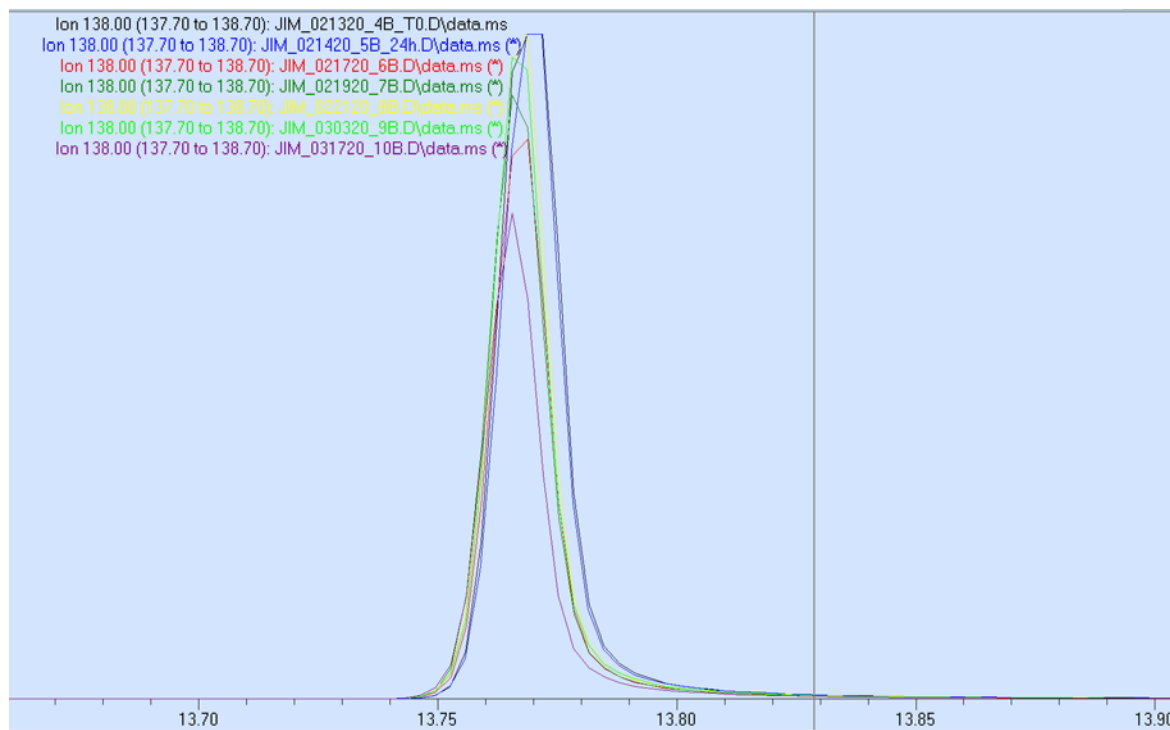


Figure 2-11: Seven overlaid GC/MS chromatograms for the seven samples taken from JIMM organic layer over a 33-day period.

2.6 Forced Hydrolysis

Because hydrolyzed JIMM was not produced under the tested conditions, the purposeful hydrolysis of JIMM was performed to confirm production of JIMM-OH. This was accomplished by hydrolyzing JIMM in a mixture of methanol and hydrochloric acid as described by the following steps.

8.5 milligrams of JIMM was mixed with 3 mL of methanol and 3 mL of 6 molar hydrochloric acid. The mixture was stirred at room temperature for 3 days. Following the hydrolysis period, the methanol was evaporated using a stream of dry nitrogen gas. 3 mL of hexane was added to the remaining aqueous solution and the mixture was stirred vigorously for 10 minutes at room temperature to separate out the hydrolysis product. The hexane layer was separated and evaporated to dryness to produce the final product.

P-NMR and H-NMR (see Figure 2-12) confirmed the 100% conversion of JIMM to JIMM-OH through hydrolysis. This demonstrates the combination of strong acid and a source of hydrolysis

(methanol) can remove the amine group from the system to produce the hydrolyzed JIMM-OH. We suspect this reaction to be active when in contact with the nitric acid during separation processes.

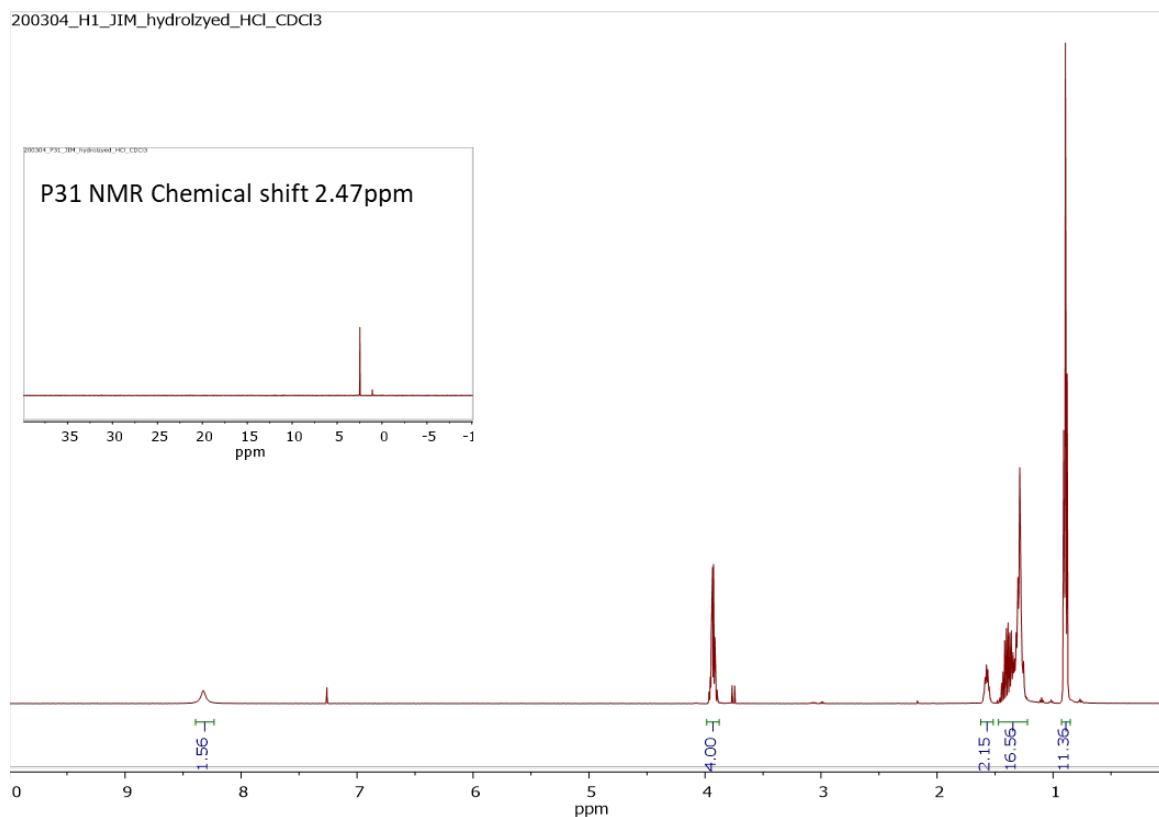


Figure 2-12: P-NMR and H-NMR spectra of JIMM subjected to forced hydrolysis. The depicted spectra confirm the complete hydrolysis of JIMM to JIMM-OH.

3.0 Conclusions

We have examined some of the properties and degradation pathways for JIMM as they relate to potential storage and solvent extraction scenarios. We have found that, while generally stable under storage conditions, JIMM is reactive with glass and will adsorb strongly onto the silanol groups on the surface of glass structures. We have also determined that the strong acidic and oxidizing conditions experienced during a typical solvent extraction scenario may cause hydrolysis of JIMM, leading to complete conversion to the hydrolyzed product.

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