Analytical Chemistry Research 9 (2016) 1–7

Contents lists available at ScienceDirect

Analytical Chemistry Research

journal homepage: www.elsevier.com/locate/ancr

Extraction and recovery of 2-butoxyethanol from aqueous phases containing high saline concentration

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ARTICLE INFO

Article history:
Received 29 April 2016
Received in revised form
13 July 2016
Accepted 14 July 2016
Available online 16 July 2016

Keywords:
2-butoxyethanol
GC/MS
Solid-phase extraction
Liquid-liquid extraction

ABSTRACT

Ethylene glycol monobutyl ether (EGBE), also known as 2-butoxyethanol (2-BE), has been identified as a contaminant in hydraulic fracturing fluids. In order to determine the presence of 2-BE in hydraulic fracturing chemical additives, a reliable method for recovering 2-BE from aqueous phases by liquid-liquid extraction combined with gas chromatography/mass spectrometry (GC/MS) was established. The liquid-liquid extraction method was applied to samples matrices containing various amounts of salt. Using methylene chloride for liquid-liquid extraction in a sample to solvent ratio of 1:3, ≥99% 2-BE recovery may be achieved with less than 5% standard error. The limit of detection was determined to be 0.957 mg L^{-1} 2-BE. Accuracy was determined to be 2.58% and precision was determined using the coefficient of variation, which was 3.5%. The method was used to recover 2-BE in a hydraulic fracturing chemical additive called Revert Flow and to quantify the weight percent of 2-BE in the chemical additive. Weight percent of two additional components of Revert Flow, D-limonene and 1-butoxy-2-propanol, were also determined. We also used the method to determine the abiotic of 2-BE in water, which was 5.55 days. The persistence of 2-BE in hydraulic fracturing fluid was also investigated and determined that 2-BE is more persistent in this environment.

1. Introduction

2-BE is commonly used as an additive in many products and industries, including the natural gas industry for hydraulic fracturing fluids, agricultural herbicides and pesticides, food processing additives, and the aerospace, automotive, and military industries for corrosion resistant coatings [1–7]. In addition, 2-BE has been added as a dispersant in solutions used to clean up oil and gas spills as authorized by the EPA [8]. Human exposure to 2-BE can occur through skin contact, inhalation, or ingestion [9,10]. Exposure to 2-BE can have harmful effects to human health, principally the central nervous system, blood, and the kidneys [11–17]. Threshold and permissible exposure limits have been set between 5 and 20 ppm [18–20].

As one of the chemical ingredients in hydraulic fracturing fluids used for natural gas production [22–26], 2-BE is completely miscible in water and most organic solvents [27]. It exhibits surfactant properties, forming micelles at concentrations greater than 120 g L^{-1} [28]. In a progress report published by the United States Environmental Protection Agency (EPA) in 2012 describing the potential impacts of hydraulic fracturing fluids, 2-BE was listed as the fourth most often appearing chemical in products used by the oil and natural gas industry [29]. Considered a potential indicator for hydraulic fracturing fluid spills, 2-BE was also listed as a chemical requiring development of analytical methods for detection and quantification. Predictive studies have found 2-BE to be potentially mobile allowing for a higher probability of exposure via groundwater contamination [30]. For that reason, developing a method to detect 2-BE in aqueous saline solutions, such as hydraulic fracturing fluids, using common laboratory techniques is crucial to monitoring the environmental fate of this chemical.

Previously established analytical methods to detect 2-BE use analytical techniques that are not readily available in most laboratories because they are very complex and very expensive. Techniques that have been used to detect 2-BE and include gas chromatography – flame ionization detection (GC/FID), “purge and trap” GC/MS, solid phase extraction liquid chromatography – tandem mass spectrometry (SPE-LC-MS/MS), direct injection liquid

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http://dx.doi.org/10.1016/j.ancr.2016.07.001
2214-1812/

chromatography – tandem mass spectrometry (LC/MS/MS), and nuclear magnetic resonance (NMR) spectroscopy are listed in Table 1 [7,8,31–40]. In order to analyze 2-BE in oil spill seawater samples, Ramirez et al. developed an online solid phase extraction tandem liquid chromatography mass spectrometry (SPE-LC-MS/MS) method with a limit of detection (LOD) reported as 7 ng L^{-1} [8]. This method allowed for minimal sample preparation and increased analytical speed. The EPA has used direct injection LC/MS/MS in order to detect 2-BE in the water and waste generated by the BP oil spill with reporting limits of 125 μg L^{-1} [31,32].

In order to detect 2-BE in hydraulic fracturing fluids, Llewellyn et al. used comprehensive 2D gas chromatography coupled with time-of-flight mass spectrometry (GCxGC/TOFMS) [33]. Use of GCxGC/TOFMS required modification of EPA Method 3510C in order to extract 2-BE from solution. EPA Method 3510C is a general procedure for extracting organic compounds from large volumes of sample. The method requires several pH adjustments as well as solvent exchange and methods to concentrate the extract. GCxGC/TOFMS provides very high resolving power enabling detect 2-BE at concentrations in the nanograms per liter range when a surrogate standard was added to the sample prior to extraction. However, Llewellyn et al. noted that these multi-dimensional MS techniques are not available in most commercial laboratories [33].

Previous methods do not evaluate the effectiveness of 2-BE separation from water, which would allow 2-BE to be detected and quantified by GC/MS, a more common analytical technique compared to previously mentioned methods. The objective of this study was to develop a method for separating 2-BE from water and high salinity solutions to be quantified by GC/MS. This study uses liquid-liquid extraction (LLE) and several organic solvents to separate 2-BE from water and aqueous solutions containing ionic species. Several applications were also investigated, including extracting 2-BE from a hydraulic fracturing chemical additive and studying the fate of 2-BE in water over time. In the hydraulic fracturing chemical additive, other organic components were identified and two, D-limonene and 1-butoxy-2-propanol, were quantified using the method described. This study also examines the effectiveness of extracting 2-BE from other sample matrices allowing for 2-BE studies in other applications, such as fluids from microbial degradation processes found in wastewater treatment plants.

2. Materials and methods

2.1. Materials

The chemicals used in this study including Optima grade methylene chloride, acetone, hexane, methanol, ethyl acetate, HPLC grade chloroform, hydrochloric acid, potassium chloride, potassium sulfate, potassium bromide, sodium bicarbonate, ferric sulfate, aluminum sulfate, sodium chloride, and ≥95% practical grade 2-butoxyethanol (2-BE) were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). Revert Flow was received from Weatherford International (Houston, Texas, USA). D-limonene and >95% 1-butoxy-2-propanol were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA) in order to verify and quantify their presence in Revert Flow. Vitamin Supplement and Trace Mineral Supplement were obtained from American Type Culture Collection (ATCC) (Manassas, Virginia, USA). Biomass was acquired from the Kuwahee Wastewater Treatment Plant in Knoxville, TN. Deionized water was produced using a Milli-Q Plus water purification system (Darmstadt, Germany).

2.2. Standards and sample preparation

Stock solutions of 2-BE were prepared by dissolving a known mass of 2-BE in Optima grade methylene chloride, methanol, hexane, or ethyl acetate or chloroform. Standards were made by diluting the stock solutions in the solvent to prepare calibration curves. Calibration curves were made for each solvent due to differences in the solvent matrix. 2-BE and Revert Flow samples were made by dissolving known amounts of the compound in water or water containing known concentrations of sodium chloride, brine solution, or Vitamin and Mineral Supplement. The concentration of Revert Flow that was added to hydraulic fracturing brine was 1 gallon per 1000 gallons of water, which was the concentration used in the hydraulic fracturing industry suggested by chemical additive supplier. Standards for the other constituents, D-limonene and 1-butoxy-2-propanol, quantified in Revert Flow were prepared in methylene chloride using standard dilutions. Table 2 displays the concentrations of salts that composed the brine solution [47–49]. Constituents of the Vitamin and Mineral Supplement may be found in Supplementary materials (Table S2) [50]. Solutions were allowed to mix for a minimum of 12 h.

2.3. Liquid-liquid extractions of 2-BE from aqueous solutions

LLEs of the solutions containing 2-BE were carried out using dichloromethane, hexane, ethyl acetate, chloroform or acetone. For

Table 2
Composition of hydraulic fracturing brine used in this study.

Brine constituent	Concentration (M)
Sodium chloride	1.71×10^{-2}
Potassium chloride	2.68×10^{-5}
Potassium sulfate	1.43×10^{-4}
Potassium bromide	1.26×10^{-4}
Sodium bicarbonate	1.79×10^{-4}
Ferric sulfate	3.75×10^{-5}
Aluminum sulfate	4.38×10^{-5}
Hydrochloric acid	1.92×10^{-5}
Total concentration	1.77×10^{-2}

Table 1
Current methods used to detect 2-BE in samples with different media types.

Sample type	Method	Detection limit	Ref
Opossum kidney cell culture	GC/FID	5.0 mg L^{-1}	[34]
Water	"Purge and trap" GC/MS	0.1–200 μg L^{-1}	[35,36]
Sea water oil spill cleanup	SPE-LC-MS/MS	20 ng L^{-1}	[8]
2-BE in methanol and aerosol samples	GC/MSD	0.1 ng μL^{-1}	[37]
Water	Direct Inject LC/MS/MS	125 μg L^{-1}	[31]
HF fluids	LC/MS/MS		[32]
Water	NMR		[38]
Air samples of cleaning products	GC/MS	1 mg L^{-1}	[7,39]
Aerosol samples of cleaning products	Direct GC/MS	16 μg mL^{-1}	[40]
Marcellus Shale HF waters	GCxGC/TOFMS	≈0.01 ng L^{-1}	[33]

each of the different solvents, 3 mL of the 2-BE solutions were placed into a scintillation vial and weighed. Then 3 mL of organic solvent was added to the vial containing the sample. The vials were vigorously mixed for 30 s using a 115V Mini Vortex Mixer (Fisher Scientific, Pittsburgh, PA 15275, USA). The solutions were allowed to come to equilibrium by setting the vials on a bench top for 10 min. The solutions were then separated using a 6 mL polypropylene syringe (Fisher Scientific, Pittsburgh, PA 15275, USA). The organic fraction was placed into a separate collection vial and the water fraction was placed back into the original vial. These steps were performed three times per sample, so that the total volume of the organic fraction in the collection vial was 9 mL after analysis of extraction steps showed that all 2-BE was recovered with 3 washes. After all washes were performed, the final organic fraction was weighed. Samples were analyzed immediately or frozen prior to analysis. Equations used for determining 2-BE concentration and mass balance calculations for extraction efficiency are shown in the Supplementary materials (Calculations S1 and S2). Standard error (SE) was calculated using Equation (1) and is represented in the figures using error bars.

$$SE_{\bar{x}} = \frac{s}{\sqrt{n}} \tag{1}$$

where s is the standard deviation, $\bar{x}$ is the mean, and n is the number of observations.

2.4. GC/MS method

GC/MS analysis was carried out on an Agilent 7890B Gas Chromatograph (GC) equipped with a 5977A Mass Selective Detector (MSD) system and a 7963 auto-sampler (Santa Clara, CA 95051, USA). The column was an Aligent J&W DB-1 capillary column, which operates at temperatures up to 325 °C and is cross-linked, non-polar, low bleed, and solvent rinsable. The column was 60 m × 0.25 mm inner diameter (I.D.) with a 0.25 μm film thickness. The carrier gas was ultra-high purity helium purchased from Airgas Corporation (Knoxville, TN 37921, USA). The GC was operated in split-less mode and the flow rate of the carrier gas was maintained at 2.5 mL min^{-1} throughout the sample run. The pressure maintained in the instrument was 234.2 kPa. The initial temperature of the GC was 40 °C and was held for 4 min. The temperature ramp was 5 °C/min to 230 °C, which was held for 2 min. The injection volume was 3.5 μL using a 10 μL syringe. The 2-BE peak on the chromatogram was between 9.5 and 10 min. Spectrum analysis was performed using the National Institute of standards and Technology (NIST) library and the most abundant peak in 2-BE's spectrum was found at the mass to charge ratio (m/z) 57.1. The abundance of this peak was recorded for all data collected and used to quantify the 2-BE in each sample.

For the unknown compounds in the chemical additive Revert Flow, the NIST library was used for identifications. Version 02 of the NIST/EPA/NIH Mass Spectral Library was used. Identifications were based on matching mass spectra of unknowns with those in the spectral database.

2.5. Validation

To validate the LLE method using methylene chloride, precision and accuracy were determined by extracting a solution contain a known concentration, 271 mg L^{-1}, of 2-BE in deionized water and in water containing 12.8 M sodium chloride. The extractions were performed six times on each solution by two different people. Reproducibility was calculated by determining the relative standard deviations (RSDs). The RSDs were calculated using Equation (2):

$$\%\,RSD = 100 * \frac{s}{\bar{x}} \tag{2}$$

where s is the standard deviation and $\bar{x}$ is the mean [43]. Accuracy was calculated using Equation (3):

$$Accuracy = 100 * \frac{\bar{x} - known\ value}{known\ value} \tag{3}$$

where the known value is the concentration of 2-BE in the aqueous solution [43].

The LOD was determined by injecting a standard sample 7 times. Equation (4) was used to calculate LOD:

$$LOD = \frac{3s}{m} \tag{4}$$

where m is the slope of the calibration curve [36].

3. Results and discussion

3.1. Gas chromatograms and mass spectrum

Fig. 1a displays the gas chromatogram of a 0.973 mg L^{-1} 2-BE standard in methylene chloride. The retention time of 2-BE in this chromatogram is 9 min Fig. 1b displays the mass spectrum of 2-BE for this same chromatogram. Calibration curves were determined for 2-BE using the mass spectra abundance of the most abundant signal, 57.1 m/z, and the total mass signal, 118 m/z. Linearity for both calibration curves were determined by calculating the square of correlation coefficient (R^2). The calibration curve using the 57.1 m/z signal gave a R^2 value of 0.955 while the 118 m/z signal gave a R^2 value of 0.978. Therefore, the 118 m/z signal was used in order to quantify 2-BE in this study.

3.2. Liquid-liquid extraction recovery

Fig. 2a shows the overall percent of 2-BE recovered by each organic solvent tested. The extraction with dichloromethane achieved 99.6% overall recovery of 2-BE from the water solution, while 100%, 42.6%, and 8.3% overall recovery of 2-BE was achieved using chloroform, ethyl acetate, and hexane, respectively. The cumulative extraction efficiency for each solvent was 35.1% using hexane, 75.9% with ethyl acetate, 100% for methylene chloride, and 99.9% using chloroform.

Fig. 2b displays a plot of extraction efficiency versus number of extractions for the extraction using all four organic solvents tested [43]. As seen in this plot, extraction efficiency dramatically increases with the first two extractions for methylene chloride and chloroform. Hexane and ethyl acetate did not perform as well as methylene chloride and chloroform. After 5 extractions, ethyl acetate achieved 75.9% efficiency, while hexane only achieved 35%. This is attributable to the differences in relative polarity between 2-BE and these solvents as shown in the Supplementary material Table S1. The relative polarity of 2-BE to water is 0.602, while the relative polarities of hexane, ethyl acetate, chloroform, and methylene chloride are 0.009, 0.228, 0.259, and 0.309 [45,46]. Solvents with a relative polarity closer in value to that of 2-BE performed better as extraction solvents.

3.3. Validation

The overall LOD for the liquid-liquid extractions using methylene chloride in a solvent to sample volume ratio of 3:1 was

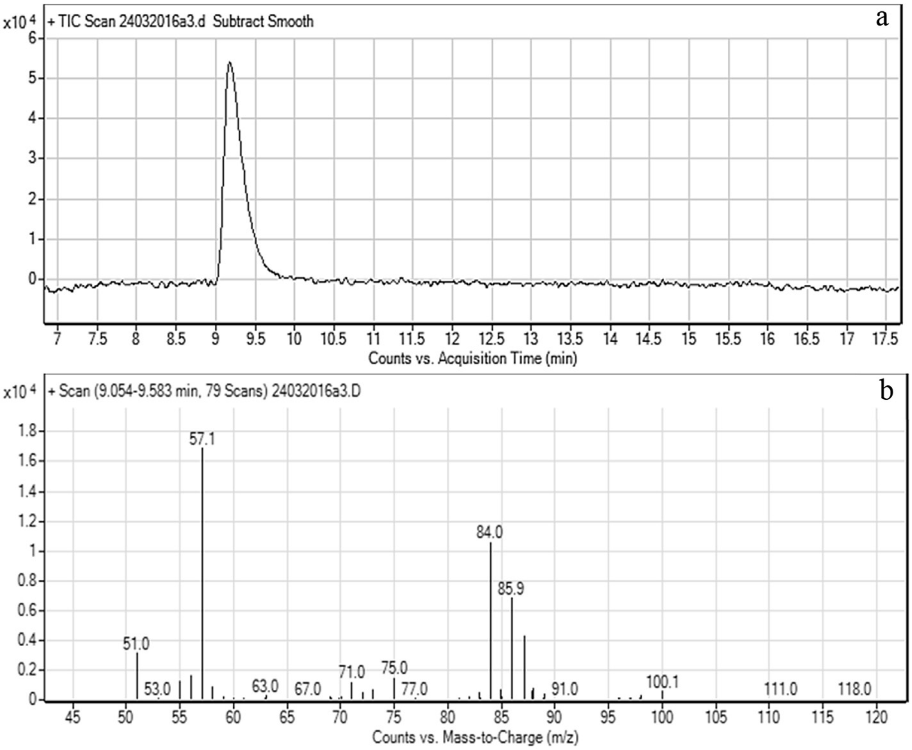

Fig. 1. (a) Gas chromatogram of a 0.973 mg L^{-1} 2-BE standard in methylene chloride. (b) Mass spectrum of the peak with a retention time of 9 min in the gas chromatogram.

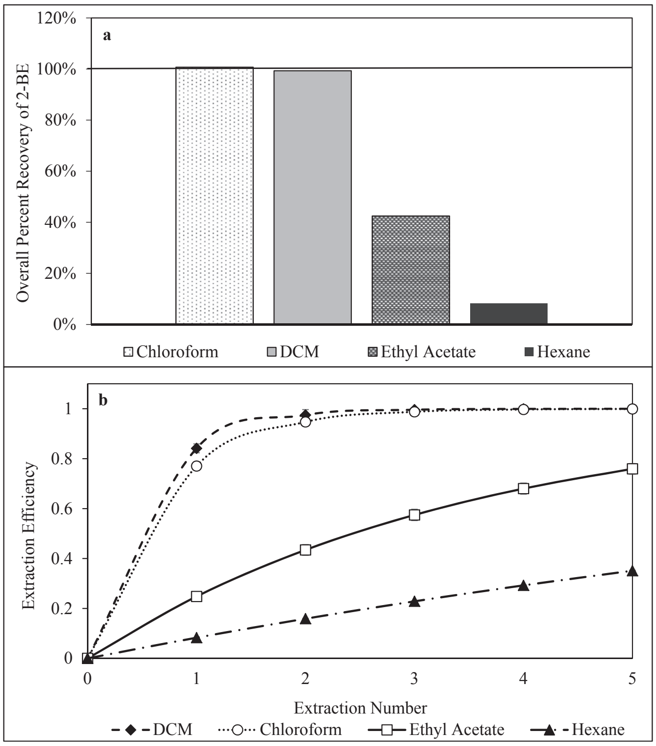

Fig. 2. (a) Overall percent recovery of 2-BE for LLE using four different organic solvents, chloroform, methylene chloride, ethyl acetate, and hexane. The initial concentration of 2-BE in the original water sample was 143 mg L^{-1}. Error bars represent standard error. (b) Plot of extraction efficiency versus the number of extractions performed for the liquid-liquid extraction using methylene chloride in Section 3.3.

determined to be 0.957 mg L^{-1}, which was lower than the method using GC/FID established by Hildenbrand et al. [34]. The LOD established in the study presented was also less than those developed to quantify 2-BE in air, aerosol, and methanol samples using GC/MS, as outlined in Table 1 [7,37,39].

Method performance was evaluated using accuracy and precision for data generated using samples extracted from deionized water and 12.8 M sodium chloride by LLE. Results indicate that the LLE method using methylene chloride is accurate and precise with values below 5%. The accuracy was determined to be 2.58%. The RSD was determined to be 3.5%, showing that there is low variability in the measurements.

3.4. Recovery from various sample matrices

Fig. 3 displays the percent recovery of 2-BE from samples in different matrices, including a set of controls consisting of 2-BE in deionized water, different concentrations of sodium chloride, hydraulic fracturing brine solution with various salt constituents, and from active and inactive wastewater treatment plant biomass samples. In the hydraulic fracturing brine, the overall concentration of constituents other than 2-BE totaled 17.7 mM. As shown in Table 2, the hydraulic fracturing brine mostly consists of inorganic salts, whereas the wastewater treatment plant samples also contain organic matter in addition to inorganic salts. Initial concentration of 2-BE varied in each sample matrix. The initial concentration of 2-BE in hydraulic fracturing brine samples and their control samples, which contained no brine, were between 95 and 155 mg L^{-1}. Samples containing 0.001 and 0.1 M sodium chloride and their controls, which contained no sodium chloride, had an initial 2-BE concentration of 500 mg L^{-1}. Initial concentration of 2-BE in active biomass, inactive biomass, and control samples, which only contained vitamin solution, was between 28 and 50 mg L^{-1}. Recovery of 2-BE from all solutions tested was 97% or greater ($n \geq 3$). In some cases, the recovery was greater than 100%, which may be due to evaporation of the methylene chloride during the extraction

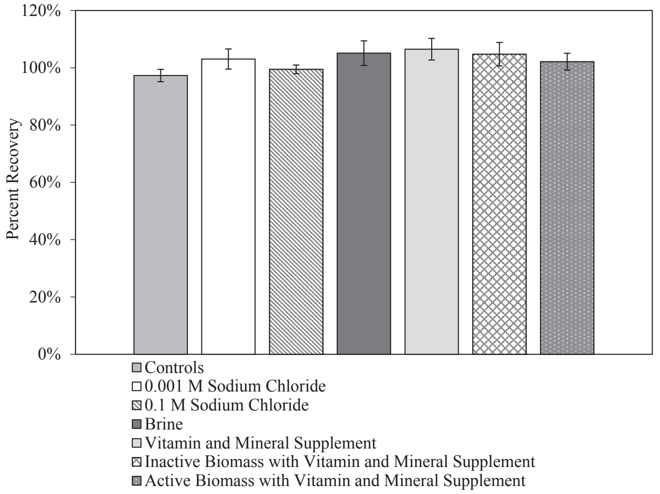

Fig. 3. Percent Recovery of 2-BE from each high saline sample matrix tested in this study. Error bars represent the standard error.

process. Standard error was calculated and was below 5% for each sample type. The data show that the method can be used for a variety of different sample matrices.

3.5. Application

3.5.1. Quantification of 2-BE in hydraulic fracturing chemical additive

Revert Flow is added to hydraulic fracturing fluids to reduce surface tension. It also improves production from unconventional reservoirs, enhances water removal, and prevents water blocking. Revert Flow was extracted from hydraulic fracturing brine. Fig. 4a displays the resulting gas chromatogram of Revert Flow. 2-BE was identified as the peak with retention time 8.748 min Fig. 4b displays the mass spectrum of 2-BE for this peak. Table 3 displays the compounds identified in the chemical additive. The mass spectra of the Revert Flow components may be found in the Supplementary materials Figures S1–S5. The weight percent of 2-BE in Revert Flow was determined to be 3.31 ± 0.00019 wt % (n = 3). Extraction efficiency for 2-BE was also determined and is shown in Fig. 5. After four washes with methylene chloride, 99.9% efficiency was obtained (n = 3). Though, 94.5% of the total initial moles of 2-BE were recovered after the first wash with methylene chloride. As shown in Fig. 4b and Table 3, Revert Flow contains a number of potentially more concentrated organic chemical additives than 2-BE. This makes extracting 2-BE more difficult than when it is the only constituent in solution.

Two of these contaminants, D-limonene and 1-butoxy-2-propanol, were also quantified and evaluated for extraction efficiency. D-limonene is a monoterpene used in cosmetics and food products and poses little to no risk to human health [51,52]. 1-butoxy-2-propanol is a glycol ether and also appears to pose little risk to human health [53]. Both of these chemicals have been reported as present in hydraulic fracturing fluids [26,54,55]. Their mass spectra obtained from analysis of Revert Flow may be found in the Supplementary materials Figures S1 and S2. It was determined that D-limonene and 1-butoxy-2-propanol make up 31.8 ± 0.019 and 18.7 ± 0.0361 wt % (n = 3), of Revert Flow, respectively. As

Table 3
Compounds identified in the hydraulic fracturing chemical additive “Revert Flow”.

Retention time (minutes)	Compound identification	NIST probability (%)
8.734	2-butoxyethanol	85.10
10.744	1-butoxy-2-propanol	93.8
11.253	di-sec-butyl ether	22.8
15.591	D-limonene	33.4
18.252	1-octanol	47.3
26.439	1-decanol	28.9

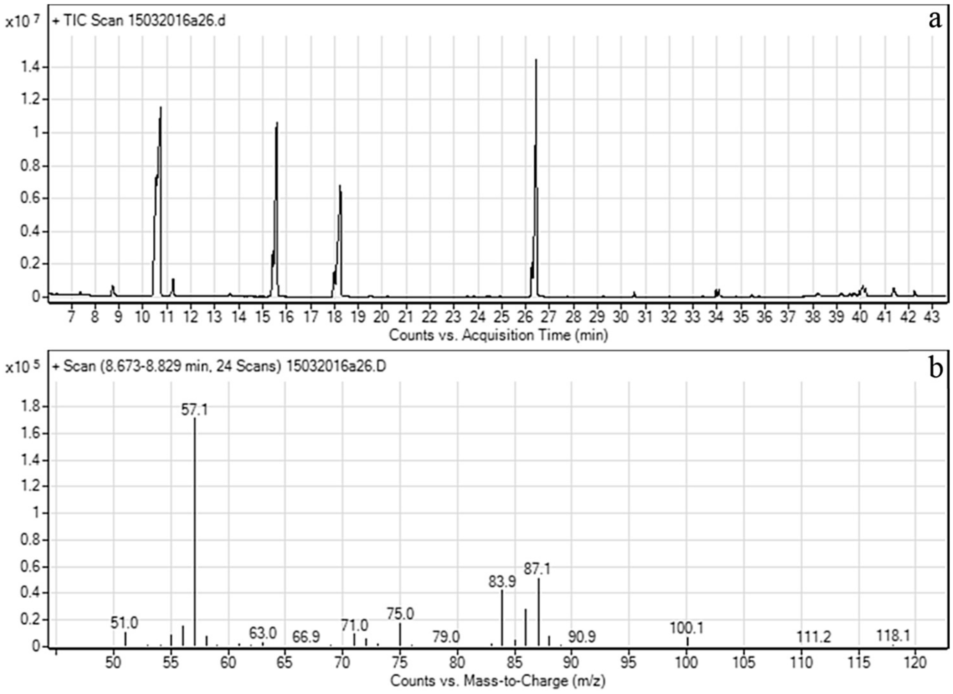

Fig. 4. (a) Gas chromatogram of 2-BE containing hydraulic fracturing chemical additive, Revert Flow. 2-BE has a retention time of 8.748 min. (b) Mass spectrum of the compound identified as 2-BE in Revert Flow.

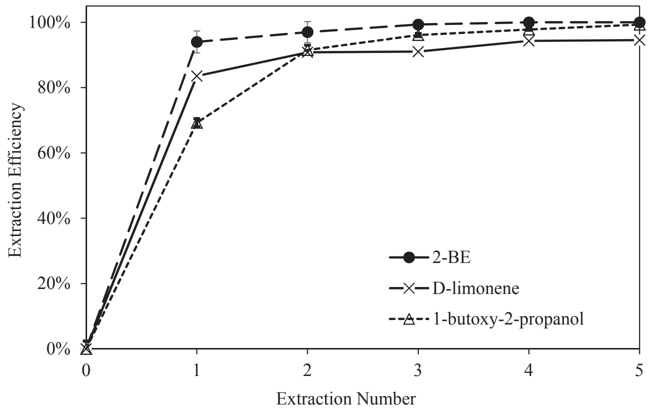

Fig. 5. Extraction efficiency of 2-BE, D-limonene, and 1-butoxy-2-propanol from Revert Flow in hydraulic fracturing brine. Error bars represent standard error.

shown in Fig. 5, extraction efficiency of D-limonene and 1-butoxy-2-propanol from Revert Flow were also determined. After 5 washes with methylene chloride, 94.5% overall efficiency was obtained for D-limonene and 99.3% was obtained for 1-butoxy-2-propanol ($n = 3$). This suggests that more washes with methylene chloride would be required to extract all of the D-limonene and 1-butoxy-2-propanol from the water into the organic phase. When studying hydraulic fracturing fluids, this must be taken into consideration if components in addition to 2-BE are of interest for quantification.

3.5.2. *Comparison of 2-BE stability*

The stability of 2-BE is important as breakdown of the compound makes it difficult to detect over time. Since 2-BE has been used as an indicator for hydraulic fracturing fluid migration [33], testing the stability of 2-BE can help determine sample lifetime for these fluids. Replicates ($n = 3$) were used to determine the stability of 2-BE in water sealed with a rubber stopper and exposed to oxygen in the atmosphere over time using a needle. Fig. 6 displays the concentration of 2-BE over time while the solution is continuously mixed. Using first-order reaction kinetics, the half-life of 2-BE in deionized water was determined to be 5.55 days. In the brine solution of Revert Flow containing 2-BE, the weight percent of 2-BE in Revert Flow decreased from 3.31% to 3.09% after 8 days of mixing. This suggests that the 2-BE half-life is dependent of the solution matrix, and other constituents such as hydraulic fracturing brine and chemical additives may increase the persistence of 2-BE in water. The other constituents quantified in Revert Flow, D-limonene and 1-butoxy-2-propanol, appear to have less stability than 2-BE in the hydraulic fracturing fluid environment over the 8 day period. The weight percent of D-limonene decreased from 31.8% to 18.2% and 1-butoxy-2-propanol decreased from 18.7 to 9.94%.

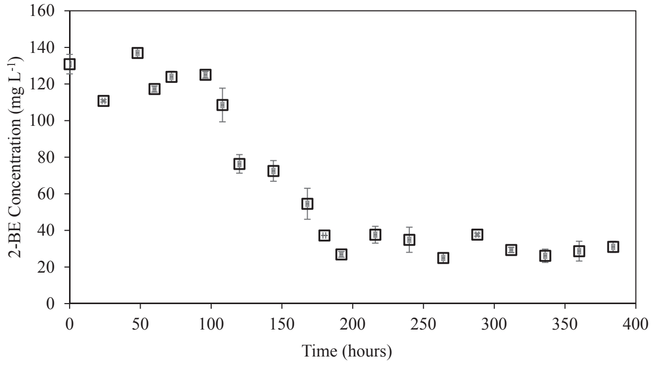

Fig. 6. Stability of 2-BE in deionized water over the course of 16 days. Standard error is represented by error bars.

The persistence of 2-BE by abiotic hydrolysis is much less than the persistence of 2-BE in anaerobic degradation, which has previously been used to estimate 2-BE persistence [30]. Rogers et al. estimated 2-BE persistence and exposure risk by calculating the tenth-life of 2-BE as 0.51 years in an anaerobic biodegradation setting [30]. In this study, we have determined that the abiotic hydrolysis tenth-life of 2-BE is 18.4 days (equation in Supplementary materials Calculation S3). When hydraulic fracturing fluid contaminated waters are in contact with oxygen, 2-BE may not be as strong as an indicator for contamination as previously thought.

4. Conclusions

This liquid-liquid extraction method with methylene chloride was a reliable method to monitor 2-BE in various water samples. The method showed a limit of detection of 0.957 mg L^{-1}. The method is reliable, convenient, and uses GC/MS, a more common laboratory technique than previously established methods. Using this method, we were able to establish the abiotic hydrolysis half-life for 2-BE, which was 5.55 days. We were also able to detect and quantify 2-BE, D-limonene, and 1-butoxy-2-propanol in a hydraulic fracturing chemical additive called Revert Flow. It was determined that Revert Flow is composed of 3.31 wt % 2-BE, 31.8 wt % D-limonene, and 18.7 wt % 1-butoxy-2-propanol. Future studies should further investigate the best extraction method for D-limonene and 1-butoxy-2-propanol and the persistence of both additives in order to compare how strong of an indicator that they could be for hydraulic fracturing contamination. The results of this study show that the stability of 2-BE is dependent upon other constituents in solution and that 2-BE persistence increases when ions and other organics are present.

Conflict of interest

There is no conflict of interest to report.

Acknowledgements

Funding for this project was provided by the University of Tennessee Knoxville's Institute for a Secure and Sustainable Environment (ISSE) and the Science Alliance.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ancr.2016.07.001.

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