

THE EFFECT OF TEMPERATURE, TURBULENCE, AND PH ON THE SOLUBILITY OF MTBE

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ABSTRACT

Methyl tertiary butyl ether (MTBE) is a fuel oxygenate whose discharge is inevitable in the environment, consequently posing serious health and environmental effects. The solubility of this volatile organic compound (VOC) has not been studied extensively, the few studies available present contrasting views. This study used a spectrophotometer to determine the effects of pH (5, 7 & 9), mixing rate (400 rpm & 600 rpm), and time (1 hour) on the solubility of MTBE in water. We calculated the λ_{max} and the molar absorptivity of MTBE as 190 nm and 167 M-cm- respectively. MTBE spiked at pH 9 gave the highest absorbance, while the results obtained at pH 5 gave the lowest absorbance. However, MTBE spiked at pH 7 was more soluble and relatively stable. A low mixing rate of 400 rpm enhanced the solubility of MTBE indicating that turbulence reduces the solubility of MTBE in water. Moreover, our results indicate that low temperature enhances the solubility of MTBE. The solubility of MTBE at 25 °C using a mixing rate of 400 rpm and 600 rpm was 0.08 g/L and 0.044 g/L respectively. Additionally, the solubility at 30 °C using a mixing rate of 400 rpm and 600 rpm was 0.068 g/L and 0.12 g/L respectively.

Keywords: MTBE, VOC, Solubility, Spectrophotometer.

INTRODUCTION

Lead was used in fuel as an additive to enhance combustion in automobile engines during the past decades. However, the advent of fuel oxygenates has rendered lead useless due to its health implications and environmental pollution problems. Methyl tertiary butyl ether (MTBE) is the most common fuel oxygenate since the passage of clean air act in the United State (Pla *et al.*, 2000; Safarzadeh-Amiri 2001). The global production of MTBE/per year is over 20 million tons, 100 percent of which is commonly used as additive (Rosell *et al.*, 2006). MTBE, the product of the reaction between methanol and isobutylene, helps raise the octane number in fuels while reducing harmful automobile emissions (Levchuk *et al.*, 2014). MTBE is a colorless clear liquid with an inherent smell and has a molecular formula and a molecular weight of $C_4H_9OCH_3$ ($C_5H_{12}O$) and of 88.15 g/mole respectively. It is widely used as a solvent in many industries besides from its applications as a fuel oxygenate. MTBE is equally flammable and has a high vapor pressure (204 mm Hg at 20 °C). The solvent has a boiling point of 55 °C (131 °F) at atmospheric pressure and a freezing point of -109 °C (-164 °F) (USEPA 1999).

The release of MTBE into the environment either through direct release or accidental discharge is inevitable due to its global production and utilization. The discharge of MTBE into the environment is mainly via leakage from storage tanks or transportation related issues (Rosell *et al.*, 2006). MTBE is an organic compound soluble in both surface and groundwater than all other organic components constituting gasoline (Rakshit *et al.*, 2013). MTBE is an

environmental pollutant and a possible carcinogen; USEPA has categorized MTBE as a compound with a potential danger to human health (USEPA 2000; Chen et al 2008). USEPA has established the allowable limit of MTBE in drinking water as 15 ug/L and a range of 0.02-0.04 mg/L as an approximate "threshold" for humans to detect the taste and odour of MTBE in drinking water. Due to its solubility and resistance to microbial degradation, cases of surface water, wastewater and groundwater contaminated with MTBE have been recorded previously (Salabat 2007; Miermans *et al.*, 2000; Achten *et al.*, 2002). Human exposure to MTBE is mostly via inhalation upon contact at a workplace, consumer use of products containing MTBE, or through environmental release. MTBE is readily absorbed and metabolized by the body.

The physicochemical parameters of MTBE such as solubility, volatility, low henrys constant, and molecular size has made MTBE highly undesirable to clean up using conventional methods such as chemical oxidation, air stripping and adsorption techniques (Fischer *et al.*, 2004; Rakshit *et al.*, 2013). The use of nanoparticles and photocatalysis to selectively isolate MTBE from contaminated water is a promising alternative (Boulamanti and Philippopoulos 2008; Barreto *et al* 1995; Chan and Lynch 2003). However, to assess impacts of MTBE to the environment, it is imperative to understand its behavior upon contact with water. The solubility of MTBE in water has not been studied extensively largely because MTBE is an organic compound making it susceptible to degradation or vaporization. These are the major reasons why researchers are reluctant to explore its solubility in great details. However, studies have shown that MTBE is persistent in groundwater and has serious health related problems. Despite the existing effects and potential dangers of MTBE, studies on its solubility are still lacking. The few literature available present contrasting results relative to temperature and henry's law solubility constant.

Moreover, most of the studies conducted on the solubility used more modified equipment such as GC-MS and GC-FID to quantitatively determine the solubility of MTBE in water. This study used a different approach to determining the solubility of MTBE in water. We used a spectrophotometer, a device that uses the principle of light to monitor the changes in the absorbance of spiked MTBE in water samples. We tried to mimic what happens in real life situation as MTBE tumbles in either surface or ground water in an event of leakage or spills. We maintained an initial concentration of MTBE and varied the pH, mixing rate, temperature, as a function of time. We believe that temperature may not be the only factor affecting the solubility of this volatile organic compound in a confined medium.

MATERIALS AND METHODS

Materials

Thermo scientific (Cimarec) hot plate and stirrer, pH meter (H12216 pH/ORP/ISE Meter Hanna Instruments), Spectrophotometer (Analytical Jena Record 50), concentrated MTBE 99.8%, deionized water, 0.01N H₂SO₄, 0.01N NaOH, Stirring bars coated in Teflon (round with glide ring of diameter 26mm and length 50mm), 160 mL sealed bottles, cuvettes, pipettes and measuring cylinders.

Method

pH adjustment

Three separate 160 mL sealed bottles were filled with 150 mL deionized water and the pH was adjusted using the pH meter to 5, 7 and 9 respectively using prepared diluted acid and

base solutions. A sealed bottle filled with 160 mL of deionized water was left without pH adjustment to serve as the blank solution.

Determination of λ_{max} of MTBE

Lambda max of MTBE is the wavelength where MTBE has the maximum absorption. Determining lambda max is cardinal to the success of any experiment involving the determination of absorption or solubility of a compound. We made an MTBE solution of 100 ppm and the spectrophotometer was zeroed using a blank solution. The absorbance spectrum (a graph of wavelength against absorbance) was then run for the 100 ppm solution of the MTBE and the readings were taking.

Working conditions

We made a 100 ppm MTBE solution separately into three sealed bottles and the pH of the sealed bottles was adjusted to 5, 7, and 9. The sealed bottles were closed to avoid vaporization of the MTBE and placed immediately on the hotplate coupled stirrer. We adjusted the hotplate coupled stirrer to 25 °C at a mixing rate of 400 rpm initially and we left the plate to stand for 10 min to ensure an even distribution of heat before the actual analysis. The sealed bottles adjusted to pH (5, 7, and 9) were then placed on the hotplate coupled stirrer and the absorbance of each bottle was taking at 10 min interval for one hour. The spectrophotometer was zeroed each time a sample was taken using the blank solution and readings were recorded in triplicates. The procedure was repeated at a mixing rate of 600 rpm to examine the effect of mixing rate on the solubility and readings were taken 10 min interval for one hour. To examine the effect of temperature on solubility we adjusted the temperature to 30 °C and varied the mixing time and pH and readings were taken from the spectrophotometer in triplicates. Lastly, we increased the mixing rate from 400 rpm to 600 rpm and maintained the temperature at 30 °C and readings were taken from the spectrophotometer in triplicates.

RESULTS AND DISCUSSION

Lambda max result

The absorption spectrum of MTBE is showed in **Fig. 1**. The volatile organic compound showed a maximum absorption of UV light at a wavelength of 190 nm. We conducted the subsequent experiments at 190 nm in order to get the maximum sensitivity. The result coincides with the range reported by Kavanaugh *et al* 2004 in their book titled “Removal of MTBE with advanced oxidation”. They mentioned that MTBE does not absorb UV above 200 nm. We recommend a highly sensitive spectrophotometer that can detect absorbances at wavelengths below 100 nm to better resolve and clarify all impending issues relative to the lambda max of MTBE.

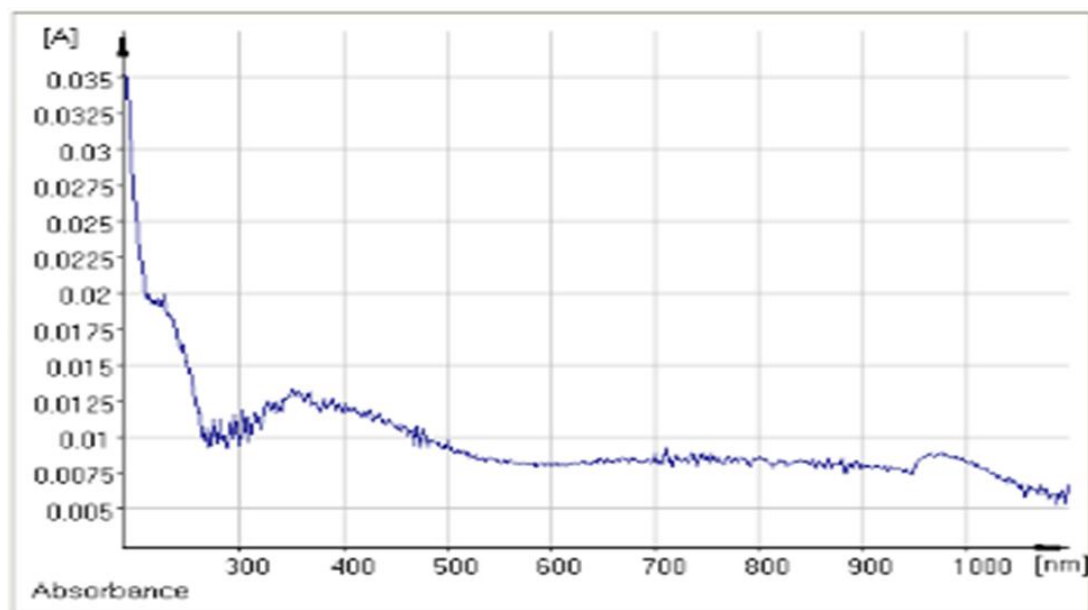


Figure 1: The absorption spectrum (Absorbance vs. wavelength) of MTBE.

Result on molar absorptivity

The calibration curve and the equation of the line graph are given in **Fig 2**. The correlation coefficient (R^2) is 0.9253 under the current conditions; the result shows a little linearity though no literature has reported on the molar absorptivity of MTBE. We used the molar absorptivity calculated from **Fig 2** to determine the solubility of MTBE.

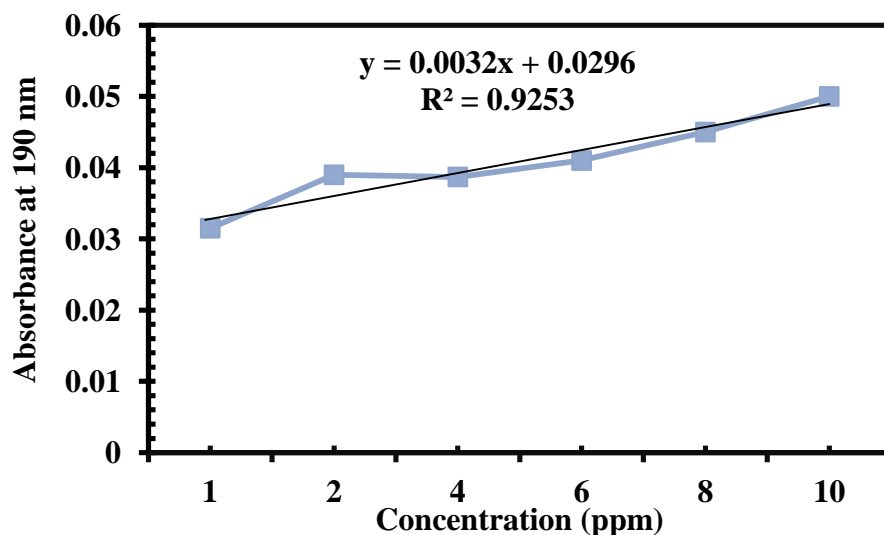


Figure 2: The calibration curve of MTBE (Absorbance vs. Concentration) at 190nm.

Beer-Lambert law states that when a beam of monochromatic light is passed through a solution, the intensity of the light decreases exponentially with the absorbance increase in the concentration of the absorbing substances. Absorbance is directly proportional to concentration (A vs C).

$$A = \log \frac{\text{Incident light } I_0}{\text{Transmitted light } I_t} = \log \frac{1}{\text{Transmittance}} = -\log T = \epsilon b C$$

$A = \epsilon b C$ where b = path length (cm) and ϵ = molar absorptivity (M-cm-) but in a graph of A vs C , ϵb is the slope, therefore

$\epsilon b = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.049 - 0.032}{10 - 1} = \frac{0.017}{9 \text{ ppm}}$ converting ppm to g/L will yield $\frac{0.017}{0.009 \text{ g/L}}$ converting g/L to the unit of molar absorptivity will change the fraction to $\frac{0.017}{0.009 \frac{\text{g}}{\text{L}} \div \text{Molar mass of MTBE} (\frac{\text{g}}{\text{mol}})}$, therefore $\epsilon b = \frac{0.017}{0.009 \frac{\text{g}}{\text{L}} \times \frac{1 \text{ mol}}{88.15 \text{ g}}} = \frac{0.017}{0.009 \frac{\text{mol}}{88.15 \text{ L}}} = \frac{0.017 \times 88.15}{0.009 \text{ mol/L}} = (167 \text{ M}^{-1})$ since the path length (b) is equal to 1cm then, ϵ (Molar absorptivity of MTBE) = $167 \text{ M}^{-1} \text{ cm}^{-1}$

Results of spectrometric analysis

The absorbance of MTBE at 25 °C, mixing rate of 400 rpm, and pH of 5, 7, and 9 for a period of one hour is given in **Fig 3**. A gradual fluctuation in absorbance at various pH (5, 7, & 9) is noticeable. However, the absorbance at various pH coincides after mixing for 40 min. The result indicates a consensus value at 40 min where MTBE seems to be completely soluble in water regardless of acidity or basicity of the medium. The mixing rate of 400 rpm contributed to the solubility of MTBE because the absorbance was linear and the readings increased from an acidic to a basic medium. The mixing rate of 400 rpm did not affect the solubility of MTBE in water. We concluded that low mixing rate seemed optimum for achieving maximum solubility of MTBE in water. Moreover, the order of solubility was pH 5 < pH 7 < pH 9. We confirmed that solubility was highest in a basic medium. We chose the absorbance of 0.15 nm to be a representative value for the derivation of solubility at 25 °C and a mixing rate of 400 rpm. The solubility of MTBE at this temperature and mixing rate, therefore, was calculated using the calculated molar absorptivity of MTBE and the result is shown below:

$$A = \epsilon b s,$$

where A is the absorbance in nm,

ϵ is the molar absorptivity in $\text{M}^{-1} \text{cm}^{-1}$, b is the pathlength in cm and

s is the solubility in mole/L

$0.15 = 167 \times 1 \times s \rightarrow s = 0.000898 \text{ mol/L}$. Converting mol/L to g/L means to multiply the result by the molar mass of MTBE (88.15 g/mol.)

$$s = \frac{A}{\epsilon b} \times \text{molar mass of MTBE} \frac{\text{g}}{\text{mol}}$$

$$s = 0.000898 \frac{\text{mol}}{\text{L}} \times 88.15 \frac{\text{g}}{\text{mol}} = 0.08 \text{ g/L}$$

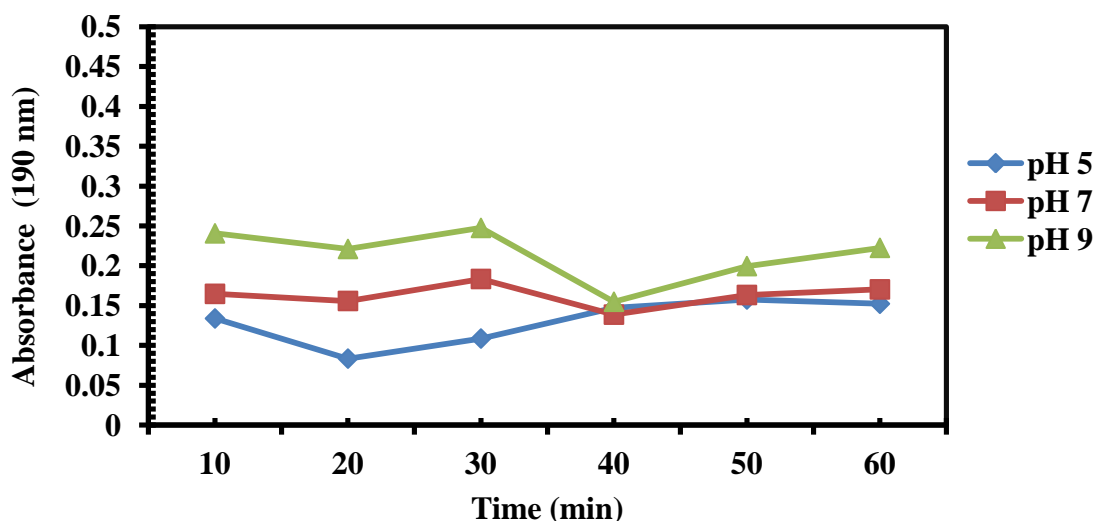


Figure 3: The absorbance of MTBE at a temperature of 25°C and a mixing rate of 400 rpm under different pH conditions at 10 min interval for 1 hour

The absorbance of MTBE at 25 °C and a mixing rate 600 rpm is depicted in **Fig 4**. The trend from various pH evaluated was slightly different from the trend obtained at a mixing rate of 400 rpm. The range was between 0.02 nm - 0.15 nm, lower than the previous experiment. The mixing rate had a noticeable effect this time compared to the readings obtained at a mixing rate of 400 rpm. The turbulence arising due to vigorous mixing may be the reason why fluctuations in absorbance readings were visible. The total solubility of MTBE was not attained after 60 min, however, the readings from various pH evaluated followed the order pH 5 < pH 7 < pH 9. Readings obtained from pH 7 were more stable compared to pH 5 & 7. The readings coincide at the same point after 30 min of vigorous mixing. The absorbance at that time was (0.08 nm), so we took the value to evaluate the optimum value to represent the solubility at this temperature and mixing rate:

$$s = \frac{A}{\epsilon b} \times \text{molar mass of MTBE} \frac{g}{mol}$$

$$s = \frac{0.08}{167 \times 1} = 0.0005 \frac{mol}{L} \rightarrow 0.0005 \frac{mol}{L} \times 88.15 \frac{g}{mol} = 0.044 \text{ g/L}$$

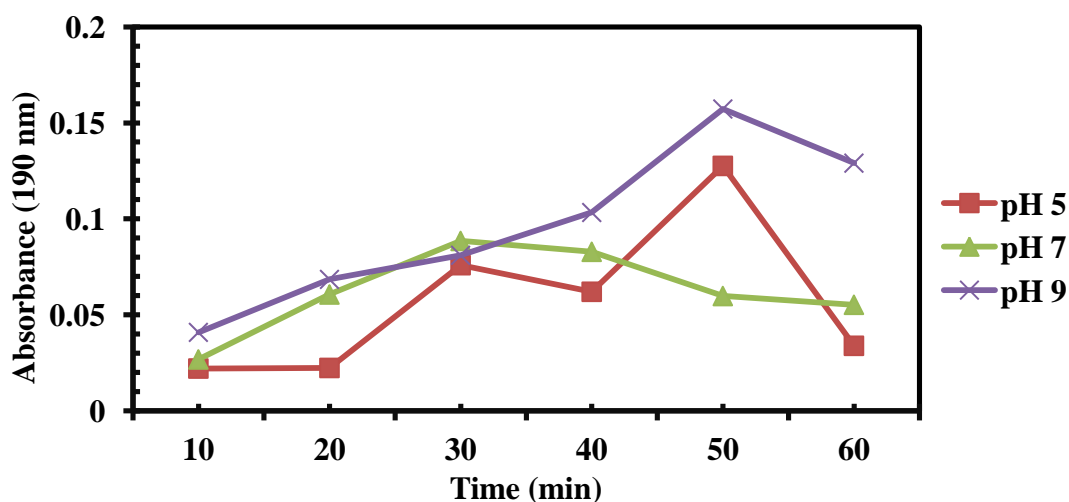


Figure 4: The absorbance of MTBE at a temperature of 25°C and a mixing rate of 600 rpm under different pH conditions

The absorbance of MTBE at 30 °C and a mixing rate of 400 rpm for the various pH evaluated are given in **Fig 5**. The range of absorbance where all the readings fall is between 0.02 nm – 0.2 nm. MTBE spiked in water at pH 5 and pH 7 reached maximum solubility in this experiment at an absorbance of approximately 0.13 nm after 30 min of mixing. Absorbance readings of MTBE spiked at pH 9 showed an increasing trend throughout the experiment much higher than the other pH used. However, a drop in absorbance to 0.05 nm after 50 min of mixing was noticeable. The unusual drop was due to turbulence which may hinder detection of MTBE at high concentration at that time. The result confirmed that low mixing rate aids in solubilizing MTBE and maintaining the stability of the volatile organic compound in a liquid medium. The experiment at this temperature showed a rather interesting result and the whole pH used had almost the same absorbance readings after 30 min of mixing, which is why the absorbance of 0.13 nm was selected as the optimum absorbance of this experiment.

$$s = \frac{A}{\epsilon b} \times \text{molar mass of MTBE} \frac{g}{mol}$$

$$s = \frac{0.13}{167} = 0.000778 \frac{mol}{L} \rightarrow 0.000778 \frac{mol}{L} \times 88.15 \frac{g}{mol} = 0.0686 \frac{g}{L}$$

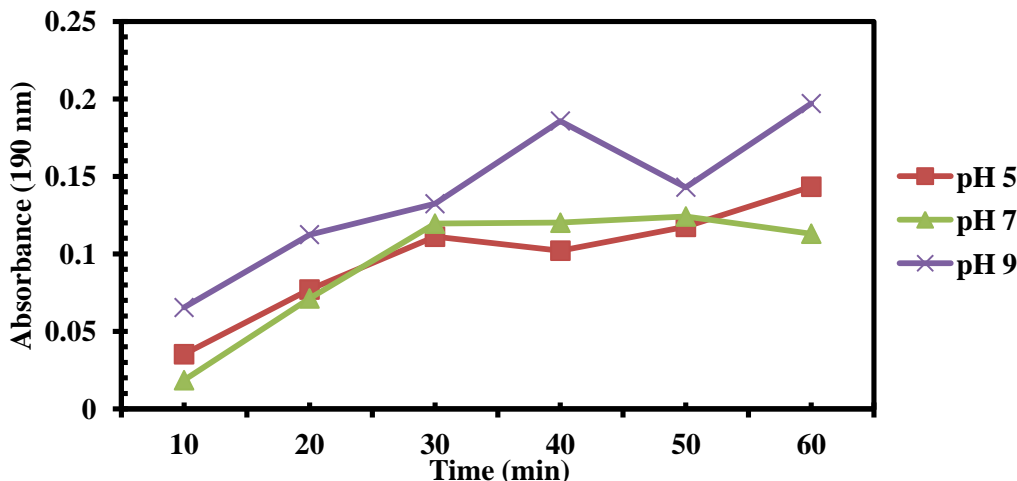


Figure 5: The absorbance of MTBE at a temperature of 30 °C and a mixing rate of 400 rpm under different pH conditions

The final experiment evaluated the effect of high temperature (30 °C) and high mixing rate (600 rpm) on the solubility of spiked MTBE in water at various pH. The result of the experiment is shown in Fig 6. The range of absorbance for all the pH was between 0.1 nm to 0.49 nm. The current experiment gave the highest absorbance readings but the trend was haphazard and random in appearance signifying a lack of stability in the spiked MTBE at the current conditions. The result in fig 6 showed the effect of both turbulence and high temperature on the solubility of MTBE. Oscillatory readings were noticed in pH 9 and pH 5 at 40 min and 50 min respectively. The result may be due to the rapid revolutions which might hinder the optimum solubility of the organic compound. Readings from MTBE spiked at pH 7 were not linear compared to be previous experiments conducted. The readings from this experiment were the least accurate in the various combinations evaluated. The result showed how a high temperature and a high mixing rate can affect the solubility of MTBE in water rendering MTBE to either vaporize or spread unevenly in the water body. However, the readings we obtained at 30 min of mixing were very close, so we took that absorbance reading (0.23 nm) to serve as the representative reading for the solubility of MTBE at 30 °C and a mixing rate of 600 rpm. The solubility was calculated below:

$$s = \frac{A}{\epsilon b} \times \text{molar mass of MTBE} \frac{g}{mol}$$

$$s = \frac{0.23}{167} \times 88.15 \frac{g}{mol} = 0.12 \text{ g/L}$$

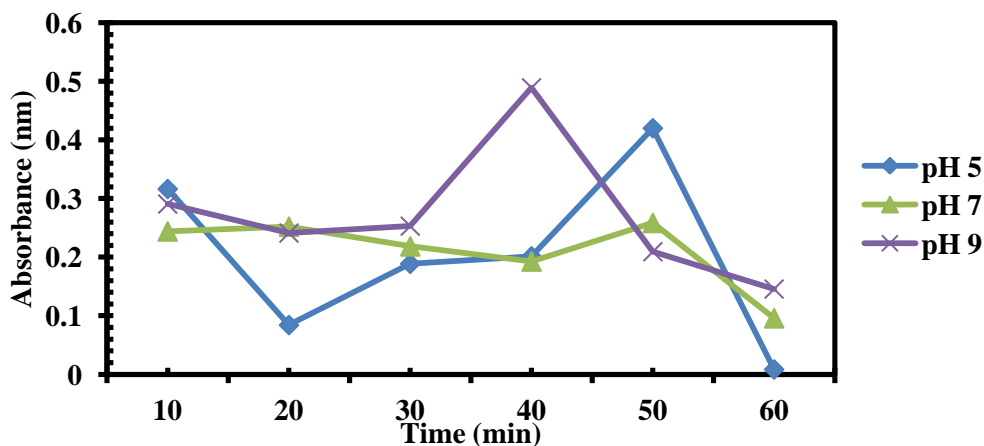


Figure 6: The absorbance of MTBE at a temperature of 30 °C and a mixing rate of 600 rpm under different pH conditions

The solubility of MTBE is an area with contrasting reports as reports present alternating results. However, much of the work done showed that the solubility increases with decreasing temperature. Fischer *et al.*, 2004 reported that the solubility of MTBE at 5 °C and 20 °C was 62.1 g/L and 35.5 g/L respectively. They believed that the high solubility of MTBE at low temperature is the reason why plumes of MTBE are noticeable during oil spills. The result means that the behavior of MTBE in terms of its solubility is largely dependent on the temperature and the environment. Reports by Kinner 2001 and USEPA 1999 indicated that the solubility of MTBE in water at 20 °C was 6.30 g/L and 0.43 g/100g respectively. Zogorski *et al* also reported that the solubility of MTBE at 25°C was 51 g/L while Merck 1989 in his publication showed the solubility of MTBE as 0.4 g/1000g of water. A report by Gilbert and Calebrese (1992) showed the solubility of MTBE at 20 °C to be 4-5 %. These results justify a lack of consistency in the determination of MTBE's solubility largely due to its volatile nature, method of detection, and the conditions used during the determination. Here, we have shown the additional effects of turbulence and pH to the determination of MTBE's solubility in water bodies. We believe this study mimics the actual environment in an event of spills or leakage of MTBE into water bodies. In general, determination of solubility using UV/Vis technique may not be as sensitive as other sensitive techniques such as chromatographic techniques, gravimetric techniques, potentiometric and computational models.

CONCLUSIONS

This paper used the principle of spectroscopy to determine the solubility of MTBE under different conditions of pH (5, 7 and 9), mixing rate (400 rpm and 600 rpm), temperature (25 °C and 30 °C), initial concentration (100 ppm) and time (1 h). We have determined for the first time the lambda max and molar absorptivity of MTBE. The results indicated the effect of mixing rate and pH on the overall absorbance of the volatile organic compound. Our result confirmed that the mixing rate of 400 rpm was the optimum for the determination of MTBE's solubility. MTBE spiked at pH 9 had the highest absorbance reading but less soluble and had a degree of instability, MTBE spiked at pH 7, on the other hand, showed the maximum solubility and stability. The solubility of MTBE at 25 °C and a mixing rate of 400 rpm, 25 °C and a mixing rate of 600 rpm, 30 °C mixing rate of 400 rpm, 30 °C mixing rate of 600 rpm were $0.08 \frac{g}{L}$, $0.044 \frac{g}{L}$, $0.0686 \frac{g}{L}$, and $0.12 \frac{g}{L}$ respectively. Most of the experiments reached equilibrium after 30 min of mixing. The results showed the combined effects of time, temperature, pH and the mixing rate on the overall solubility of MTBE in water. The low absorbance readings suggest the insensitivity of the method used. The spectroscopic determination may not be selective and sensitive to determine the solubility of MTBE. Other sensitive methods such as GC, GC-MS, miniaturized shake-flask method, and a semi-automated potentiometric acid/base titrations might provide a clearer picture.

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