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Raman Spectroscopy for Monitoring Aqueous Phase Hydrogen Sulphide Scavenging Reactions with Triazine: A Feasibility Study

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Triazine is one of the most commonly used scavengers for removal of hydrogen sulphide in the offshore oil and gas industry, but the kinetics of the scavenging reactions are still poorly understood. In this work the feasibility of Raman spectroscopy for on-line monitoring of the aqueous phase reaction between 1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine (HET) and HS⁻ was studied. It was found that the development of specific peaks in the Raman spectra reveals clear patterns related to the changes of concentration of HET and HS⁻ with time. On this basis, a qualitative evaluation of the dependence of the reaction kinetics on temperature and pH was carried out. No change in Raman peaks was observed at 40 °C for reaction time of 30 minutes, but a reaction was observed at 50 °C. Furthermore, a decrease in the reaction rate as the initial pH increases was observed in the pH range 8.5 to 10.3. No change in peaks was observed at pH 10.3 within 30 minutes.

1. Introduction

Hydrogen sulphide (H₂S) is an extremely toxic and corrosive gas, often found in reservoir fluids in the offshore oil and gas industry in concentrations above acceptable thresholds for material integrity, health and safety, environmental and sales reasons. The most common H₂S abatement method in offshore oil and gas production is the use of water-soluble non-regenerative scavengers, usually based on s-triazines formulated from monoethanolamine (MEA). Within this family of scavengers, the most common is 1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine (HET). It is formulated as aqueous solution and it is typically injected in wet gas streams, where it allows reaching specifications for H₂S removal. However, there is a tendency to inject far more HET than stoichiometrically required (Kelland, 2014), leading to high operating costs. Further, despite low toxicity of triazines, they are not unproblematic to use, and both spent and unspent scavenger may end up both in the oil and the surrounding sea via the produced water (Agbroko et al., 2017). In addition, spent scavengers show a tendency to precipitate leading to fouling problems (Madsen and Søggaard, 2014). The multiple reaction scheme governing the H₂S scavenging with HET was reported in the literature, as shown in Figure 1.

HET reacts with HS⁻ in aqueous phase to form 3,5-bis(2-hydroxyethyl)hexahydro-1,3,5-thiadiazine (thiadiazine). Thiadiazine may further react with HS⁻ to form 5-(2-hydroxyethyl)hexahydro-1,3,5-dithiazine (dithiazine) (Bakke et al., 2001). The last theoretical product, reported not to be observed, is s-trithiane (trithiane) (Madsen and Søggaard, 2014). At low pH, HET is not stable and undergoes hydrolysis to MEA and formaldehyde (Buhaug, 2002), even though this reaction can be neglected at pH above 10 (Bakke et al., 2001).

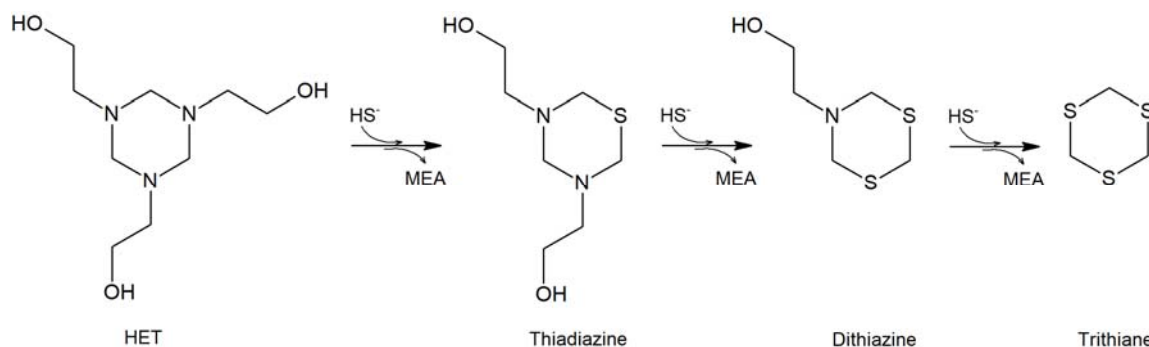


Figure 1: Scavenging reaction pathway for 1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine. Inspired from Madsen and Søgaard (2014).

Despite HET has been used for decades for removing H_2S , rate equations for the scavenging reactions have not been found in the literature, except for the first reaction which was observed to be pseudo-first order with respect to HET for large excess of HS^- and constant pH (Buhaug, 2002). The lack of more detailed kinetic expressions, allowing to account for, e.g., excess of HET and variable pH, does not enable optimization of the scavenging process at field conditions.

This problem can be solved by using spectroscopic methods, which allow to monitor chemical processes in-situ (van der Berg et al., 2013). Raman spectroscopy is one of the strongest candidates as it provides a signal with selective peaks (in contrast to another wide-spread solution, NIR) and, at the same time, can be used with fibre collecting signal via glass and in water solutions. Raman spectroscopy is already widespread for process monitoring in, e.g., pharma and food industry (You, 2017), but very little research has been found on using Raman spectroscopy for monitoring H_2S scavenging processes. Recently, Raman spectroscopy was applied in order to quantify amounts of HET and dithiazine in spent triazine samples off-line (Perez-Pineiro et al., 2018). The method showed some potential for the early stages of the scavenging process, while interference, possibly due to high concentrations of MEA in highly spent samples, made the quantification difficult for later stages of the scavenging. The objective of this work is to carry out a preliminary investigation of the feasibility of Raman spectroscopy for on-line monitoring of the reaction between HET and HS^- in a non-intrusive and time-resolved manner.

2. Materials and methods

The experimental work consisted in preparing solutions of HET and HS^- , mixing them in a vial and initiating the reaction by lowering pH. The experiments were performed at different initial pH values, temperatures and initial concentrations of reactants. The method used for the experimental work is still under development.

2.1 Chemicals

1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine (CAS 4719-04-04) was purchased from Sigma-Aldrich (product ID COM497512403, purity 75 %), sodium sulphide ($\text{Na}_2\text{S}\cdot\sim 3\text{H}_2\text{O}$, product code 83756.230) from VWR Prolabo Chemicals and hydrochloric acid 37 % (HCl) from Fisher Scientific. The amount of Na_2S in the sodium sulphide product was deduced from the sodium content measured by means of ICP-AES.

2.2 Spectra acquisition

Raman spectrometer RXN1 (Kaiser Optical Systems, Inc., MI, USA), equipped with 785 nm laser as an excitation light source and fibre connected non-contact probe, was used to acquire Raman spectra. The obtained spectra covered the range of 3425 to 100 cm^{-1} (Raman shift) with resampling interval = 1 cm^{-1} . The optimal settings for acquisition time and number of spectra were evaluated experimentally in order to achieve reasonable signal-to-noise ratio. The spectra were preprocessed using Savitzky-Golay smoothing filter (filter width = 11 points, linear fit), Alternating Least Squares baseline correction (penalty = 0.001, lambda = 1000) and normalized using standard normal variate. All transformations, calculations and plots were carried out in MATLAB 2018b using toolbox "mdatools" (Kucheryavskiy, 2019).

2.3 Reaction experiments

Certain amounts of sodium sulphide (0.5 to 1 g, corresponding to 3.1 to 6.2 mmol) and HET (0.4 to 1 g, corresponding to 1.3 to 3.4 mmol) were dissolved in demineralized water in two batches with final volume of 5

mL each. The starting pH of the HET solution was around 10, while it was around 12 for the sulphur-containing solution. The two solutions were then mixed, giving a starting pH of around 11, placed in a water bath to be brought at the reaction temperature, and kept stirred using a magnetic stirrer. The Raman probe and a pH meter monitored the system (Figure 2), while the temperature was kept constant by the bath. No reaction is expected during the heating time, due to the high pH of the solution (Bakke et al., 2001). When the solution reached the

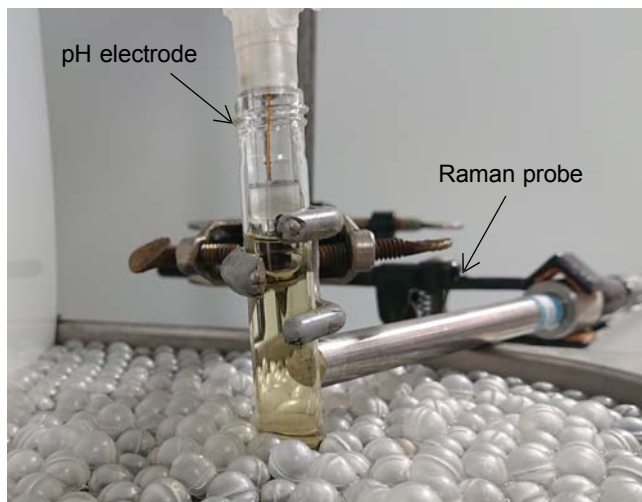


Figure 2: Experimental set-up. Water bath, vial with solution, Raman probe, and pH electrode.

desired temperature, the reaction was initiated by adding HCl, thus lowering the pH to the desired starting value. However, when adding the acid, evaporation of H_2S was observed despite the HS^- being the most abundant sulphur species. This was explained by localized low pH values during HCl addition. Hence, the starting concentration of H_2S might differ between experiments, even with the same initial concentration, due to different evaporation losses. The Raman spectrometer was started, setting the starting time ($t = 0$) when acid is added. The spectrometer obtained one spectrum every minute, averaged from 3 scans accumulation with 5 seconds exposure time each. The pH of the mixture was recorded from $t = 15$ s and at the start of each scan to the end of the experiment.

3. Results and discussion

The feasibility of Raman spectroscopy was investigated by carrying out a number of experiments characterized by different temperatures (in the range 40 to 60 °C) and initial pH (8.5 to 10.3), corresponding to typical field application values. Reaction times were varied in the range 30 to 120 minutes. The molar ratio HET/ HS^- was estimated to be in the range 0.2 – 1.4 in the runs.

Prior to the reaction runs, the Raman response of HS^- , HET and MEA was obtained on pure solutions of said species and the results compared to the literature. The investigation of the Raman response of HS^- was done by varying the concentration of HS^- in aqueous solution. It was observed that the Raman peak at 2572 cm^{-1} changes intensity with change in concentration of HS^- . This is supported by the literature reporting H-S bonds to be in the region of 2540 to 2600 cm^{-1} (Socrates, 2001). The peak at 2572 cm^{-1} is thus an indicator of HS^- . The more complex molecular structure of HET, containing several types of bonds, led, as expected, to more peaks in the Raman spectra. Several of these peaks, however, were observed either completely or partially overlapping with peaks associated with MEA. In the pure spectrum of HET two peaks not overlapping with MEA were however identified, corresponding to Raman shift 650 cm^{-1} and 790 cm^{-1} . As the intensity of these peaks was observed to vary with the concentration of HET, these peaks were selected as indicators of HET. In mixtures with HS^- , the peak at Raman shift 650 cm^{-1} was seen to shift horizontally in the spectra, with a new Raman shift observed at 630 cm^{-1} , whereas the 790 cm^{-1} peak did not change. The latter was therefore chosen as a suitable indicator for HET. No distinct peak belonging to MEA and not overlapping with HET was found.

Figure 3 shows the developing of Raman spectra in one of the experiments. The blue spectra refer to initial times, while the red spectra refer to final times. As can be seen from Figure 3a, there is a clear trend for the intensity of several specific peaks, located at Raman shifts 575 cm^{-1} , 630 cm^{-1} , 675 cm^{-1} , 790 cm^{-1} and 2572 cm^{-1} . The peak at 2572 cm^{-1} , Figure 3c, is HS^- , which is decreasing over time. The peaks at 630 cm^{-1} and 790 cm^{-1} are both decreasing, in line with the expected decrease of HET.

The observed decrease in intensity of the peaks associated to HS⁻ and HET is therefore an indication of the occurrence of the scavenging reaction. In Figure 3b two peaks (575 cm⁻¹ and 675 cm⁻¹) are observed increasing over time. These peaks are not observed in neither HET, MEA or HS⁻ spectra. According to the literature, the peak at 575 cm⁻¹ is associated to a C-S bond, whereas the peak at 675 cm⁻¹ is associated to C-S-C bonds (Socrates, 2001). In addition, Perez-Pineiro et al. (2018) have associated the peak at 675 cm⁻¹ to dithiazine, i.e. a secondary product of the scavenging reaction (see Figure 1). The C-S-C bond is however present in both dithiazine and thiadiazine. Even though the results of this work do not elucidate a correspondence to dithiazine or thiadiazine, the development of these sulphur-containing bonds are strong indicators of the occurrence of the scavenging reaction.

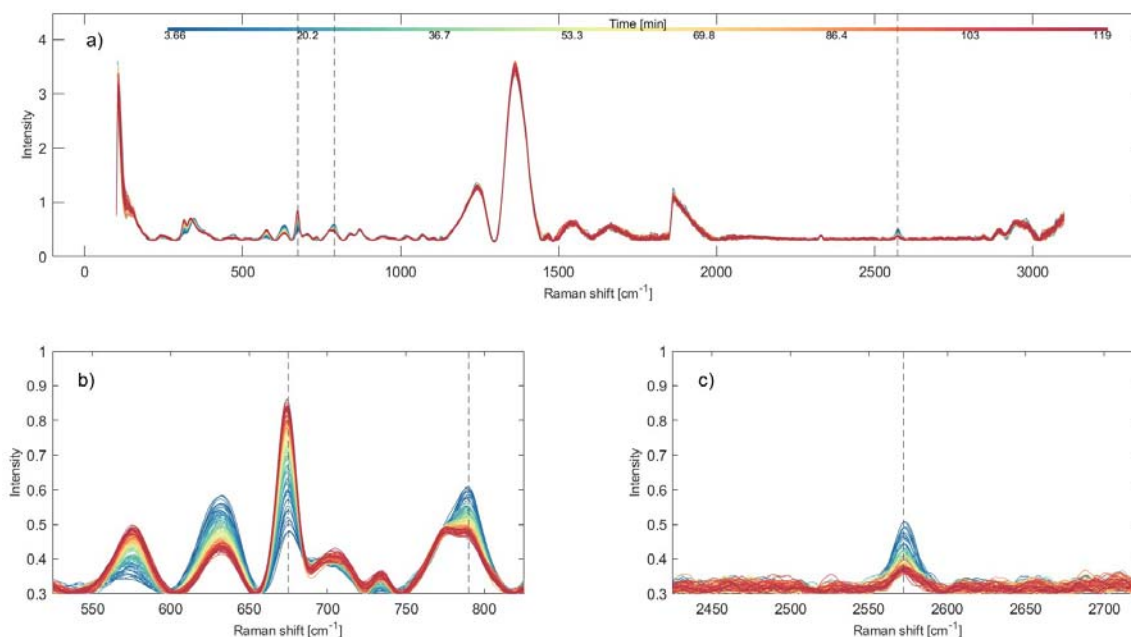


Figure 3: Raman spectra of the scavenging reaction; a) Full spectrum; b) Indicator peaks for HET and scavenging products; c) HS⁻ peak. Experiment at 45 °C, initial pH 9.3 and run for 120 minutes.

In this preliminary study, it was chosen to focus on the trends of variation of three of the above-mentioned peaks, being the Raman shift at 2572 cm⁻¹, 790 cm⁻¹, and 675 cm⁻¹. The hypothesis is made that the intensity variation of these peaks is an important indicator of the variation of the concentration of three key species: HS⁻, HET and a scavenger product, respectively. The hypothesis is that there is a linear correlation between the concentration of a chemical species compound and the intensity of the associated peak, as reported in Eq(1):

$$I_{\text{species}} - I_{\text{baseline}} = K_{\text{species}} \cdot C_{\text{species}} \quad (1)$$

where I_{species} is the intensity of a peak linked to a species, I_{baseline} is the baseline intensity, K_{species} is the Response Factor for a species, and C_{species} indicates the concentration of the species.

Figure 4 shows the development of I_{species} of the selected peaks against time, for reaction experiments at the same temperature (45 °C). As can be seen, the peaks of Raman shift 2572 cm⁻¹ (HS⁻) and 790 cm⁻¹ (HET) are decreasing, while the peak at Raman shift 675 cm⁻¹ (product) is increasing. In addition, the comparison between Figure 4a (pH 8.6) and Figure 4b (pH 9.3) shows a rate of decrease of the peak intensities associated to reactants about 1.5 times higher at the lower initial pH, for similar HET load in the system. This is in line with previous findings, reporting the triazine scavenging reaction to proceed at lower rates as pH increases (Bakke et.al., 2001).

Furthermore, when Figure 4b (HET load 3.49 mmol) and Figure 4c (HET load 1.71 mmol) are compared, a slower decrease of the peaks of the reactants is observed for the lower HET concentration, at similar pH. The same tendency is observed if evaluating the increasing peak (675 cm⁻¹), at different pH but similar starting concentrations. This peak increases with a higher rate at the lower initial pH. Overall, these observations support the hypothesis that a methodology based on Raman spectroscopy can be used for quantitatively tracking the scavenging reaction.

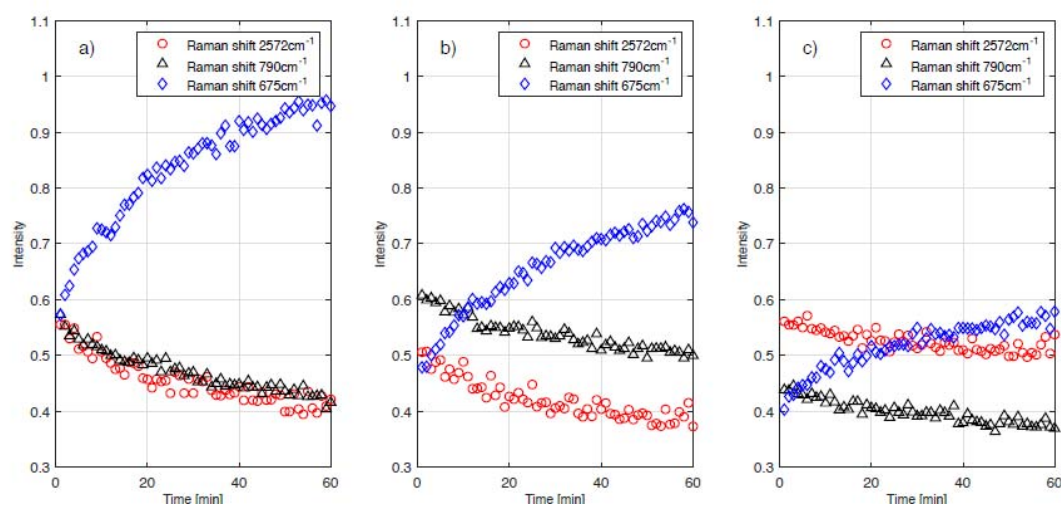


Figure 4: Trend with time of the Raman shift at 2572 cm^{-1} (HS⁻), 790 cm^{-1} (HET) and 675 m^{-1} (product). Reactions at $45\text{ }^{\circ}\text{C}$. a) HET load 3.48 mmol ; $\text{pH}(t=0) = 8.6$; b) HET load 3.49 mmol ; $\text{pH}(t=0) = 9.3$; c) HET load 1.71 mmol ; $\text{pH}(t=0) = 9.2$.

In Figure 5, the effect of the reaction temperature is shown, for three experimental runs at approximately same pH (9.8). In these experiments, only the change in HET and the peak associated to the scavenging products is evaluated. As can be seen, there is a clear indication that the reaction is temperature dependent, since no change in intensity of neither HET nor the product at $40\text{ }^{\circ}\text{C}$ (Figure 5a) is observed. At $50\text{ }^{\circ}\text{C}$ there is a clear trend of decreasing HET and increasing product peaks (Figure 5b). At $60\text{ }^{\circ}\text{C}$ there is still a clear trend of the product (676 cm^{-1}) increasing, yet no clear trend of a decrease in the reactant, which has no clear explanations presently. Finally, the effect of pH was investigated, for same temperature ($50\text{ }^{\circ}\text{C}$) and HET load with excess of sulphur..

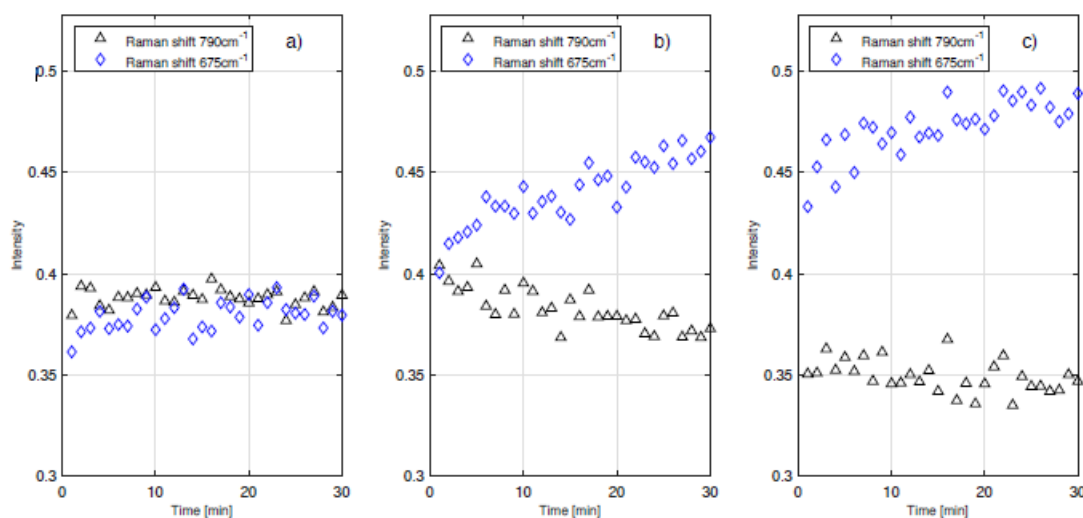


Figure 5: Change in intensity for selected peaks for reactions at pH 9.8, excess of sulphur, and reaction times of 30 min. The reaction temperature was: a) $40\text{ }^{\circ}\text{C}$; b) $50\text{ }^{\circ}\text{C}$; c) $60\text{ }^{\circ}\text{C}$

Results are shown in Figure 6. If the initial pH is above 10 (Figure 6c), little or no change in the peaks for HET (790 cm^{-1}) and the products (675 cm^{-1}) is observed. If the initial pH is lowered to around 9.5 (Figure 6b), there is a slight decrease in the intensity of the HET peak and a corresponding increase in the peak intensity of the product. This development of the intensities is even greater if the initial pH is lowered to 8.45 (Figure 6a), indicating a strong pH dependency of the scavenging reaction.

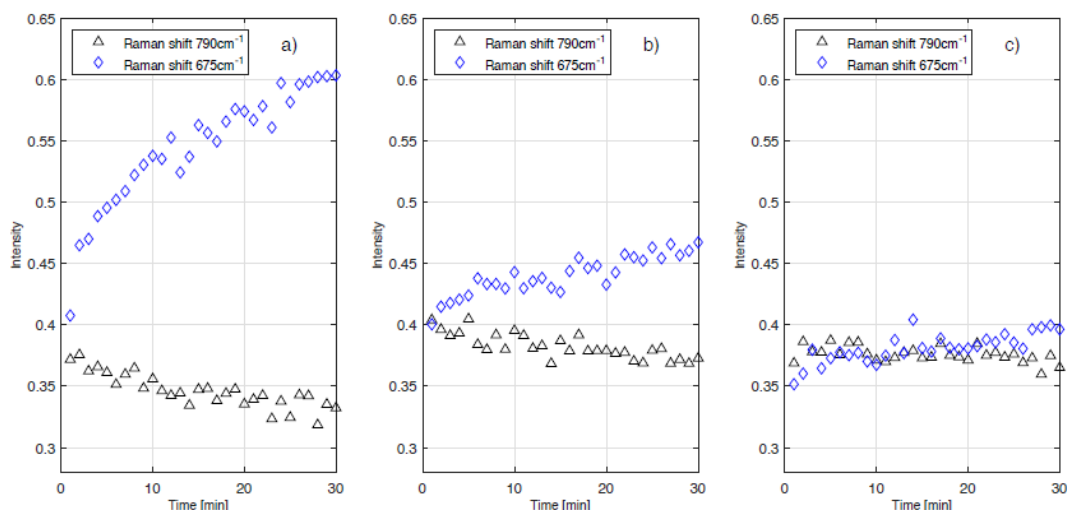


Figure 6: Change in intensity for selected peaks at temperature 50 °C with initial pH a) 8.45; b) 9.5; c) 10.32.

4. Conclusions

This study shows promising results with regards to the application potential of Raman spectroscopy for on-line quantitative monitoring of H₂S scavenging using HET. Two peaks closely linked to the reactants were observed to change over time and associated to HS⁻ (2572 cm⁻¹) and HET (790 cm⁻¹). Another peak (675 cm⁻¹) closely linked to scavenging products, being characteristic of C-S-C bonds, was observed to increase over time. The rate of variations of the peak intensities varied with temperature, initial pH, and initial reactant concentrations consistently with previous literature findings. In particular, the reaction was not observed at 40 °C, but it was clearly observable at 45 °C and above. Moreover, the variations of the intensity of the selected peaks was found to increase as pH decreases. In particular, at initial pH values above 10 the peak intensity did not change, whereas at initial pH of 8.6 the rate of variation was 50 % higher than for pH 9.3, for reaction runs at 45 °C.

Acknowledgments

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