ACT LAUNCH Project No 299662

Lowering **A**bsorption process **UN**certainty, risks and **C**osts by predicting and controlling amine degradation

Deliverable Nr. D3.1.3
Foaming in PZ affected by degradation and impurities removal by adsorption

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Executive summary

Experiments were conducted to measure foaming and foam break time of 5 m piperazine (PZ) in two recent lab campaigns. This report summarizes those measurements made during April-May 2022 (Y.L. Chen) and October-November 2022 (Carter) and benchmarks them to those made by Xi Chen [1]. Foaming and foam break time were measured in 5 m PZ at a loading of 0.3 mole CO_2/mole alkalinity. Additional experiments were conducted with varying concentrations of formaldehyde added to the solvent to simulate changes in foaming behavior with degradation. The calculated foaminess of the test solutions as measured by Y.L. Chen differed from the 2011 findings of X. Chen with no clear trend. However, foam break time trends followed those of X. Chen up to the addition of 150 mM formaldehyde, when the data points diverged. The October-November 2022 measurements made by Carter generally matched the April-May 2022 measurements with the exception of the extremes of 0 and 150 mM formaldehyde additions.

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1   Introduction

Foaming can cause many problems in process engineering in distillation and absorber columns with severe consequences such as reduced separation efficiency and a reduced capacity. Foaming can be caused by various contaminants such as liquid hydrocarbons, iron sulfide, and amine degradation products [2]. X. Chen measured the effects of additives such as formaldehyde, formic acid, and heptane on foaming in neat PZ solution [1]. Two recent studies in the lab were performed to replicate the work of X. Chen and to continue the study of the effects of contaminants on foaming.

2 Experimental Methods

2.1 Experimental Setup

The recent foaming experiments were performed using the setup described by X. Chen [1]. The experimental setup included a 1000 mL graduated cylinder, a water bath maintained at 40 ℃, a sparger with a fine fritting, and a gas flowmeter. The setup is shown in Figure 1 below. Tubing connected to a nitrogen source was attached to the bottom of a gas flowmeter. Tubing was also attached to the top of the gas flowmeter with the other end attached to the sparger. The gas flowmeter was secured using a clamp and a rubber stopper was used to keep the sparger in place.
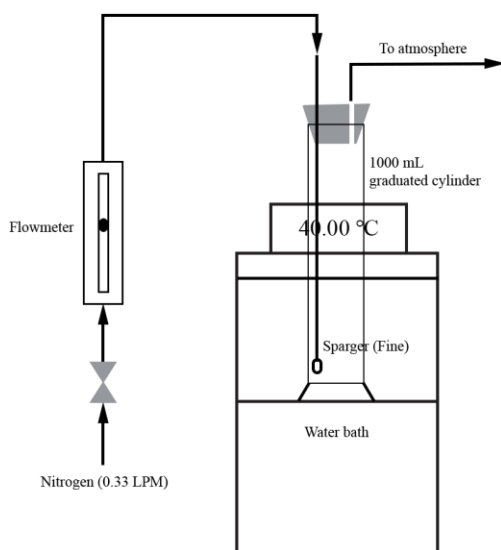

Figure 1: Diagram of the foaming experiment setup

2.2 Materials

PZ (99%, Alfa Aesar) and formaldehyde (37 wt % water solution, Certified A.C.S, Fisher Chemical) were used without further purification for the April-May 2022 tests. The PZ solution used was 5 m with a loading (α) of 0.3 moles CO_2/mole alkalinity.

2.3 Experimental Procedure

400 mL of the test solvent were poured into the 1000 mL graduated cylinder which was then placed into the water bath and heated to 40 ℃. Once the temperature reading on the water bath reached 40 ℃ and stabilized, the valve to the gas flowmeter was opened to introduce nitrogen to the solution. The gas flow rate was set to approximately 0.33 LPM (~ 2×10^{-3} m/s with respect to the cross-sectional area of the graduated cylinder). The timer was started once bubbles were observed. Total liquid volume of liquid and froth in the cylinder was recorded every minute. The experiment was run for 25 minutes. The volume

appeared to reach steady state at around 5 or 6 minutes, so the last 15 minutes were averaged as a steady-state value.

Measured amounts of formaldehyde and any other substances were added to the graduated cylinder in between runs using a pipette. The formaldehyde was thoroughly mixed into the solvent once nitrogen was bubbled through the solution.

2.4 Data Analysis

Foaminess (F, m2 · s) is defined as:

$$F = \frac{V_t - V_0}{G} = \frac{V_g}{G}$$

where:

Vg (m3) = the volume of gas trapped;
V0 (m3) = the original volume of solution at the start of the experiment;
Vt (m3) = the total volume of liquid plus bubbles in the graduated cylinder throughout the experiment; and
G (m/s) = the superficial velocity of the nitrogen gas.
The break time of foam was also measured. Break time, t (s), is defined as the length of time required for the foam to completely break apart and collapse after nitrogen gas flow is stopped [1].

3   Results

3.1   April-May 2022 Experiments

Results of foaming experiments conducted in April-May 2022 by Y.L Chen will be referred to as the "April-May 2022" results. For these experiments, only 5 m PZ with α = 0.3 mol CO_2/mol alkalinity was used. The primary goal was to replicate the experimental apparatus of X. Chen and compare new measurements to his 2011 findings [1]. X. Chen used 8 m PZ with α = 0.3 CO_2/mols alkalinity including when he made measurements with additives including formaldehyde.

In the April-May 2022 tests, the foaminess of the 5 m PZ with no additives was greater than the foaminess measured in runs where formaldehyde was added to the solution. When 50 and 100 mM formaldehyde was added, foaminess increased. However, when 150 mM formaldehyde was added to the solvent, the foaminess decreased. The foaminess of 5 m PZ was also greater overall than the foaminess of 8 m PZ [1]. This mismatch in results was unanticipated; the foaminess was expected to be higher in the more concentrated PZ (8 m) tests as a result of higher viscosity.

The break time trend in the April-May 2022 data followed the trend observed by X. Chen more closely than it did the foaminess trends. Up to a concentration of 100 mM formaldehyde, the break time data from April-May 2022 closely followed X. Chen. However, at 150 mM formaldehyde, the break time decreased. This paralleled the decrease in foaminess between 100 mM and 150 mM formaldehyde.

Figure 2 is a plot of foaminess and break time as a function of formaldehyde concentration. The data from X. Chen were plotted on the same figure. Table 1 summarizes foaminess and break time for the four runs plotted in Figure 2.
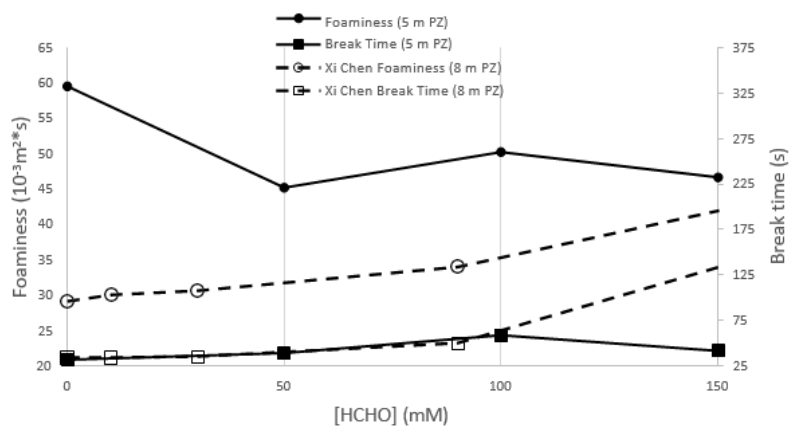

Figure 2: Foaminess and break time as a function of formaldehyde concentration for 5 m PZ with α = 0.3 at 40 °C. Foaminess and break time from X. Chen are included for comparison [1].

Table 1: Summary of foaminess and break time for 5 m PZ solution with α = 0.3 and with different additives at 40 ℃.

Amine/m	Additives/mM	Foaminess ($10^{-3}m^2$ s)	Break time (s)
PZ/5	None	59.52	31.63
PZ/5	Formaldehyde/50	45.18	38.75
PZ/5	Formaldehyde/100	50.21	58.53
PZ/5	Formaldehyde/150	46.63	41.42

A one-time test was conducted with an increased rate of nitrogen flow (0.5 LPM) in a PZ solution with a concentration of 150 mM formaldehyde to understand if foaming would increase with increased gas flow. The break time remained approximately the same, but the foaminess decreased. A higher volume of foam formed at the higher flow rate, but the calculated value of foaminess (*F*) was lower due to the gas rate (*G*) in the denominator being higher. Table 2 summarizes these findings.

Table 2: Comparison of foaminess and break time for 5 m PZ solution with α = 0.3 and 150 mM formaldehyde at 40 ℃ with N₂ sparging at different flow rates.

N₂ Flow Rate (LPM)	Foaminess ($10^{-3}m^2$ s)	Break time (s)
0.33	46.63	41.42
0.50	38.97	42.16

3.2 October-November 2022 Experiments

Foaming tests were conducted in a newly constructed apparatus during October-November 2022. These tests were performed in a similar experimental setup in a 1000 mL graduated cylinder with nitrogen sparged at rates of 0.33–0.40 LPM for 25 min. Measurements were performed at 40, 50, and 60 °C. Repeat measurements were then made with the addition of formaldehyde (37 wt % formaldehyde in water) at 50, 100, and 150 mM. Those results are plotted under the name Carter against the previous work of Chen and the April-May 2022 results in Figure 3. Carter's results match those of Y.L. Chen (April-May 2022) with 0 and 150 mM formaldehyde but diverge for 50 and 100 mM formaldehyde. Chen (2011) provides the only results showing a consistently increasing foaminess factor from 0 to 150 mM formaldehyde.
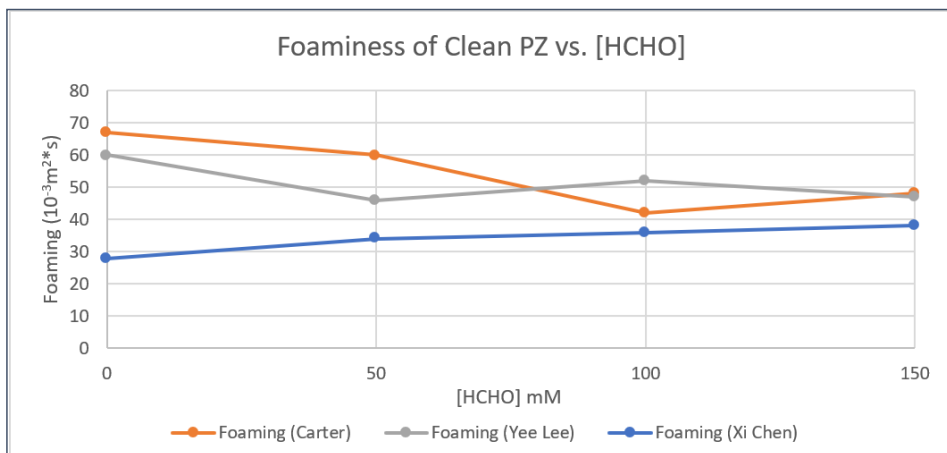
Figure 3: Foaming in 5 m PZ at 40 °C as a function of formaldehyde addition

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4 Discussion

The differences in foaming results are likely due to inconsistent quality or purity of starting PZ, the difference between 5 m PZ and 8 m PZ (the latter was used by Chen), and differences in the three apparatuses, among other possible factors.

All the foaming measurements used PZ solvent created from reagent grade flakes in the lab, but the April-May 2022 tests were conducted on a solvent created in November 2021, possibly allowing degradation to occur that affected foaming results. Further, because these tests were conducted at three different times, it is likely that the PZ flake sources were different, and this would have affected the outcome of the foaming tests due to differences in surface tension of the solvents.

As noted, X. Chen [1] used 8 m PZ while 5 m PZ was used in both 2022 campaigns. According to Freeman, the viscosity of 5 m PZ at a loading of 0.22 mols CO_2/mol alkalinity and 40 °C is 3.23 mPa-s [3]. Although she did not measure its viscosity at 8 m, Freeman did make measurements of 7 m and 9 m PZ at similar loadings and 40 °C and determined the viscosities to be 6.35 mPa-s and 11.1 mPa-s, respectively. It is generally believed that foaming will be a function of both solvent viscosity and surface tension. These viscosity measurements demonstrate the different physical behavior of PZ solvent when concentration is increased [3]. When plotted together (Figure 3), the data indicate that the more concentrated solvent (8 m), which likely had higher viscosity, also exhibited the greatest foaminess.

Finally, differences in experimental apparatuses may have produced different foaming results. One likely source of differences in results is differences in the sparging stones between each of the three apparatuses. Chen (2011) used a gas diffusing stone with an average pore size of 60 um. A sparger with a pore size of 25-50 um was used at the start of the April-May 2022 tests, but no foaming occurred while using it, demonstrating the sensitivity to sparge bubble size of foaming. A similar experience was reported in the October-November 2022 tests wherein a sparge stone with 70-100 um pore size was first used, with little or no foam produced. When the stone was replaced with one having a pore size of 30-60 um, foaming occurred in the experiments. Unevenness in the sparge stone pore size(s) likely was a factor in the development of stable foam in each of the experiments.

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5 Conclusions

The foaminess and foam break time of PZ solutions were measured in three separate lab campaigns. The calculated foaminess of the test solutions as measured by Y.L. Chen and Carter differed from that of X. Chen with no clear trend. However, foam break time trends followed those of X. Chen up to the addition of 150 mM formaldehyde, at which point the data points diverged. The October-November 2022 measurements made by Carter generally matched the April-May 2022 measurements with the exception of the extremes of 0 and 150 mM formaldehyde additions. The differences in results from the three different foaming data collection events are likely a result of several factors including inconsistent quality or purity of starting PZ solvent among the three data collection campaigns, the difference between 5 m PZ and 8 m PZ, the latter of which was used in the foaming tests of Chen from 2011, and differences in the three apparatuses.

The sparge stones used in each of the three lab setups were different, likely resulting in important differences in nitrogen bubble size and consistency, thereby affecting the formation and stability of foam in PZ solvent.

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