Foaming of CO₂ Loaded Amine Solvents Degraded Thermally Under Stripper Conditions

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Foaming of amine solutions remains a problem for natural gas sweetening and post-combustion carbon capture. New amine-based solutions are being developed to replace monoethanolamine (MEA). This work tested the foaminess of MEA and three alternatives (methyldiethanolamine (MDEA), 1-(2-aminoethyl)piperazine (AEPZ), 2-amino-2-methyl-1-propanol (AMP)) before and after thermal degradation; two methods were used to describe the foaminess. Foam was only formed after thermal degradation. The first method suggests foaminess where AEPZ > MDEA > MEA; AMP, by contrast, did not conform to this model and formed stable foam. The second method, using liquid physical properties, found that solutions containing more degradation products (MEA, MDEA, AMP) show different foaminess than those without *i.e.* the changing chemistry during degradation strongly impacts the foaminess observed. The foaming of these degraded samples demonstrates complexity which cannot be replicated by simple model solutions. This study is therefore more representative of the foaming behavior seen in industrial cases.

Foam, Amine, Post-combustion carbon capture

Introduction

The role of foaming has been a long-known but poorly understood problem in industrial operations with amine systems. Natural gas sweetening plants using amine solvents experience the problem of foaming¹. The same problems have been reported in liquid amine solutions for use in carbon capture. The formation of foam directly results in loss of solvent and indirectly in a change to the solution composition, thereby contributing to a reduction in efficacy and financial losses. The source of these problems has been reported to result from the changing components in the solution system¹.

In aqueous amine solutions used for carbon capture processes, impurities arise from sources including the gas stream itself, as well as the metal infrastructure. In both cases, the result of contact with the solvent is its subsequent degradation. Additionally, the heating process required directly degrades the amine solvent². As a result, the aqueous amine solution contains an increasing quantity of a wide range of impurities during its operational lifetime.

To demonstrate the influence of impurities experimentally, otherwise untreated carbon dioxide (CO₂) loaded aqueous amine solutions with additives included, have been previously tested. The foam formation, with the addition of impurities, has been measured experimentally for monoethanolamine (MEA)^{3,4}, diethanolamine (DEA)^{4,5}, methyldiethanolamine (MDEA)^{4,6}, piperazine (PZ)⁷. However, these works only demonstrate the artificial inclusion of impurities in solution; degraded solvents have never been explored.

A thorough parametric study of the behavior of MEA as a function of various essential variables in the foam process has been considered³. However, the use of alternative amine solvents is growing in popularity for carbon capture and the foam behaviors are not known to be directly comparable. The foaminess at 7 m (molal) MEA solution shows a smaller foaminess coefficient than 8 m PZ solution under the same conditions (where foaminess is defined as the Bikerman coefficient normalized by the same coefficient for a neat solution)⁷. In one study it is suggested that MEA is the foamiest, as compared to

other aqueous binary solutions, where MDEA had a foaminess coefficient half that of MEA, and neither DEA nor 2-amino-2-methyl-1-propanol (AMP) showed any foaminess (using the Bikerman coefficient as the foaminess metric)³. However, a ternary aqueous mixture of MEA and AMP (2:1) showed nominal foaming of less than a sixth that of the binary aqueous MEA solution. In contrast, a different study suggests that an aqueous solution, where the amine was 20% MEA, 30% DEA, and 50% MDEA, shows no notable foam whatsoever (as demonstrated by foam height in a 1000 mL graduated cylinder)⁴.

This study presents four thermally degraded binary aqueous amine solutions of MEA, MDEA, AMP, and 1-(2-aminoethyl)piperazine (AEPZ). The use of these degraded solutions demonstrates foaminess which is more representative of the solutions which are used in large-scale plants for the purposes of carbon capture. Similar samples have shown to be accurately representative of the thermal degradation found in larger pilot plant scale trials. The measurement of foaminess will be represented using traditional metrics, as well as with relationships accounting for the liquid solution's physical properties.

Foam Theory

The widely used Bikerman model⁸ was developed to demonstrate a relationship between the foam formation (by height, H) and the superficial gas velocity, j , to give a resulting foaminess coefficient, Σ .

$$\Sigma = \frac{H}{j} \quad \text{Equation 1}$$

The use of this metric is conditional on the height of the bulk liquid being ‘sufficiently large’ and the velocity of the gas flowing through being ‘not too minimal.’ It is then suggested that the foaminess is independent of gas flow rate through the liquid and the total volume of liquid used; additionally, the tube shape and dimensions are said to have no impact. Recently, concerns have been highlighted over the failure of Bikerman’s model to account for the environmental conditions, particularly humidity⁹. As a result of these and other limitations, other empirical models have been suggested as replacements for the Bikerman model, to incorporate more physical properties.

More recently, a semi-empirical method has been developed to use physical properties further in their relationship to foam formation¹⁰. This model uses the Capillary number Ca , which is a balance of viscous and surface tension forces, with a ratio of the foam height (H) to bubble radius (r) on the left hand side of the expression. This is balanced on the right hand side with a ratio of the Reynolds, Re , and Froude, Fr , numbers to provide a balance between the gravitational and viscous forces, where the pre-exponential factor, K , and exponent, n , are fitted.

$$Ca \left(\frac{H}{r} \right) = K \left(\frac{Re}{Fr} \right)^n \quad \text{Equation 2}$$

$$\text{where } Ca = \frac{\mu(j-j_m)}{\sigma} ; Re = \frac{\rho(j-j_m)r}{\mu} ; Fr = \frac{(j-j_m)^2}{gr}$$

In the fitting of this model using traditional foaming solutions, the resulting correlation had the parameters $K = 2905$ and $n = -1.8$. This model was more recently applied for binary aqueous MEA solutions where it was suggested that $K = 4394$ and $n = -1.3$ (for the range $2.0 \times 10^{-3} < Ca < 6.3 \times 10^{-2}$, $5.0 < Re < 276.4$, $0.01 < Fr < 0.89$) where the bubble radius was not measured experimentally¹¹. The bubble size, r , in this model is an average as dictated by Pilon. The bubble size distribution is not currently

accounted for. However, the size and distribution of the bubbles are very significant and equally have been shown to be important in foam stability.

Experimental Methods

The solvents MEA (Sigma $\geq 99\%$), AMP (Sigma $\geq 90\%$), AEPZ (Sigma $\geq 99\%$), and MDEA (Sigma $\geq 99\%$) were used as received. Solutions (3 M) for solvents of interest were made with DI water. For measurement of physical properties before degradation, each solution was purged with nitrogen (N_2) (20 mL min^{-1} at room temperature and 0.5 barg) to remove air. Solutions' physical properties were tested prior to carbon dioxide (CO_2) loading. Subsequently, samples were loaded with CO_2 (20 mL min^{-1} at room temperature and 0.5 barg) overnight to attain full saturation. A condenser was used to minimize water loss (all at atmospheric pressure). The physical property measurements were then repeated twice more.

Thermal degradation

A custom designed 500 mL stainless steel vessel (Longshore Systems Engineering) was used for the thermal degradation tests. The vessel includes two temperature controllers (PT1000) with a heating jacket for temperature control; a liquid recirculation pump (TCS Micropumps), a pressure transducer (RDPE), and mass flow controllers (MKS) for N_2 and CO_2 individually.

Prior to experimentation, each reactor was cleaned and all consumables replaced (to avoid cross-contamination). The reactor was loaded with the 3 M aqueous amine solution. A flow rate of 20 mL min^{-1} of N_2 was bubbled for two hours to remove any air from the liquid and reactor headspace. The reactor temperature was increased to 120°C and subsequently CO_2 bubbled through until saturation of the liquid was exceeded and a vessel pressure of 3.5 bar was reached (conditions which mimic the stripper unit in a post-combustion carbon capture plant). A small sample was withdrawn once the target pressure was reached (and the solution was considered to be fully loaded with CO_2) and CO_2 added

again to return to 3.5 bar. After 28 days, the liquid was collected for foaming testing and chemical analysis (results of which is including as supporting information).

Foam apparatus and testing

The foam vessel (Figure 1) (inner diameter = 20.4 mm) was loaded with 100 mL of solution and a water bath was used to maintain the heating jacket at 40°C (similar conditions to those in the absorber unit of a post-combustion carbon capture plant). Nitrogen flow (at room temperature and 0.5 barg) commenced, bubbling at a low flow rate of 10 mL min⁻¹ through a frit (diameter = 10 mm, pores = 100 – 160 µm) into the solution with the rate controlled by a flow meter. If no foam was produced after five minutes the flow rate was increased to 25 mL min⁻¹ and subsequently in steps of 25 mL min⁻¹ until foam was observed. The initial flow rate at which foam was observed was recorded (Figure 2). A minimum of five photographs of the top of the liquid and foam region were recorded initially and at intervals of 30 seconds for the first 90 seconds. This was followed by recordings at three minutes, five minutes, and at five-minute intervals thereafter for a total of thirty minutes. The height of foam was found to plateau within five to ten minutes for all samples. This process was repeated for flow rates at appropriate intervals until the onset of slugging in the column. Slugging was defined as the point at which the bubbles coalesced into a large bubble taking up a significant portion of the column diameter. The column was then drained and cleaned. Measurements were subsequently repeated, independently, twice.

Figure 1: Glass foam measuring apparatus with temperature controlled jacket and frit for gas dispersion

at the inlet.

Figure 2: Photograph of foam formation for AEPZ with a gas flow rate of 50 mL min^{-1}

Physical Property Measurements

All physical property measurements were made at 40°C , consistent with the foam experimental conditions, and run three times in independent experiments. Density was measured using a densimeter (Anton Paar DMA 5000); surface tension (equilibrium) was measured using a force tensiometer with a Wilhemy plate (Biolin Scientific) in air; viscosity was measured using appropriately sized glass capillary viscometers in a temperature controlled oil bath.

Results and Discussion

Undegraded samples

Under the foaming conditions specified for testing of the aqueous amine solutions, no stable foaming behavior was observed for any of the four solutions. The lack of foaming under such conditions with no additives is consistent for MEA, MDEA, and AMP under similar conditions^{3,4}. It has been previously demonstrated that the conditions under which foaming is tested greatly influence the foam formation. The sensitivity of foam formation to testing variables and environmental factors is critical, giving rise to complexities in comparisons across the literature.

It is observed that under testing conditions the four aqueous amine solutions show relatively similar densities (Table 1). An increase in density would be associated with increasing foam thickness due to a faster rate of drainage. The reduction of drainage rate can be associated with an increasing viscosity. As such, it would suggest that AEPZ would be the most likely of the four aqueous amines solutions to form foam. There remains disagreement on the role of surface tension in its contribution to foaming. Additionally, surface tension measurements of loaded solutions are extremely sensitive, with significant sources of error. Unloaded measurements show higher surface tension measurements.

Table 1: Physical properties of 3 M aqueous amine solutions at 40°C before and after CO₂ loading

Amine	Unloaded Solutions			CO ₂ Saturated Solutions	
	Density (kg m ⁻³)	Kinematic Viscosity (mm ² s ⁻¹)	Surface Tension (mN m ⁻¹)	Density (kg m ⁻³)	Kinematic Viscosity (mm ² s ⁻¹)
MEA	998.7 ± 0.1	1.04 ± 0.01	58.22 ± 0.06	1069.3 ± 0.1	1.27 ± 0.01
MDEA	1022.0 ± 0.1	2.31 ± 0.01	49.35 ± 0.03	1088.0 ± 0.1	2.55 ± 0.01
AEPZ	1026.9 ± 0.1	4.98 ± 0.01	50.82 ± 0.11	1129.9 ± 0.1	6.42 ± 0.01
AMP	988.3 ± 0.1	1.97 ± 0.01	39.86 ± 0.06	1086.7 ± 0.1	3.16 ± 0.01

Degraded Samples

Four solvents were observed before and after degradation to determine the foam height, recorded as a function of nitrogen gas flow rate, in an unpacked column. Those solvents tested after full saturation of CO₂, but before the thermal degradation process, showed no foaming under the conditions tested.

However, all four solvents subjected to thermal degradation demonstrated foaming. The range of flow rates tested was dictated by the onset of foam and the onset of slugging in the column.

Three of the degraded solvents (MEA, MDEA, and AEPZ) show reasonably linear relationships between the nitrogen flow rate and the resulting foam height measured (Figure 3). The Bikerman model (Equation 1) uses such a relationship to determine a foaminess coefficient. In such a case, AEPZ would be considered the foamiest overall with a 0.11 min Bikerman foaminess factor, followed by MDEA with 0.04, and finally MEA with 0.01. These three solvents also showed very limited foam stability. In all cases, regardless of flow rate, for the solvents MEA, MDEA, and AEPZ the breaktime was found to be less than ten seconds. As would be expected, at the onset of slugging all three solvents were found to no longer demonstrate any foam formation.

The degraded solvent AMP shows a categorically different behavior from that observed with the other solvents discussed. The degraded AMP has significantly larger films with much more variability in the foam size and stability. Separation of the foam was regularly observed; the foam initially moved upwards in the column, away from the foam contiguous with the bulk liquid. Gravitational forces then returned the foam down the column and the two portions reunited. These distinctions amongst the solvents are clear in Figure 3 where AMP does not show the linearity suggested by the Bikerman model.

Figure 3: Foaminess of thermally degraded samples of MEA, MDEA, AEPZ, and AMP solutions shown where height is plotted against nitrogen flow rate to extract the foaminess coefficient suggested by the Bikerman foam model. Standard deviation includes three individual experiments for each of which five measurements were taken at each flow rate. Error bars not visible are smaller than the marker.

The empirical nature of the Bikerman model provides some confidence in the known relationship between nitrogen gas flow rate and foam observed. However, at the same flow rates tested there is no foam for solutions before thermal degradation - a critical finding. As such, this strongly indicates that the tendency of foaming in an untreated solution is not comparable and provides little insight into the behaviors observed industrially. However, the Bikerman model's insufficiencies are clear with its failure to accommodate for the physical liquid behaviors, bubble size, and environmental conditions during the experiment. As such, results in the literature are likely to be inconsistent if only this model is considered.

For the four thermally degraded solvents studied, it is shown that all fit the Pilon exponential model (Equation 2) exceptionally well (Figure 4). It is observed that, in the model fit, the exponent fitting

parameter for three of the four (MEA, MDEA, AMP) solvents falls within a small range of -1.211 to -1.307. These values are somewhat lower than those previously observed for traditional foaming solutions¹⁰. The three degraded amine solutions showed significant numbers of degradation products. Such an array of components in the system is dramatically different from traditional foaming solutions with many fewer constituents. It is important to note, that the fourth solvent AEPZ shows a somewhat smaller exponent (-1.626). By contrast to the three other solvents, AEPZ is far less reactive under the same thermal degradation conditions. There were observed to be fewer degradation products, though they were present in reasonable quantities (results of this analysis are included in the supporting information).

Figure 4: The experimentally measured foam height of thermally degraded solutions of MEA, MDEA, AEPZ, and AMP for which Ca , Re , and Fr were determined and subsequently plotted according to the exponential model proposed by Pilon et al. (Equation 2) where $R^2 > 0.98$ for all four cases.

The sign of the exponent highlights the balance between viscous and gravitational forces. For all these cases the gravitational term dominates over the viscous forces. This is particularly true for AEPZ where the exponent is smaller. As this value is closer to the results found for traditional foaming solutions, this provides additional support that AEPZ may behave more like foaming solutions used for the original fitting of the model. Such distinctions critically demonstrate that these degraded amine solutions cannot be treated as traditional foaming solutions due to their more complex array of constituents.

The pre-exponential factors determined for these four degraded solvents are found to be smaller than those previously reported for non-degraded solvents. Again it is seen that MEA, MDEA, and AMP all show pre-exponential factors of the same order of magnitude while that of AEPZ appears between one and two orders larger. The results found for AEPZ again appear more consistent with traditional foaming solutions and some previously cited amine results. This consistent disparity points to the significantly different nature of the degraded AEPZ solution as compared to MEA, MDEA, and AMP collectively. The vastly different physical properties (Table 2), particularly the very high kinematic viscosity, contribute to such distinct differences for AEPZ as compared to the other degraded amine solvents.

Table 2: Physical properties of 3 M aqueous amine solutions at 40°C after degradation

Amine	Density (kg m^{-3})	Kinematic Viscosity ($\text{mm}^2 \text{s}^{-1}$)	Surface Tension (mN m^{-1})
MEA	1078.8 ± 0.1	1.94 ± 0.01	29.50 ± 0.05
MDEA	1040.0 ± 0.1	4.41 ± 0.01	39.00 ± 0.04
AEPZ	1132.9 ± 0.1	31.63 ± 0.01	26.81 ± 0.09
AMP	1014.3 ± 0.1	4.21 ± 0.01	33.04 ± 0.03

The pre-exponential factor is strongly influenced by the bubble radius. This work determined the average bubble size using images collected of the foam formation. However, in foams of this nature, the bubble size is not consistent and represents a wider range than might be observed in other systems. As

a result, the fitting of this parameter results in an average rather than a representation of the whole. A more accurate representation of the bubble size would require a modification to this model where bubble size is expressed as a function. In turn this would allow an improved understanding of the pre-exponential factor's physical meaning.

The differences observed in both the exponent and pre-exponential factor suggest that a specific value cannot be used generally. This is particularly true for these complex degraded amine solutions. Furthermore, even in the case of MEA the use of additives does not produce equivalent results to those found for degraded solvents. Such distinctions are critical as these complex mixtures much more closely resemble those found industrially, which prove problematic.

Conclusions

The thermal degradation of four amine solutions containing MEA, MDEA, AEPZ, and AMP, respectively, has been shown to increase foaminess as compared to the non-degraded counterparts. The Bikerman model highlights this and finds that MEA, MDEA, and AEPZ behave linearly in increasing foam formation with an increasing N_2 flowrate, as is expected. However, AMP is observed to form significant and highly stable foam irrespective of flow rate. This finding suggests significant foaming problems are likely to be associated with the use of AMP for large-scale industrial plants. In an alternative method for the consideration of foaminess, the use of a semi-empirical model linking physical properties showed similar fitting parameters for thermally degraded MEA, MDEA, and AMP solutions whereas AEPZ appears to behave more closely to traditional foaming solutions. Such inconsistencies between thermally degraded amine solutions and traditional foaming theory suggests that further investigations are required to improve an understanding of the intrinsic solution differences creating this divide. Furthermore, the distinctions, in both models, highlight that foaming properties in degraded amines are not consistent as a collective. This demonstrates that until a better understanding

is developed, each solution must be treated individually when being considered for industrial applications.

Acknowledgements

The authors wish to acknowledge Prof. M. Trusler for use of his laboratory facilities as well as Dr. J. Zhang and Dr. J. Hall.

Associated Content

Supporting Information Available: The four thermally degraded solutions were analyzed by gas chromatography–mass spectroscopy at the completion of the 28-day experiment. The resulting spectra are included showing the extent of degradation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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