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Effect of pH and time on hydrodynamic properties of dodecylamine

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Abstract: Gas holdup and froth height in the presence of dodecylamine (DDA, $pK_a = 10.63$) are reported at three pH values. The results revealed a strong time effect for DDA: stability was reached at pH 3; not at natural pH, for example, gas holdup declining to the water only value; and at pH 11, while stability was reached quickly gas holdup was now less than in water alone indicating coalescence. In the first two cases, the time effect is attributed to loss of amine from the system as molecular amine, observed at natural pH as precipitates on the column wall. An argument for precipitation at pH < pKa is presented. At pH 11, coalescence is attributed to the oily nature of the molecular amine present as colloidal aggregates. Noting a difference in literature steady state gas holdup data at natural pH, it is speculated that varying steady states can be reached that corresponds to different levels of amine loss.

Keywords: dodecylamine, pH, frother function, gas holdup, froth height

1. Introduction

For this special issue in honour of Janusz Laskowski we have chosen a subject to which he has made significant contributions: frothers. Through the contributions of Laskowski and co-workers (Laskowski 1998, Cho and Laskowski, 2002, Laskowski 2003, Melo and Laskowski, 2007, Castro et al., 2013,) he has reminded us that while frothers play key roles understanding of how they act remains limited, which has stimulated the recent surge in frother-related research. Long understood that frothers reduce bubble size to a transition concentration where the bubble size was minimum and constant (Klassen and Mokrousov, 1963; Finch and Dobby, 1990), Laskowski was the first to recognize the utility of this transition in characterizing frothers. In a seminal paper Cho and Laskowski (2002), knowing that coalescence suppression was central to frother action (Harris, 1976), reasonably argued that the transition concentration corresponded to complete suppression of coalescence, and introduced it as the 'critical coalescence concentration' or CCC. A graphical method of determining CCC was described, which led to subsequent mathematical (curve-fitting) methods (Nesset et al., 2006; Gomez et al., 2014). Building on this, Laskowski (2003) modified frother characterization, which had focussed on properties of the froth zone, to include CCC, that is, a property related to the pulp zone. Frother characterization employing both pulp and froth zone properties are now the norm, sometimes referred to as 'hydrodynamic characterization' (Cappuccitti and Finch, 2008). The measures in the pulp zone are bubble size (to derive CCC) and/or gas holdup (collectively referred to as 'gas dispersion properties' (Wills and Finch, 2016)) and for the froth zone they include dynamic foamability index (Laskowski, 2003), froth height (Cappuccitti and Finch, 2008; Alvarez-Silva et al., 2014; Zhou et al., 2016), froth half-life (time for froth to reduce to half its equilibrium height when air is shut off) (Tan et al., 2005), and water overflow rate (Moyo et al., 2007; Zhang et al., 2010). In an example of the utility of this approach, Cappuccitti and Finch (2008) used froth height vs. gas holdup to rank frother 'strength' and successfully identified a frother to replace MIBC.

Other reagents can exert frother-like properties. Collectors, for example, are now being scrutinized using the same techniques developed for frothers (Ravichandran et al., 2013; Zhou et al., 2016). The fatty acids and fatty amines exhibit frother properties (Atrafi et al., 2012; Corona-Arroyo et al., 2015) but unlike conventional frothers that are non-ionic, the properties of these weak acids and bases depend on

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pH. Two recent papers have examined dodecylamine (DDA) at roughly the same pH, pH 7 (Corona-Arroyo et al., 2015) and natural pH (ca. pH 7.4) (Zhou et al., 2018). The purpose of this paper is to determine frother properties of DDA as a function of pH using the froth height vs. gas holdup (i.e., hydrodynamic characterization) technique of Cappuccitti and Finch (2008). In doing so it became evident that there is a significant time effect.

2. Experimental

2.1. Apparatus

Figure 1 shows the setup used to measure gas holdup and froth height. The Plexiglas column was 7.62 cm (3 inches) in diameter and 485 cm (with launder) in height. The air, controlled with an air flow meter, was dispersed through a cylindrical stainless steel porous sparger centrally located at the column base. Gas holdup (ε_g) was measured using differential pressure (Bailey PTSDDD differential pressure transducer) over a 120-cm section starting 174 cm above the sparger (P_1) with a temperature sensor located 15 cm above P_1 for temperature correction. A short section of upward-curved plastic tubing was installed on the inside wall (inset Fig. 1) to prevent bubbles entering the tapping and degrading pressure measurement. All instruments were connected to iFix software to monitor with data extracted to Excel on a desktop. The air flow rate was 5 dm^3/min (giving air superficial velocity, J_g, 1.8 cm/s) controlled by a mass flow meter for all experiments. The overflow recycle to the tank was used to remix the column contents to repeat some measurements.

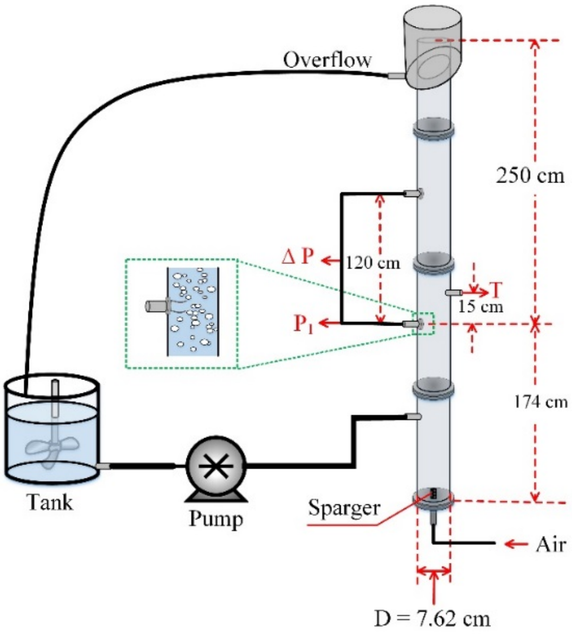

Fig. 1. Experimental setup to measure gas holdup and froth height

2.2. Procedure

Reagents: The DDA was the hydrochloride salt, with pH controlled by hydrochloric acid and sodium hydroxide. All reagents were reagent grade supplied by Fisher Scientific Canada.

Solution preparation: Solutions were prepared using Montréal tap water. All experiments were conducted using air-water (i.e. no solids) system at room temperature, 21 ± 4 °C. The solution (100 dm^3) was prepared in the tank and pumped into the column using a Masterflex Easyload pump. As the salt, the amine dissolved readily. Three pH levels were tested: 3, natural (pH 7.3-7.6), and 11, (HANNA HI 8424) at concentrations up to 20 ppm (based on the hydrochloride) (Castro et al., 1986). For some conditions the column contents were re-mixed, and the measurements repeated, referred to as cycle 1, 2 etc. At completion of an experiment, the circuit was drained and cleaned thoroughly.

Measurements: Differential pressure (Δp) was measured and gas holdup was calculated by $Eg.1$: $\varepsilon_g(\%) = 1 - (\Delta p/(\rho g \Delta h)) \times 100$, assuming solution density, ρ = 1g/cm^3, Δh = 120 cm). Using a ruler, froth height measurements were started after J_g reached 1.8 cm/s, in some cases tracked at 20 s intervals for several mins.

3. Results

3.1 Natural pH

The immediate observation was the impact of time (Fig. 2): Gas holdup initially increased then declined towards the value in water only (ca. 8 %); and froth height also initially increased in the case of 10 and 20 ppm, then declined, in all cases, to zero. Froth images (at 20 ppm, Fig. 3) visualize these changes: from an initial froth with small, uniform bubble size that grows in height to one with large bubbles present to eventually, after 20 mins (1200 s), no froth at all but leaving a trace of yellowish precipitates on the column wall. The precipitates could be re-dissolved in water at natural pH but not in base solution, supporting that the precipitates were molecular DDA. This behaviour was repeatable: by rinsing down the precipitates with the same solution and re-mixing (using the overflow recycle), Figure 4 shows the gas holdup trends over 3 cycles.

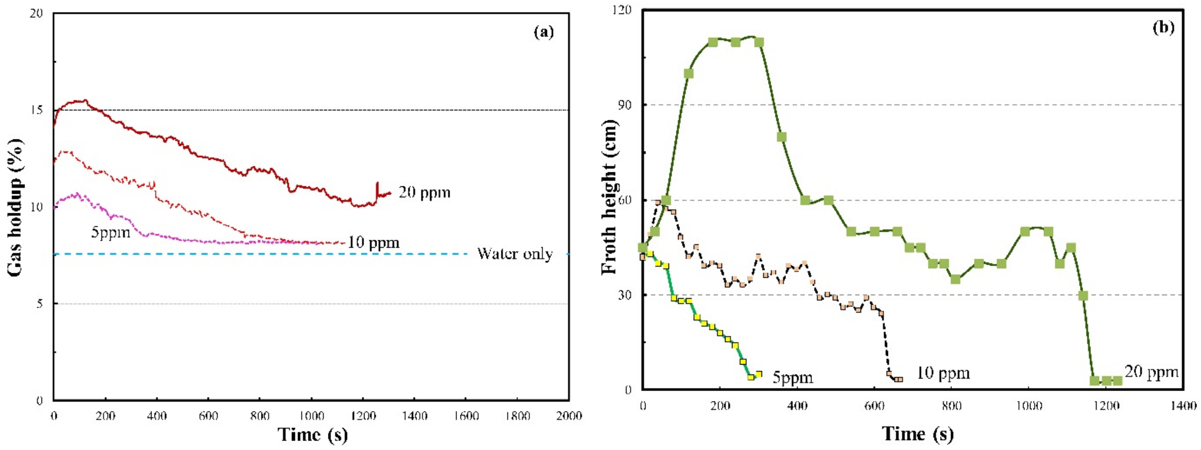

Fig. 2. Variation with time and concentration at natural pH: (a) Gas holdup; and (b) Froth height

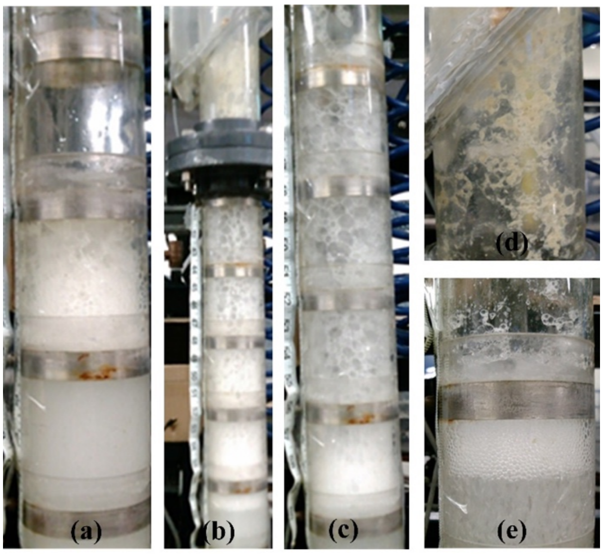

Fig. 3. Images of the froth with 20 ppm DDA at natural pH over time (view in conjunction with Fig 2(a)): (a) the start (i.e., on reaching J_g = 1.8 cm/s); (b) 4 mins (240 s), close to max height; (c) 11 mins (660 s), significant decline in height with evidence of large bubbles; (d) yellow precipitates left on column wall; and (e) 18 mins (1080 s), froth virtually disappeared

(a)

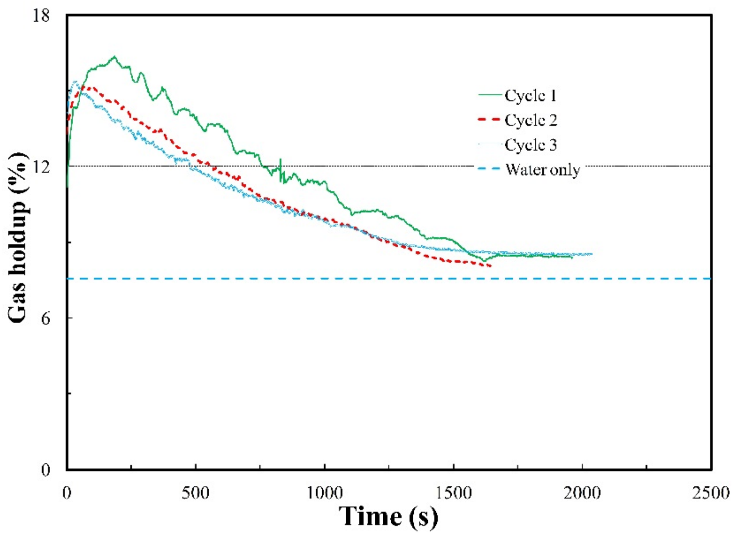

Fig. 4. Gas holdup as a function of time for three cycles

3.2. pH 3 and pH 11

Figure 5 compares the gas holdup trend with time for 20 ppm at the three pHs. Compared to natural pH, at pH 3 holdup stabilized at ca. 16% (twice that in water alone), while at pH 11, an initial spike was followed by holdup rapidly declining to less than the water only value with large bubbles evident accumulating and creating turbulence just below the froth. Froth height was more stable at both pH 3 and 11 compared to natural pH: for 20 ppm at pH 3, froth height dropped from a maximum ca. 60 cm near the start to stabilize at ca. 30 cm, while at pH 11, the froth layer was stable at about 25 cm with a foamy structure, reminiscent in our experience (Cappuccitti and Finch, 2008) with froths produced with a 'strong' polyglycol frothers such as F150 (or PPG 425). Precipitates were less evident at the acid and alkaline pHs.

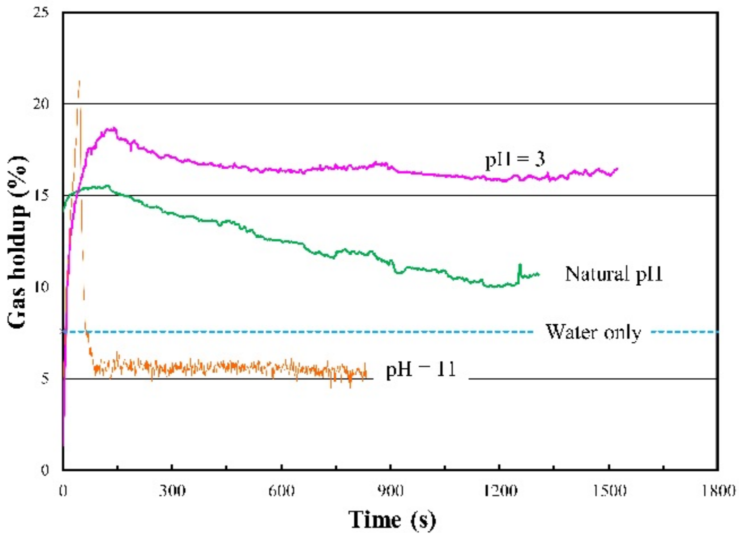

Fig. 5. Effect of pH on gas holdup as a function of time in 20 ppm DDA (including water only for reference)

4. Discussion

4.1 Effect of pH and time

An effect of pH on the properties of DDA is to be expected as you transit pH 10.63 (i.e., pK_a = 10.63 (Somasundaran and Wang, 2006)), where ionic DDA transforms (by hydrolysis) to neutral molecular DDA which has low solubility. An impact of pH is well known in flotation. In the classic demonstration of the electrostatic model of flotation using the goethite/DDA system, Iwasaki et al. (1960) also showed that recovery dropped sharply above ca. pH 11, attributed to molecular DDA carrying no (positive) charge and being poorly soluble. Others have shown that flotation recovery tends to maximize around the pK_a, speculated as due to formation of ion-molecular complexes that act as strong collectors (Pugh, 1986; Rao and Forssberg, 2007). Fundamental properties also change. For example, surface tension passes through a minimum ca. pH 10.5 attributed again to presence of ion-molecular species (Castro et al., 1986; Finch and Smith, 1973); and bubble surface charge passes from positive, due to adsorption of the amine cation, to negative above ca. pH 10, the usual sign in the presence of non-ionic surfactants (Yoon and Yordan, 1986). Considering the present gas holdup results, we see a trend with increasing pH: from some stability at pH 3, less stability at natural pH, to rapid change then stability at pH 11. What was unexpected is this role of time.

In other contexts, however, time is recognized as a factor in the properties of DDA. Referred to as 'dynamic' surface tension, while there is little time-dependence at acid pH (Burcik and Vaughn, 1951; Finch and Smith, 1972), it becomes very evident at ca. pH 10, taking some 100 s to reach equilibrium tension, attributed to large size of the ion-molecular species reducing mass transfer rate (Finch and Smith, 1972). Time-dependent (dynamic) contact angles, where the angle decreases to zero over time, have been reported in presence of DDA (Lai and Smith, 1966), a phenomenon explained by time-dependent surface tension (Finch and Smith, 1972). The time effect in the present context, however, has an origin different from just mass transfer.

Previous work characterizing frothers using gas holdup has noted a time effect, gas holdup decreasing with alcohols to that in water alone (within 30 mins for 10 ppm MIBC) but being stable for up to 50 hrs with polyglycols (Azgomi et al., 2009). The higher volatility of alcohols relative to polyglycols points to an explanation. It begins with frother adsorbing on the bubbles and transferring to the froth. In the absence of volatility (polyglycols) this process rapidly reaches equilibrium between solution and froth (even allowing for the greater transfer to the froth experienced by the more surface active polyglycols compared to alcohols (Gélinas and Finch, 2007)) and gas holdup stabilizes. In contrast, for the volatile alcohols, this translates into loss to atmosphere and thus equilibrium is not reached, rather depletion of frother occurs, as actually measured in the case of MIBC (Azgomi et al., 2009), reducing the solution concentration over time causing an increase in bubble size with increased rise rate and consequently a reduction in gas holdup. Thus, the difference is loss of frother in one case (alcohols) and not in the other (polyglycols). We are now in a position to examine the present results for DDA.

Ionic dodecylamine, even relative to most frothers, is strongly surface active (decreases surface tension) thus adsorption on the bubble and transfer to the froth occurs. At natural pH, something then happens to disrupt establishment of equilibrium, namely precipitation of molecular amine in the froth. Why this occurs at pH well below the pK_a requires some speculation. The cationic amine will impart a positive charge on the bubble which induces a counter charge provided by OH^- ions; that is, local to the bubble surface the pH is higher than in the bulk, evidently approaching the pK_a value, and given the elevated DDA concentration in the froth conditions are primed to induce precipitation. In this manner amine is continuously lost (precipitated) from solution and gas holdup declines, eventually to the water-only value implying complete loss of amine. At pH 3 it is reasonable to anticipate it is more difficult for the local (bubble surface) pH to approach pK_a and consequently the rate of amine 'loss' is less and equilibrium, that is, steady gas holdup and froth height, is attained.

Conditions at pH 11, that is, above pK_a are different in that precipitation has already occurred, and molecular amine is present in solution, which associates as insoluble oily colloidal aggregates ('droplets') (Castro et al., 1986). Knowing that oil droplets induce coalescence (Ross, 1950, Stewart and Arnold, 2009, Coca-Prados and Gutiérrez-Cervelló, 2010) the rapid decline in gas holdup to below that of water-only, which indicates bubbles are larger than in water alone, can be pinpointed to the molecular amine colloids. Molecular amine being present from the beginning means there is no 'loss' and stable gas holdup (albeit much reduced) and stable froth height can be maintained.

The strong influence of time, especially at natural pH precluded achieving the initial goal of the test work, namely establishing the froth height – gas holdup trend ('hydrodynamic curve') by which to compare against conventional frothers, and other flotation reagents.

4.2. Proffered explanation of difference in published DDA 'frother' data

Reporting as Sauter mean bubble diameter (D_{32}), Figure Fig. 6 compares the bubble size vs. concentration results found by Corona-Arroyo et al. (2015) and Zhou et al. (2018) for DDA and MIBC. The setups were very different, the former using a mini Jameson Cell, the latter a mini mechanical cell, which helps account for the large difference in initial (zero concentration) bubble size, but despite this the MIBC results show a similar CCC (ca. 8 ppm) and minimum bubble size (ca. 0.75 mm). The difference in setup, therefore, does not seem to be the origin of the quite different results for DDA, in the one case finding it more effective in reducing bubble size than MIBC (Corona-Arroyo et al.) and in the other less effective (Zhou et al., 2018).

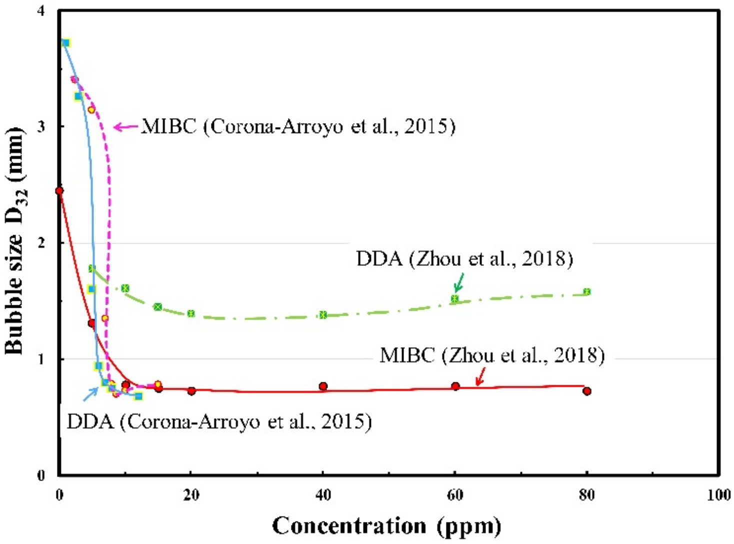

Fig. 6. Comparison of results for bubble size as a function of concentration for MIBC and DDA (data from Corona-Arroyo et al. (2015) and Zhou et al. (2018))

In both setups, however, the measurements were made at a steady state, but the present results may mean that different 'times' at which steady state is imposed are involved. The apparently more active DDA in the Corona-Arroyo et al. case suggests this time is relatively short with little DDA 'loss' (as precipitates), while the less active DDA found by Zhou et al. suggests a relatively long time, and more loss of amine. If this explanation is correct, it does mean that the different test rigs may be responsible, the times involved in a Jameson will be less than in the mechanical cell, which corresponds to the more active DDA in the first case compared to the second. In testing with alcohol frothers, we are always conscious of the effect of loss (due to volatility) and limit the testing time, or if feasible add excess frother to compensate for loss. Precautions may be useful in testing DDA where there is clear evidence of loss, in this case due to precipitation.

5. Conclusions

Two frother-related properties of dodecylamine (DDA, $pK_a = 10.63$), gas holdup and froth height, were determined using an air-water system in a bubble column at three pH values, 3, natural, and 11. An impact of pH was evident, as expected for this weak base, but there was an unexpected large effect of time: at pH 3 stability was reached, at natural pH stability was not reached, gas holdup declining to the water-only value and froth height approaching zero; at pH 11 steady state was reached quickly but gas holdup was below that in water only. Observing precipitation in the froth at natural pH, the decrease in both gas holdup and froth height with time was attributed to loss of amine from solution. A mechanism to explain precipitation at $pH < pK_a$ is proposed. At pH 11 molecular amine present as colloids evidently causes coalescence, a phenomenon well known in presence of oil droplet dispersions. Noting differences in literature steady state gas holdup results for DDA, it is postulated that a steady state can be reached that corresponds to different levels of amine loss and thus amine activity apparently varies.

Acknowledgements

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