Frother structure–property relationship: Effect of alkyl chain length in alcohols and polyglycol ethers on bubble rise velocity

Yue Hua Tan, James A. Finch *

Department of Mining and Materials Engineering, McGill University, 3610 University, Montreal, Quebec H3A 0C5, Canada

ABSTRACT

In mineral flotation, frothers are used to produce fine bubbles, reduce bubble rise velocity, and stabilize the froth, three properties that enhance the flotation process. These properties depend on the frother structure and this paper is part of an investigation into the frother structure-property relationship. The property here is bubble rise velocity and the structural variation is alkyl chain length of two frother families, alcohols and polyglycols. Single bubble rise velocity profiles were determined in a 350 cm column. Velocity at 300 cm as a function of concentration is determined and as a measure of the impact of structure on reduction in bubble rise velocity the concentration at minimum velocity (CMV) is estimated. The effect of increasing alkyl chain length is to decrease CMV by about ca. 90% in alcohols and ca. 70% in polyglycols for every one carbon addition. Taking log CMV as a function of the number of carbons in the alkyl chain gives a series of self-similar linear plots. An argument relating bubble rise velocity to surfactant molecule packing on the bubble surface is proposed.

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1. Introduction

Surface active agents known as frothers play a critical role in most mineral flotation systems. The main functions of frothers are to reduce bubble size, to slow bubble rise velocity, and to stabilize froth, which together enhance particle collection rate (Klimpel and Isherwood, 1991). The correct frother selection can be vital to maximize flotation performance. Progress has been made devising lab tests to screen frothers (Laskowski, 2003; Cappuccitti and Finch, 2008; Doucet et al., 2009), but being able to formulate a frother structure to meet specific requirements would represent an important breakthrough (Zimba et al., 2007). However, the relationship between frother structure and flotation performance is unclear. Understanding the effect of frother structure on the frother functions (or properties) noted above should help identify the relationship.

The frother molecule has two parts: a hydrophobic (non-polar) hydrocarbon (usually alkyl) chain and a hydrophilic (polar) head. The general understanding is that the frother molecule adsorbs at the water/air interface with the polar group oriented to the water-side and the hydrocarbon chain to the air-side. As a consequence, water/air interface-related properties are modified, causing the noted effects on the bubbles and froth. The ability of

surfactants to change the properties of interfaces is dependent on their chemical structure (Rosen and Dahanayake, 2000; Somasundaran and Wang, 2006).

Water/air interfacial properties are related to the hydrocarbon chain length of the surfactant, which is recognized in processes such as flotation, flocculation and foam separation (Rao and Leja, 2004), and in phenomena such as surface tension, adsorption, and micelle formation (Lin et al., 1974; Briggs et al., 1995). As an example in flotation, Fuerstenau (1976), testing a homologous series of alkyl amine surfactants, showed that the concentration at equal recovery of quartz decreased as hydrocarbon chain length increased; and as an example in micelle formation, for a homologous series of linear single-chain surfactants, Klevens (1953) showed that the critical micelle concentration (CMC) decreased logarithmically with increasing carbon number.

The frother functions also reflect their structure. However, commercial frothers are often not pure and are too few to identify a structure-property relationship. Systematic variation in structure, such as chain length, and position of branched hydrocarbon groups and hydroxyl groups, is required. That is, more surfactants from the frother families need to be tested. In a previous study, Zhang et al. (2012) investigated a range of surfactants from two frother families, alcohols and polypropylene glycol ethers, and reported the effect on the critical coalescence concentration (CCC), the concentration giving minimum bubble size in a flotation system. We have extended the families to include diols and polyethylene glycol

* Corresponding author.
  E-mail address: jim.finch@mcgill.ca (J.A. Finch).

ethers and use single bubble rise velocity as the property, which is sensitive to surfactant structure (Sam et al., 1996; Tomiyama et al., 2002; Krzan and Malysa, 2002; Krzan et al., 2004; Parkinson et al., 2008). The purpose of this paper is to determine the effect of alkyl chain length in alcohols and polyglycol ethers on single bubble rise velocity.

2. Experimental part

2.1. Reagents

Table 1 lists the 28 surfactants from the alcohol and polyglycol ether families used in the study. In the alcohols there were two sub-groups: four 1-alcohols (general structure formula: $C_nH_{2n+1}OH$, n = 4–7) from Fisher Scientific Company (Canada Ltd), and four 1,2-diols (two hydroxyl groups at one end, i.e., the 1,2 positions) ($C_{n-2}H_{2n-3}CHOHCH_2OH$, n = 3–6). All were from Sigma-Aldrich Corporation (Canada) and of the highest purity available (98–99.9%). The polyglycols were also in two sub-groups: nine polypropylene glycol alkyl ethers (PPGAE: $C_nH_{2n+1}(OC_3H_6)_mOH$), and 11 polyethylene glycol alkyl ethers (PEGAE: $C_nH_{2n+1}(OC_2H_4)_lOH$). The polyglycols are further divided based on the number of propylene oxide (PO: $-OC_3H_6-$) groups (m = 1, 2, 3) or ethylene oxide (EO: $-OC_2H_4-$) groups (l = 1, 2, 3). The surfactants represent those that are readily available (n = 2 in PPGAE is not, for example), and can be safely disposed. All polyglycols were from Sigma-Aldrich Corporation (Canada) with a purity of 98.5–99.7%.

The table effectively includes two commercial frothers (i.e., having the same reported structure): DF200 (tripropylene glycol methyl ether[2]; n = 1, m = 3) (Wiese and Harris, 2012; Corin and Wiese, 2014; Nyabeze and McFadzean, 2016), and Nasfroth 240 (triethylene glycol butyl ether[3]: n = 4, l = 3) (Jávor et al., 2012), as well as 1-hexanol[1] which has some industrial applications (Liu and Somasundaran, 1994; Monte and Oliveira, 2004; Ngoroma et al., 2013; McFadzean et al., 2016).

2.2. Single bubble column setup

The setup used to determine the local rise velocity as a function of distance, or velocity profile, is shown in Fig. 1. It comprises a circular Plexiglas column 6.35 cm diameter by 350 cm high (20 L capacity) surrounded by a square Plexiglas water jacket ($8 \times 8 \times 350$ cm). The water jacket maintains a uniform temperature ($23 \pm 1 \,^\circ C$), and eliminates the optical distortion associated with curved surfaces. An overflow outlet was positioned at the 350 cm level to give a reproducible water column height (i.e., reproducible hydrostatic pressure) above the bubble generating capillary. A measuring tape placed along the central axis of the column locates the position of the bubble, which is recorded on video tape. A glass capillary with nominal internal diameter 51 μm was used to generate bubbles using dry air delivered from a compressor. Two measurements of bubble size were made at right angles near the capillary to give a mean value which was corrected to conditions at the 350-cm level (top of water column) giving a diameter of 1.45 ± 0.061 mm (standard deviation based on 30 measurements). A 1.45 mm bubble is in a range where velocity is sensitive to surfactant addition (Clift et al., 1978) and is relevant to the size of bubble in flotation systems, typically 0.5–2.5 mm (Finch and Dobby, 1990). The 20-L test solution was prepared with Montréal tap water (Remillard et al., 2009). The minimum input gas rate to just generate a bubble was applied, which also respected the bubble frequency of <80 bubbles/min recommended by Sam et al. (1996). A digital video camera (CCD Canon GL2, 30 frame/s) stage mounted on a chain controlled by a variable speed motor was driven manually to track the bubble rise.

The experiment was initiated by activating the camera at the moment of bubble release with the experimenter adjusting speed to maintain the bubble in the field of view. The images were continuously displayed on a monitor (Sony PVM-1340) through a signal sender and receiver set (Radio Shack 15-2572). After recording, the images were processed offline to give position, and from sequential images, the local velocity.

Table 1
Reagents used in the study.

Family	Name			Chemical formula	n	m or l	Molecular weight
Alcohol	1-Butanol			C_4H_9OH	4	–	74.12
	1-Pentanol			$C_5H_{11}OH$	5		88.15
	1-Hexanol[1]			$C_6H_{13}OH$	6		102.17
	1-Heptanol			$C_7H_{15}OH$	7		116.2
1,2-Diol	1,2-Propanediol			$CH_3CHOHCH_2OH$	3	–	76.09
	1,2-Butanediol			$C_2H_5CHOHCH_2OH$	4		90.12
	1,2-Pentanediol			$C_3H_7CHOHCH_2OH$	5		104.15
	1,2-Hexanediol			$C_4H_9CHOHCH_2OH$	6		118.17
PPGAE	Propylene glycol	Methyl	Ether	$CH_3(PO)OH$	1	1	90.12
		Propyl		$C_3H_7(PO)OH$	3		118.17
		Butyl		$C_4H_9(PO)OH$	4		132.20
	Dipropylene glycol	Methyl		$CH_3(PO)_2OH$	1	2	148.2
		Propyl		$C_3H_7(PO)_2OH$	3		176.25
		Butyl		$C_4H_9(PO)_2OH$	4		190.28
	Tripropylene glycol	Methyl[2]		$CH_3(PO)_3OH$	1	3	206.28
		Propyl		$C_3H_7(PO)_3OH$	3		234.33
		Butyl		$C_4H_9(PO)_3OH$	4		248.36
PEGAE	Ethylene glycol	Ethyl		$C_2H_5(EO)OH$	2	1	90.12
		Propyl		$C_3H_7(EO)OH$	3		104.15
		Butyl		$C_4H_9(EO)OH$	4		118.17
	Diethylene glycol	Methyl		$CH_3(EO)_2OH$	1	2	120.15
		Ethyl		$C_2H_5(EO)_2OH$	2		134.17
		Propyl		$C_3H_7(EO)_2OH$	3		148.20
		Butyl		$C_4H_9(EO)_2OH$	4		162.23
		Hexyl		$C_6H_{13}(EO)_2OH$	6		190.28
	Triethylene glycol	Methyl		$CH_3(EO)_3OH$	1	3	164.20
		Ethyl		$C_2H_5(EO)_3OH$	2		178.23
		Butyl[3]		$C_4H_9(EO)_3OH$	4		206.28