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Frother structure-property relationship: Effect of polyethylene glycols on bubble rise velocity

Yue Hua Tan^a, Wei Zhang^b, James A. Finch^{a,*}

^a Department of Mining and Materials Engineering, McGill University, 3610 University, Montreal, Quebec H3A 0C5, Canada
 ^b Mine Management Division, Department of Mining & Mineral Resources, Chinalco China Copper Corporation Limited, Beijing 100082, China

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ABSTRACT

This paper is part of our study of the frother structure-property relationship using bubble rise velocity as the property. Single bubble rise velocity profiles were determined for surfactants of the polyethylene glycol (PEG) family in a 350-cm column, and the concentration to reach minimum velocity (CMV) measured at 300 cm is determined. The lower the CMV indicates a structure more effective in slowing bubble rise. The CMV is shown to decrease as both alkyl chain length (n, number of carbons) and number of ethylene oxide groups (l) increases. Linear correlations log CMV vs. n and l were observed; and taking literature data for critical coalescence concentration (CCC), a linear log CMV vs. log CCC correlation was found. Mechanisms controlling bubble rise velocity based on structure effects on surface tension gradients and surface viscosity are discussed. A comparison with previous findings on polypropylene glycols is included.

1. Introduction

Frothers, a class of surface active agents (surfactants), are widely used in mineral flotation. They have three principal functions: to aid formation and preservation of small bubbles; to reduce bubble rise velocity; and to stablize froth (Klimpel and Isherwood, 1991; Wills and Finch, 2016). These functions reflect their molecular structure which impacts flotation; for example, different chemistries give different flotation recovery depending on particle size (Klimpel and Isherwood, 1991). The choice of frother for a given duty remains largely empirical but progress is being made developing tests to characterise frothers to aid selection (Laskowski, 2003; Cappuccitti and Finch, 2008). From the pioneering days of Klimpel and co-workers (1988, 1991, 1995), work linking frother functions to frother structure is advancing (Zhang et al., 2012; Kowalczuk, 2013; Finch and Zhang, 2014; Corin and O'Connor, 2014; Tan and Finch, 2016a, b, c).

The use of frothers in mineral flotation practice today is dominated by two nonionic surfactant families, alcohols (general formula: $C_nH_{2n+1}OH$) and polyglycols (R(X)_yOH, where R = H, or C_nH_{2n+1} and X stands for, most commonly, propylene oxide, PO ($-C_3H_6O-$) or ethylene oxide, EO ($-C_2H_4O-$), i.e., polypropylene glycols and polyethylene glycols, respectively (Klimpel and Isherwood, 1991; Laskowski, 1998; Laskowski, 2003; Wills and Finch, 2016). In previous studies we have used bubble rise velocity as the property to investigate the structure-property link for alcohols (Tan and Finch, 2016a, b, c) and polypropylene glycols (Tan et al., 2016). The polyethylene glycol (PEG) family is the focus of this study.

Polyethylene glycols (also known as polyethylene glycol alkyl ethers, alkyl monoethers of polyoxyethylene glycols (Sokołowski and Burczyk, 1983), polyoxyethylene alkyl ethers (Bakshi et al., 2005; Ivanova et al., 2012; Sharma et al., 2014) and alcohol ethoxylates (Pletnev 2001)), consists of two parts, the alkyl chain $(-C_nH_{2n+1})$, which is hydrophobic, and the ethylene oxide (ethoxy, EO) group $(-C_2H_4O-)$ made hydrophilic by the -O- linkage. The structure of both the alkyl and EO chains controls the surfactant properties. Writing for simplicity as $C_n(EO)_1$, by varying n and 1, that is, the ratio of hydrophobic to hydrophilic groups, PEGs can range from completely miscible with water to partially soluble (Laskowski, 2001).

Several studies have reported structure effects on properties of PEGs. Crook et al. (1963) and Carless et al. (1964) showed that the critical micelle concentration (CMC) decreases with increasing EO chain length and alkyl chain length. Sokołowski and Burczyk (1983) noted that increasing alkyl chain length decreased surface tension, and Dittmann (1972) that increasing both alkyl chain length and EO chain length decreased surface tension with the former having greater impact.

Polyethylene glycols and their ethers have been studied with respect to use in flotation (Sokołowski and Burczyk, 1983; Giesekke and Harris, 1994; Sis and Chander, 2003; Kowalczuk, et al., 2015). In general, only low molecular weight PEG are employed as frothers (Pugh, 1991). Pugh (1991) testing $C_{12}(EO)_5$ found the stability of the aqueous film between

* Corresponding author.

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

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Y.H. Tan et al.

a hydrophobic mica surface and an air bubble increased with the amount adsorbed on the bubble. Comparing froth stability of $C_{12}(EO)_{10}$ with MIBC (methyl iso-butyl carbinol, the most common alcohol frother), Niewiadomski et al. (2001) demonstrated that the former provided greater froth stability at lower concentration. Aside from effects at the air/water interface, Gong et al. (2010) showed that increasing PEG addition flocculated and depressed flotation of fine quartz particles. PEGs have been used in flotation of various commodities, including coal (Ozmak and Aktas 2006), and graphite, quartz and phosphate ores (Sis and Chander 2003), and Cu/Au ores (Gong et al., 2010). An example commercial polyethylene glycol frother is Nasfroth 240 (CaH₉(EO)₃OH).

Understanding the effect of frother structure on flotation performance is of both fundamental and practical importance. The objective of this study is to establish the structure effect in the PEG family using single bubble rise velocity as the property. Also included are comparisons with literature data on polypropylene glycols (Tan et al., 2016) and with critical coalescence concentration (Finch and Zhang, 2014).

2. Experimental part

2.1. Bubble column setup

Fig. 1 shows the setup to determine the local rise velocity of a single bubble as a function of distance, or velocity profile. The experimental procedure, detailed in previous publications (Tan and Finch, 2016a, b, c), is briefly described here.

The water-jacketed (for temperature control) column was 350 cm in height of 20 L capacity. At the base, bubbles of diameter ca. 1.45 mm were formed using a glass capillary of 51 μ m internal diameter. (A 1.45 mm bubble is in a size range sensitive to surfactant addition (Clift et al., 1978) and is relevant to the size of bubbles in flotation systems (typically 0.5–2.5 mm) (Finch and Dobby, 1990).) 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). The experiment was initiated by activating the camera at the

Table 1 Polyethylene glycol ether surfactants te

Polyethylene	glycol	ether	surfacta	nts	tested.
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Name		Chemical structure			Mole weight (g/	
		Formula n		1	11101)	
Diethylene glycol Triethylene glycol	Methyl ether	CH ₃ (OC ₂ H ₄) ₂ OH CH ₃ (OC ₂ H ₄) ₃ OH	1	2 3	120.15 164.20	
Ethylene glycol Diethylene glycol Triethylene glycol	Ethyl ether	C ₂ H ₅ (OC ₂ H ₄)OH C ₂ H ₅ (OC ₂ H ₄) ₂ OH C ₂ H ₅ (OC ₂ H ₄) ₃ OH	2	1 2 3	90.12 134.17 178.23	
Ethylene glycol Diethylene glycol	Propyl ether	$C_{3}H_{7}(OC_{2}H_{4})OH$ $C_{3}H_{7}(OC_{2}H_{4})_{2}OH$	3	1 2	104.15 148.20	
Ethylene glycol Diethylene glycol Triethylene glycol	Butyl ether	C ₄ H ₉ (OC ₂ H ₄)OH C ₄ H ₉ (OC ₂ H ₄) ₂ OH C ₄ H ₉ (OC ₂ H ₄) ₃ OH	4	1 2 3	118.17 163.23 206.28	
Diethylene glycol	Hexyl ether	C ₆ H ₁₃ (OC ₂ H ₄) ₂ OH	6	2	190.28	

instant of bubble release with the experimenter adjusting speed to maintain the bubble in the field of view. The images were processed offline to give position and, from sequential images (30 frames/s), the local velocity. For each structure, the concentration of surfactant was gradually increased until the minimum velocity at 300 cm was attained, referred to as the CMV (concentration at minimum velocity). The known profile in tap water was used to judge the system was sufficiently clean before each experiment.

2.2. Reagents

Eleven polyethylene glycols ($C_nH_{2n+1}(OC_2H_4)_1OH$) with varied l (1, 2, 3) and n (1, 2, 3, 4, 6) were tested (Table 1). All reagents were from Aldrich-Sigma Corporation (Canada) with the highest purity (98–99.8%) available and used as received. Solutions were made in Montréal tap water (average values: conductivity, 314 µS/cm; pH, 7.95 (Remillard et al., 2009)) and fresh solutions were made for each profile.



Fig. 1. Experimental setup for single bubble rise velocity determination. (Adapted from Tan and Finch, 2016a)

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