Synthesis and characterization of alkyl, propoxy, ethoxy-based frothers

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ABSTRACT

In this paper we describe the synthesis and characterization of a homologous series of linear polyglycol-based frothers comprising alkyl, propoxy (propylene oxide, PO), and ethoxy (ethylene oxide, EO) groups. The identities were confirmed by proton nuclear magnetic resonance spectroscopy and total organic carbon analysis. Characterization used three parameters, bubble size, gas holdup and water overflow rate, measured in a bubble column. The results indicate that increasing number of PO groups led to significant decrease in bubble size, and increase in gas holdup and water overflow rate. Increasing the alkyl chain length, gave similar but less pronounced trends; the least effect was increasing the number of EO groups. Changing the relative position of the PO and EO group had a significant effect on all three parameters. To account for the effect of PO/EO position, a mechanism based on effect of structure on molecule packing at the air/water interface is proposed.

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1. Introduction

Frothers are surfactants used in mineral flotation to enhance performance through control of pulp zone hydrodynamics and froth properties (Klimpel and Isherwood, 1991; Laskowski, 1998; Rao and Leja, 2004; Wills and Finch, 2016). The most common frothers fall into two categories: aliphatic alcohols ($C_nH_{2n+1}OH$) and polyglycols (commonly $C_nH_{2n+1}(OC_3H_6)_mOH$ but also $C_nH_{2n+1}(OC_2H_4)_lOH$). These compounds can be represented by the general formula: $R(X)_nOH$ where R is H or alkyl ($-C_nH_{2n+1}$), and X is propoxy (propylene oxide, PO, $-OC_3H_6-$) or ethoxy (ethylene oxide, EO, $-OC_2H_4-$). The choice of frother has important implications in flotation performance (Rao and Leja, 2004). Progress has been made in laboratory testing procedures using, for example, the critical coalescence concentration (CCC) concept (Cho and Laskowski, 2002) and employing two-phase (air-water) tests to screen candidate frothers (Cappuccitti and Finch, 2008), but frother selection remains largely empirical.

Reagent optimization is a central ambition of flotation chemistry research. It entails modification of existing structures or designing new ones to provide improved performance compared to currently marketed products. Most work has been on collectors followed by modifiers with relatively little on frothers (Nagaraj and Ravishankar, 2007). From the pioneering days of Klimpel and Hansen (1988), Klimpel and Isherwood (1991), and Klimpel (1995), the situation is changing and reagent suppliers are responding with increased range of offerings. Frother, along with air, is a common operational variable used to control flotation kinetics so a focus on frothers is overdue.

The search for new frother chemistries would become less daunting if a frother structure-property relationship approach could be used. The structure represents the type, number and position of functional groups in the molecular architecture. For the property, basic work largely uses such parameters as bubble size, bubble rise velocity and gas holdup, which affect particle collection kinetics, and froth height and water overflow rate, which affect particle entrainment.

One of the first investigations into frother structure-property relationships is by Laskowski (1998, 2003). He investigated the *n*-alcohol homologous series of increasing length of alkyl chain, and members of the polypropylene glycol alkyl ether (PPGAE) homologous series of varying number of PO groups. The results indicated that increasing either length of alkyl chain or number of PO groups increased the ability to reduce bubble size and create froth. Also studied were surfactants with three functional groups, alkyl, PO and EO, including the latter two in different positions, namely, di-ethoxy mono-propoxy hexanol and mono-propoxy di-ethoxy hexanol. Results indicated that the relative position of PO and EO affected the CCC, but the actual structure (whether it is

PO or EO linked to the alkyl group?) was not clear. Melo and Laskowski (2006), along with Moyo et al. (2007) and Zhang et al. (2010), noted that PO-based polyglycols gave higher water recovery than alcohols. Zhang et al. (2012), Tan and Finch (2016a, 2016b, 2016c), and Tan et al. (2016) systematically varied the structure in alcohols and polyglycols which has, among others, identified the impact of the relative position of the OH and methyl groups in branched-alcohols, and resulted in relationships with number of carbons in the alkyl chain (n) and number of PO groups (m).

The work quoted above was largely in two-phase (air-water) systems. The evidence is that solid particles have little impact on bubble size in the pulp (Zhang and Finch, 2014), but do significantly affect froth properties (Hunter et al., 2008). Nevertheless frother type remains a factor: for example, alcohols are generally considered better at recovering fines and polyglycols better at recovering coarse particles (Klimpel and Isherwood, 1991), which may be related to polyglycols tending to recover more water, as identified in two-phase tests. Frother type also appears to influence degree of entrainment (Kracht et al., 2016).

There have been periodic attempts to create new frother chemistries in anticipation of tailored flotation properties. Klimpel and Isherwood (1991) reacted propylene oxide with aliphatic alcohols, resulting in compounds such as hexanol(PO)$_2$. This new chemistry extended the coarse particle size range of flotation, but at the expense of recovering less fine material. Harris and Jia (2000) added a sulphur atom to polyalkoxylated compounds of various configurations. They showed that these frothers increased copper and molybdenum recovery in flotation of porphyry ores. Cappuccitti and Finch (2008) reacted aliphatic alcohols C_1 (methanol) to C_4 (butanol) with between 0.2 and 5 mol of EO. Through measurements of gas holdup and froth height in two-phase tests they identified an ethoxylated butanol as a potential equivalent to MIBC, which was verified by subsequent plant evaluation. The literature, therefore, does imply potential benefits of designing new frother compounds for improved flotation performance.

From the preceding, it is noted that new chemistries tend to be reaction products of alcohols and polyglycols, either alkyl-propoxylates (abbrev: C_nPO_m) or alkyl-ethoxylates (C_nEO_l). This recognizes that frother molecules with two functional groups located at appropriate positions in the molecular architecture may offer advantages over mono-functional frothers. An extension of this thinking is to consider the family of compounds consisting of three functional groups, alkyl, PO and EO.

There is limited data on surfactants from this family used as frothers, the study noted by Laskowski (2003) being the one exception. The purpose of this paper is to synthesize frothers comprising the three functional groups in varying size and positions, specifically linear alkyl-ethoxy-propoxylates ($C_nEO_lPO_m$) and alkyl-propoxy-ethoxylates ($C_nPO_mEO_l$), to confirm their structure, and to characterize them by measuring bubble size, gas holdup and water overflow rate.

2. Experimental

2.1. Synthesis

2.1.1. Materials

The reagents used in the synthesis are listed in Table 1. The polyglycols and their ethers, alcohols, 1,2-diiodoethane and sodium hydride were analytical grade from Aldrich-Sigma Chemical Co. (Canada, Ltd) and used without further purification. The solvent tetrahydrofuran (THF) was obtained from a commercial source with high purity (>99.9%). The dialysis membrane (16 mm × 10 mm) with 100–500 Da MWCO (molecular weight cut-off) was purchased from Spectrum Laboratories Inc. The solvent deuterium oxide for the NMR measurements was 99.994 atom% D from Aldrich-Sigma Co. (Canada, Ltd).

2.1.2. Preparation and purification

By stepwise substitution, we synthesized five nonionic linear polyglycol-based products with varying numbers of repeating units in each group (alkyl, PO and EO) and varying position of EO and PO groups. The chemical structure, formulae and names of the five synthesized frothers are listed in Table 2.

To illustrate the synthesis procedure, we take dipropoxy monoethoxy propanol (DPMEPro) as an example. The three-step reaction is shown in Fig. 1. In the first step, sodium dipropylene glycol was prepared by reacting dipropylene glycol and sodium hydride in the tetrahydrofuran (THF) solvent. Sodium hydride (4.8 g) was dissolved in 20 mL THF in a flame-dried round-bottom flask (three-neck, 100 mL) agitated by a magnetic stirring bar. Dipropylene glycol (16.08 g) was then added into the flask dropwise. The solution was stirred and cooled in an ice-cooled water bath during the addition of the dipropylene glycol for 2 h, maintaining the temperature at 0 °C. In step 2, 1-propanol (7.2 g) was dissolved in 20 mL THF and sodium hydride (4.8 g) was added and stirred in another round-bottom flask (three-neck 250 mL) also held in an ice-cooled water bath to maintain 0 °C for 2 h. At the end of the 2 h 1,2-diiodoethane (31 g) in THF solution was gradually introduced to react with the newly generated sodium propan-1-olate. During the introduction, the vessel was relocated to a heating bath at constant temperature of 60 °C under continuous reflux and stirring conditions for 2 h. After step 2, the sodium dipropylene glycol (from step 1) was taken via a syringe from the 100 mL flask and transferred to the solution (1-(2-iodoethoxy) propane) dropwise with continuous stirring. The solution rapidly became viscous.

Table 1
Reagents used in synthesis.

Name	Formula	Purity
Dipropylene glycol	H(OC$_3$H$_6$)$_2$OH	⩾99%
Tripropylene glycol	H(OC$_3$H$_6$)$_3$OH	⩾97%
Tripropylene glycol monopropyl ether	C$_3$H$_7$(OC$_3$H$_6$)$_3$OH	⩾97%
Ethylene glycol	H(OC$_2$H$_4$)OH	⩾99.8%
Ethylene glycol monopropyl ether	C$_3$H$_7$(OC$_2$H$_4$)OH	⩾99.4%
1-propanol	C$_3$H$_7$OH	⩾99.7%
1-pentanol	C$_5$H$_{11}$OH	⩾99.5%
1,2-diiodoethane	ICH$_2$CH$_2$I	⩾99%
Sodium hydride	NaH	⩾95%
Tetrahydrofuran (THF) (solvent)	C$_4$H$_8$O	⩾99.9%

Table 2
Synthesized frothers.

Type	n	m	l	Chemical formula	Name	Abbrev.
Alkyl-ethoxy-propoxylate	3	2	1	C$_3$H$_7$(EO)(PO)$_2$OH	Dipropoxy Monoethoxy Propanol	DPMEPro
	3	3	1	C$_3$H$_7$(EO)(PO)$_3$OH	Tripropoxy Monoethoxy Propanol	TPMEPro
	5	3	1	C$_5$H$_{11}$(EO)(PO)$_3$OH	Tripropoxy Monoethoxy Pentanol	TPMEPen
	3	3	2	C$_3$H$_7$(EO)$_2$(PO)$_3$OH	Tripropoxy Diethoxy Propanol	TPDEPro
Alkyl-propoxy-ethoxylate	3	3	2	C$_3$H$_7$(PO)$_3$(EO)$_2$OH	Diethoxy Tripropoxy Propanol	DETPPro