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A study on the flotation properties of a new sustainable frother based on cellulose and short-chain alcohol mixtures

Muhammad Wildanil Fathoni [1], *Ted* Nuorivaara[2], and *Rodrigo* Serna-Guerrero[1*]

[1]Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, PO Box 16200, FI-00076 Aalto, Finland
[2]Geological Survey of Finland, PO Box 96, FI-02151 Espoo, Finland

Abstract. Among the major challenges facing the mineral processing industry is the simultaneous need to increase productivity while reducing environmental impact. This study explores the potential of polymer-surfactant (PS) mixture composed of short-chain alcohols combined with hydroxypropyl methyl cellulose (HPMC) as a new environmentally friendly frother produced from sustainable sources. Ethanol, pentanol, and octanol were evaluated as surfactant fraction due to their availability and relatively low cost, alongside the polyglycol based commercial frother (Dowfroth 200) as a benchmark. The result demonstrates that longer-chain alcohols are more effective at preventing bubble coalescence, longer-chain alcohol achieving unimodal distributions at lower concentrations. Interestingly, HPMC exhibited unique behavior due to its macromolecular structure, forming a stable yet slow-diffusing layer around bubbles, resulting in bimodal distributions even at higher concentrations. Mixtures of HPMC and alcohols, particularly pentanol and octanol, show synergistic effects that enhance the initial stabilization of the air-liquid interface, facilitating unimodal distributions at relatively low concentrations. These findings offer valuable insights for optimizing frother formulations to improve flotation efficiency.

1 Introduction

The demand for raw materials has surged in recent years, particularly driven by global megatrends such as electrification and the push for renewable energy sources. In response, improving the capacity and productivity of concentrator plants has become critical. Alongside these developments, there is growing emphasis on environmental sustainability within the mining industry, prompting the search for greener chemical reagents for processes such as flotation. Frothers are a key category of the reagents in flotation, stabilizing the froth phase and controlling bubble size. However, most commercial frothers (alcohols, alkoxy-substituted paraffins, and polyglycol-type frothers [1]) are dominantly derived from petroleum, thus failing to meet the criteria of “green chemicals”[2].

To address these challenges, there is an urgency to develop frothers that are both effective and environmentally sustainable. One promising approach proposed by our research team involves the use of polymer-surfactant (PS) mixtures based on cellulose derivates [3-5]. Previous studies have shown that PS-mixtures increase the flotation rate and recovery of copper from ores, tailings and flash smelting slag [3, 4]. While the previous formulation utilized polyglycol-based frothers as the surfactant component, faster diffusion rate of surfactant molecules enhance initial adsorption and improve control over bubble size in PS-mixture [5]. Therefore, short-chain linear alcohols seem attractive as the surfactant fraction of the PS-mixture due to their commercial availability, smaller molecular size, and renewable sourcing potential.

Following the previous work, hydroxypropyl methylcellulose (HPMC), a biodegradable amphiphilic cellulose derivative, was selected as polymer component. Short-chain linear alcohols, i.e., ethanol, pentanol, and octanol, were chosen as surfactant fraction. Pentanol and octanol were employed due to their known ability to reduce bubble size effectively [6]. Ethanol was tested to further explore the possibility of using shorter alcohol in the PS mixture. Moreover, those alcohols can be derived from sustainable sources such as biomass refining [7-9], further supporting the sustainability goals of this approach.

The use of PS-mixtures as frothers has not been widely studied beyond our research group. A key aspect that remains to be clarified is how PS-mixtures influence bubble formation and coalescence prevention. Frothers acts as surface-active molecules used to stabilize the air/liquid interface through adsorption onto the surface of air bubble dispersed in the liquid phase. The adsorption process typically occurs in three steps: diffusion of surfactant to the interface, adsorption, and molecular re-arrangement [6]. This phenomenon directly influences bubble formation and stability.

The present study aims to evaluate the performance of these alcohol-based PS-mixtures in controlling bubble size. Bubble size distribution in a two-phase air-

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* Corresponding author: rodrigo.serna@aalto.fi

liquid system was investigated to gain deeper insights into the foam stabilization mechanism by PS-mixtures. These results can be used as basis for the understanding of these new reagents in three-phase mineral froth systems in future work.

2 Experimental

2.1 Bubble size measurement

The experimental setup consists of a stirred tank, a Plexiglas® column, and a viewing chamber developed to determine the bubble size distribution for each frother mixture (Fig. 1). During the experiment, a frother solution was prepared by adding the necessary amount of chemical solution in a 1.5 L stirred-tank to achieve the target concentration for each measurement. The solution was then fed to the Plexiglas® column using a peristaltic pump, with the column initially filled with 8 L of water. To ensure homogeneity in the system, the frother solutions was circulated for 40 minutes prior to measurement. Air with flowrate of 2 L per minute was introduced at the base of the column through 5 µm opening of porous sparger. All experiments were run at room temperature (20 – 22 °C), without any temperature control.

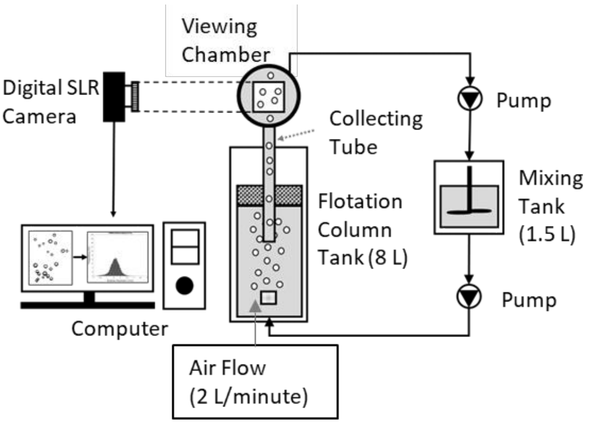

Fig. 1. Schematic diagram of laboratory column experimental setup (adapted from Nuorivaara and Serna-Guerrero [5]).

A sample collecting tube was inserted into the column at the aqueous-phase level to direct the bubbles into the viewing chamber. The viewing chamber was equipped with a red background light and a transparent glass screen. After the first minute of operations, images of the bubbles in the viewing chamber were captured every 4 seconds using a Nikon D750 digital single-lens reflex camera, with settings adjusted to an aperture of F9.0, a shutter speed of 1/20,000, and an ISO of 1000. An image processing routine programmed in MATLAB® was employed to analyze these images, determining bubble diameter and bubble size distribution. The minimum detectable bubble size with this method was 0.2 mm.

The correlation between frother concentration and bubble size was expressed in the following equation [10]:

$$D_{32} = D_l + A.\exp(-b.C) \qquad (1)$$

where D_{32} is sauter mead diameter, D_l is the minimum bubble size achieved with the frother under study, A is the range between D_{32} of pure water and D_l, b is the decay constant, and C is the frother concentration. The concentration for 95% reduction in bubble size (CCC95) value can be determined according to the following equation:

$$b = \frac{\mathrm{LN}\ 0.5}{\mathrm{CCC95}} \qquad (2)$$

2.2 Materials

The PS-mixtures evaluated in this study were composed of HPMC paired with either ethanol, pentanol, or octanol. HPMC was purchased from Sigma-Aldrich product no. 423238 with an average molecular weight of 10 kDa, methoxyl content of 29% and propylene oxide content of 7%. Pentanol and octanol were also obtained from Sigma-Aldrich (product no. 398268 and 8.20931, respectively) with a purity of ≥99%. Ethanol used was of an Aa grade from Etax, with a purity of 99.5%. Dowfroth 200 (DF200), a polyglycol based commercial frother supplied by Nasaco International LLC, served as a benchmark, assessed both in pure from and within PS-mixtures. All chemicals were used as received, without further purification. Table 1 provides details on molecular structure for the frother employed. The experiments were conducted using water purified with an Elga Purelab Option-R 7/15 down to a resistance of 15 MΩ.

Table 1. Frother used in the experiments.

Frother	Chemical Formula
Polymer/Cellulose	
HPMC	$[C_6H_7O_2(OR)_3]n$; R = H or CH_3 or $C_2H_3(OH)CH_3$
Surfactant / Short-chain alcohol	
Ethanol	C_2H_5OH
1-Pentanol	$C_5H_{11}OH$
1-Octanol	$C_8H_{17}OH$
Surfactant / Commercial frother	
Dowfroth 200 (DF200)	$CH_3(OC_3H_6)_3OH$

3 Results and Discussion

3.1 Pure chemical as frother

The steady-state bubble size distribution is a result of the surface tension of the solution and bubble interactions, such as coalescence. Both factors are influenced by the presence of frothers. Frothers reduce air-liquid surface tension, promoting the formation of smaller bubbles, while simultaneously forming a protective film around bubble surface that inhibit coalescence. The bubble size distributions for single frother species explored in this work are shown in Fig. 2, while the CCC95 value based on equation (1) and (2) are presented in Table 2.

In comparison to the pure water baseline, the addition of all frother species hereby studied modified the bubble size distribution. This trend follows the typically reported behavior of aqueous frother solutions, where the initial bimodal distribution of pure water becomes progressively unimodal, growing narrower as it approaches its critical coalescence concentration (CCC) [6, 11, 12].

Different frothers demonstrated varying capabilities of bubble size control. A unimodal distribution was achieved with as little as 1 ppm of octanol, while 4 ppm of DF200 or pentanol were necessary to produce a unimodal distribution. In contrast, ethanol required a significantly higher concentration to achieve unimodal distribution, observable only at concentration exceeding 512 ppm. At concentrations near or above the CCC the transition from a bimodal to a unimodal bubble size distribution is typically attributed to the suppression of bubble coalescence [6, 11, 12]. However, the occurrence of a unimodal distribution at concentrations below the CCC suggests a different mechanism. Below the CCC, the bubble size in flotation machines or spargers is primarily governed by coalescence, which in turn generates a secondary population of fine bubbles [12]. If the formation of such secondary population is suppressed by the stabilization of the air-liquid interface, a unimodal distribution may emerge even when coalescence still occurs. The experimental results obtained with alcohol solutions indicate that longer chain alcohols are more effective in preventing bubble break-up, enabling the formation of a unimodal distribution at lower concentrations than CCC.

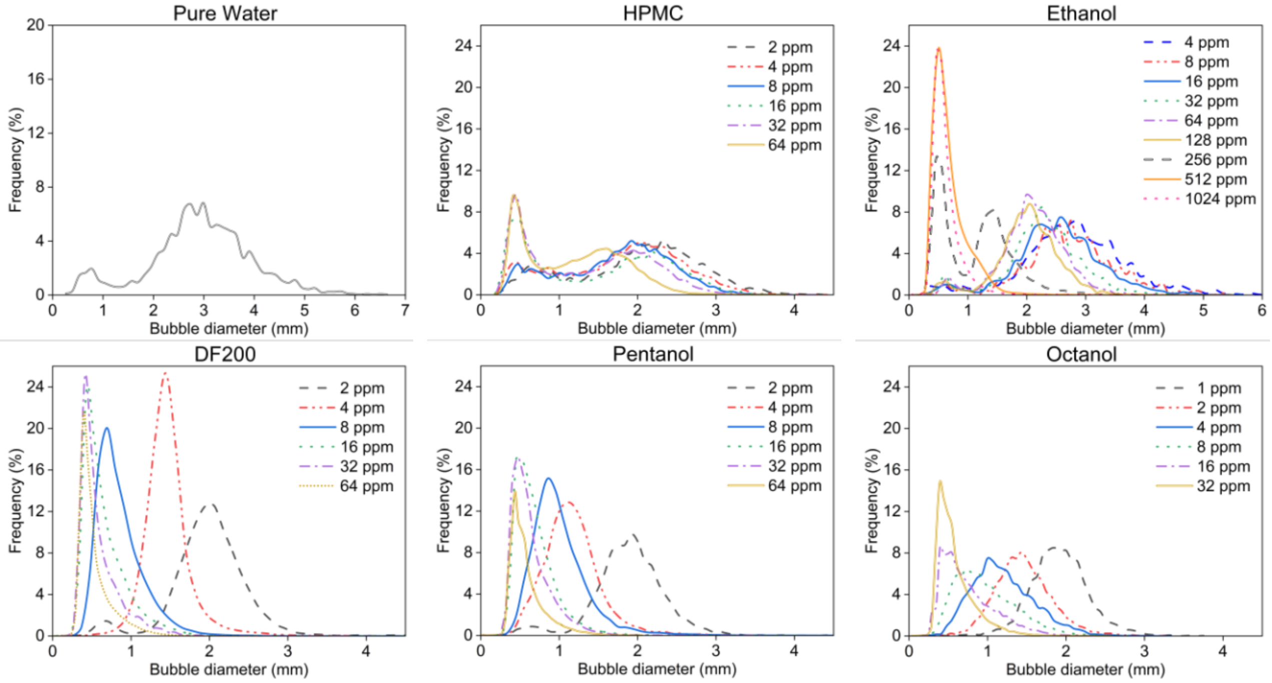

Fig. 2. Bubble size distribution at various frother concentrations.

Table 2. CCC95 value of the frothers.

Frother	HPMC	Ethanol	1-Pentanol	1-Octanol	DF200
CCC95 (ppm)	5.98	131.68	8.10	5.65	9.46

Unlike other frothers, HPMC showed an uncommon behavior, a bimodal distribution was observed even at a concentration higher than its theoretical CCC. HPMC has a large macromolecular structure that readily forms a stable protective layer around bubbles but with the caveat of a slow diffusion to the air-liquid interface [5]. Furthermore, HPMC is an amphiphilic polymer, adsorbing at the air-liquid interface according to train-tail-loop model [13]. Thus, bubbles colliding before the adsorption of HPMC will merge, generating populations of bubbles with large and fine sizes until sufficient time has elapsed for the formation of a steric protective barrier. This argument is further supported by a broad bubble size distribution observed throughout all experiments with HPMC. Even though unimodal distribution was not reached with pure HPMC, the median bubble size grew smaller as its concentration increased, in similar fashion to all other frothers.

3.2 PS-mixture as frothers

Fig. 3 presents the bubble size distribution of PS-mix of HPMC with alcohol. As seen, HPMC-pentanol produced unimodal distributions with all compositions, in contrast with pure HPMC. In PS-mix frothers, this may be explained by the rapid adsorption of the short chain alcohol at the air-liquid interface, providing some preliminary stabilization before the cellulose adsorption [14]. Furthermore, a synergistic action on the diffusion rate of PS-mixtures was also reported by Nuorivaara and Serna-Guerrero [5] which explains the absence of a significant population of large bubbles. The only exception to this behavior is the HPMC-ethanol mixture where, even at high concentrations, a bimodal distribution was observed. This suggests that the surfactant properties of ethanol are insufficient to prevent bubble coalescence before HPMC adsorbs and forms a stabilizing interfacial barrier. As a result, bubble size control is relatively weak, leading to broader bubble distribution and larger average bubble sizes compared with the other mixtures studied.

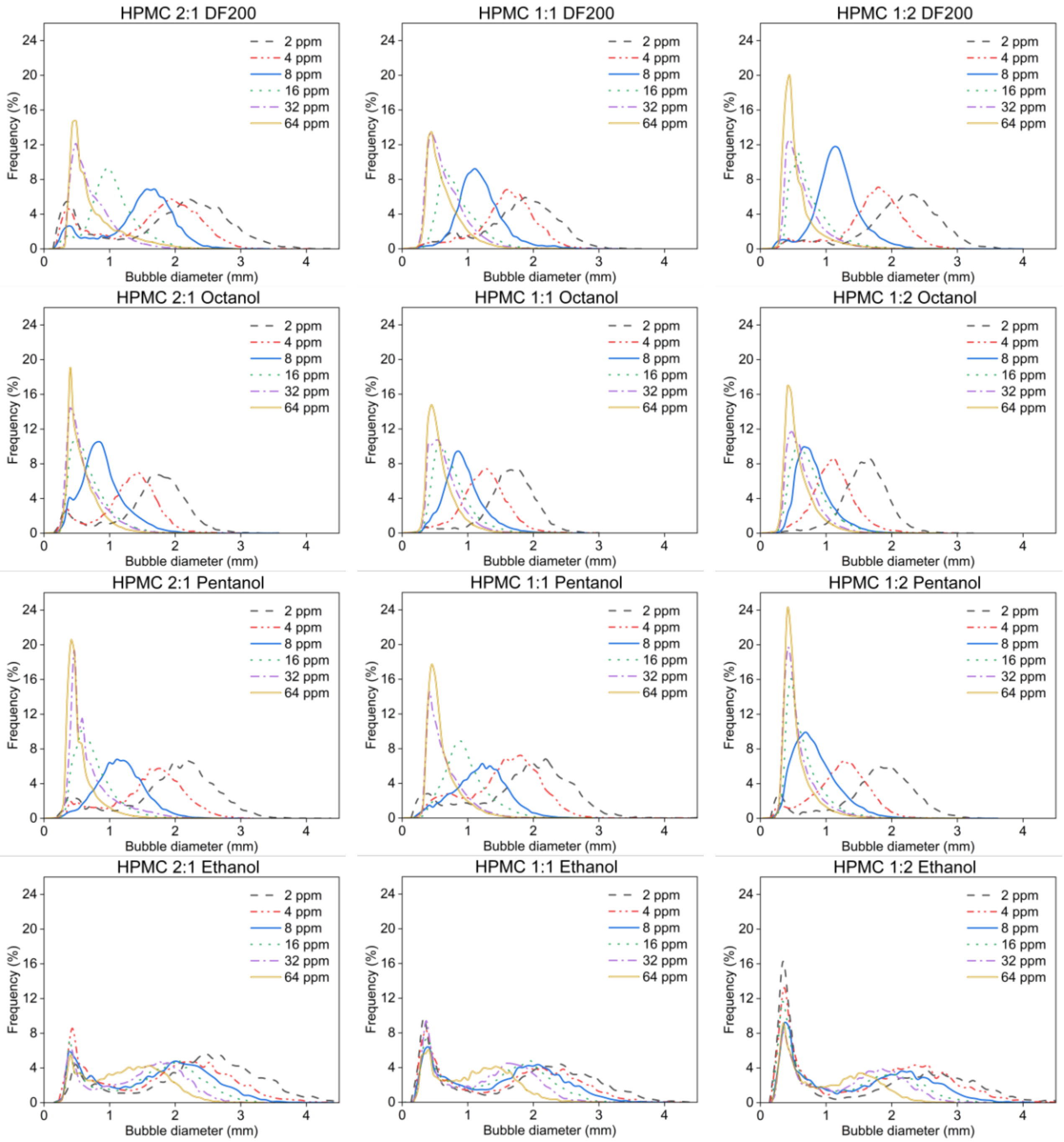

Fig. 3. Bubble size distribution of different composition HPMC and Alcohol Mixture.

The bubble size distribution results indicate the presence of two distinct phenomena at the air-liquid interface. In previous work conducted by our research team [5], evidence suggested that, although the diffusion rate of HPMC is slower than that of smaller surfactant, both molecules are present during the initial adsorption of the frother onto the bubble surface in PS-mixtures. This suggests co-adsorption at the interface, with HPMC providing a more potent coalescence prevention mechanism compared to alcohol. Consequently, at low concentrations, the bubble distribution more closely resembles pure HPMC than alcohol. Notably, while the bubble distribution at low concentrations resembles that of pure HPMC, the bubble size is significantly smaller in all mixtures, except for HPMC-Ethanol. This finding supports the earlier hypothesis that alcohol acts as an initial barrier, providing preliminary stabilization before cellulose adsorption.

On the other hand, at higher concentrations, HPMC attaches to the interfacial layer of alcohol as a sublayer [15], resulting in a coalescence prevention mechanism similar to typical surfactants but with an added protective layer. This leads to a unimodal bubble distribution with a narrow size range. These phenomena are clearly observed in mixtures of HPMC with DF200, pentanol, or octanol, where the transition from co-adsorption to sublayer formation occurs at different concentrations for each mixture. For example, this transition occurs at 16 ppm for the HPMC-pentanol mixture at a 1:1 ratio.

As previously discussed, the shift from a bimodal to a unimodal distribution is strongly correlated with the transition of HPMC from co-adsorption at the interface to forming a sublayer after interfacial of alcohol. Theoretically, a higher surfactant ratio should lower the frother concentration required for this transition, as observed in the HPMC-Octanol mixture. However, the results shown in Fig. 3 reveal a different behavior for HPMC-Pentanol and HPMC-DF200 mixture. There are two possible explanations: either the transition occurs at lower concentration than expected or despite the presence of HPMC at the interface, the protective layer it forms becomes more uniformly distributed across the bubble swarm at specific ratio and concentration, in contrast to the behavior observed with pure. A more detailed characterization and investigation of the interface would be necessary to fully explain this phenomenon, for example through a detailed examination of the interfacial structure and composition. However, such an analysis falls beyond the scope of the current manuscript.

4 Conclusions

This study investigated the potential of PS-mixture consist of HPMC and short-chain linear alcohols (ethanol, pentanol, and octanol) to control bubble size with an outlook on their use as frothers in mineral flotation. The result indicates that frother composition play critical role in controlling bubble size, with a strong correlation observed between frother composition and bubble size distribution.

Due to the combination of slow diffusion rate and the nature of amphiphilic polymer absorbed in air-liquid surface, HPMC exhibited different behavior compared to conventional frother. As a result, pure HPMC solution showed persistent bimodal bubble size distribution even at concentration exceeding the CCC. This phenomenon indicated that although large molecules of HPMC have strong ability to prevent coalescence, it is less efficient in controlling bubble size within a bubble swarm, resulting in wide distribution and larger bubble size.

The introduction of short-chain alcohol into the HPMC solution to form PS-mixture enhances the effectiveness of bubble size control. The alcohol components, having lower molecular weight and faster diffusion, aids stabilizing bubbles before HPMC forms a protective layer resulting in a smaller bubble size and narrower distribution. Each HPMC-alcohol combination exhibited distinct behavior, with specific concentrations required to achieve transition from bimodal to unimodal bubble size distribution. HPMC-pentanol and HPMC-octanol mixtures showed a promising performance, indicating their potential as more sustainable frother alternative compared to conventional petroleum derivative reagents.

Overall, this work supports the viability of PS-mixture as effective and sustainable frothers. Careful selection of polymer-surfactant pair is essential to optimize the ability of mixture to control bubble size that directly correlates with improving flotation performance.

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