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Frothers and gas dispersion: A review of the structure-property-function relationship

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Abstract: Over the past 20 years quantitative measures of frother functions have been developed to try to replace such qualitative descriptors as “weak” and “strong”. One of these metrics is the critical coalescence concentration (CCC) that quantifies a frother’s ability to reduce bubble size; another is the concentration at minimum velocity (CMV) that quantifies a frother’s ability to reduce bubble rise velocity. The experimental procedure for the two measures is briefly outlined and the measures are shown to be related. Using CMV, based on more than 50 surfactants from the two main frother families, alcohols and polyglycols, the frother structure-property-function link is investigated. The structure variables were: in alcohols, alkyl chain length, and position of the methyl branch and hydroxyl group(s); and in polyglycols, alkyl chain length, and number of propylene oxide (PO) or ethylene oxide (EO) groups. On the argument that low CMV represents the desired outcome, the main findings are: the dominant effect of alkyl chain length in both alcohols and polyglycols; that for alcohols branched-chain isomers are superior to straight chain, with the best combination being OH at the terminus and the methyl branch as far away as possible; and for polyglycols, PO-based are superior to EO-based. Interpretation of these observations included the effect of structure on the following properties: surface activity, mass transfer rate, H-bonding, and molecule packing.

Keywords: Frothers, alcohols, polyglycols, frother structure, mechanisms

1. Introduction

Since the first commercial application in Broken Hill in 1905 to re-process tailings from a gravity separation plant, flotation grew rapidly to a range of sulphide and non-sulphide minerals (Lynch et al., 2010). Accompanying this growth was the development of flotation reagents, collectors to control particle properties and, the subject of this paper, frothers to control bubble-related properties.

Frothers have three prime functions: to produce small bubbles, reduce bubble rise velocity, and stabilize froth, which together increase the efficiency of the flotation process (Klimpel and Isherwood, 1991). Initially natural products such as pine oil, frothers today are mostly synthetic aliphatic alcohols and polyglycols (Wills and Finch, 2016).

Aliphatic alcohols are typically 5 to 8 carbon atoms with general formula $R-OH$ ($R = C_nH_{2n+1}$), linear or branched. Figure 1 shows two branched members, methyl-iso-butyl-carbinol (MIBC; modern formal name: 4-methyl-2-pentanol) and 2-ethyl hexanol, and one linear alcohol, 1-hexanol, that have been widely used for decades (Crozier and Klimpel, 1989). The high concentration required with $n < 5$, and low solubility with $n > 8$ limits the range of aliphatic alcohols that can be used.

Polyglycols, most commonly polypropylene glycols (PPG, $C_nH_{2n+1}(OC_3H_6)_mOH$) and polyethylene glycols, (PEG, $C_nH_{2n+1}(OC_2H_4)_mOH$), 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, $-OC_2H_4-$). By introducing the polar ether $-O-$ linkage into the structure, the polyglycols become readily

soluble (Somasundaran and Wang, 2006), which has led to the large variety used industrially (three being illustrated in Fig. 1).

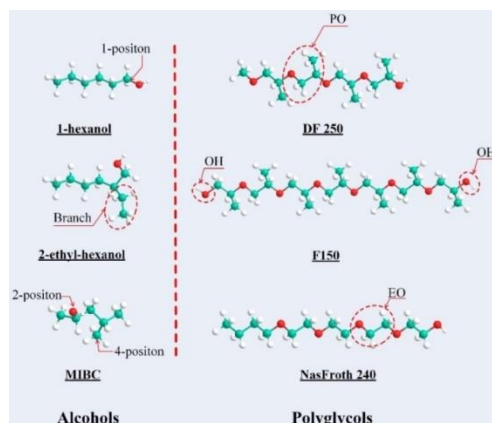


Fig. 1. Chemical structures of some commercial frothers

First available as by-products, Dow Chemical introduced a series of polypropylene glycols, Dowfroth (DF) 200, 250, 400, 1012, and 1263, the most familiar being DF250 ($\text{CH}_3(\text{PO})_4\text{OH}$, Fig. 1). While no longer available from Dow, these formulations are still widely used. Another polypropylene glycol, F150 ($\text{H}(\text{PO})_7\text{OH}$, Fig. 1) supplied by Flottec, and a polyethylene glycol, Nasfroth 240 ($\text{C}_4\text{H}_9(\text{EO})_3\text{OH}$, Figure 1) supplied by Nasaco, are also widely used.

All frothers are hetero-polar or amphipathic, that is, the chemical structure has a non-polar hydrophobic hydrocarbon (alkyl: $\text{C}_n\text{H}_{2n+1}$) part and a polar hydrophilic part, commonly $-\text{O}-$ and OH . This general understanding is sufficient to explain their surface activity, that is, adsorption at the air/water interface, as this location accommodates the hydrophilic part on the water side and the hydrophobic part on the air side of the interface.

The molecular structure will determine the magnitude of surface activity and other properties relevant to the flotation system, including: mass transfer from bulk solution and along the interface, molecule orientation and packing at the interface, and H-bonding with water molecules. Together these properties give rise to the three functions noted above. Figure 1 shows some of the structural variety: in alcohols, length of alkyl chain and position of methyl ($-\text{CH}_3$) and OH groups; and in polyglycols, length of alkyl chain, number of EO or PO groups, and PO vs. EO , where the former can be considered an EO unit with a methyl branch. Polyglycols with no alkyl chain ($n = 0$), e.g., F150 (Fig. 1), give structures with two OH s sitting at the terminal positions, a structure also found in diols (i.e., alcohols with two OH s).

Surface activity, determined by some measure related to the extent of surface tension depression (or increase in surface pressure), has been reported for some of these structures. Alcohols have received the widest study (among the most recent: Joos and Serrien, 1989; Chang et al., 1992; Firooz and Chen, 2012; Fong et al., 2015; Basařová, et al., 2016). Fong et al. (2015) include data for standard free energy of adsorption, ΔG_{ads} , which is one measure of surface activity. Where in this paper we have covered the same structures the ΔG_{ads} data are included in the tables, along with data on area occupied per molecule determined at close packing, A_{min} , taken from the same source. The data show, for example, that increasing chain length has a significant effect on increasing surface activity (making ΔG_{ads} increasingly negative), and that OH in the terminus position gives higher surface activity than in the central position, findings mirroring those for other surfactants (Cosgrove, 2005; Frank et al., 2007).

Other measures of surface activity are the Henry constant (K_H) and the Langmuir constant (K_L) (Posner et al., 1952; Hommelen 1959; Mulley and Metcalf, 1962; Carless et al., 1964; Joos and Serrien, 1989; Lee et al., 2003). At low concentration, appropriate for the situation with frothers, the Langmuir isotherm can be derived from the Henry isotherm, which is the form of Gibbs adsorption equation for dilute solutions. The Langmuir constant can then be approximated by $K_H = \Gamma_m K_L$ where Γ_m is maximum surface concentration. In general, as Γ_m varies little for surfactants, both K_H and K_L provide a measure of the surface activity, the larger the values the greater the surface activity. Chang and

Franses (1995) showed that K_L increases with alkyl chain among alcohols, diols and PEGs, increases with increasing EO in PEG, and decreases when OH moves to the center in both alcohols and diols. Other than this reference, we find no further surface activity data for PPG and PEG. Less direct evidence can be gauged from Mulley and Metcalf (1962) and Bauduin et al. (2005) who showed the effect of the alkyl chain length in polyglycols mirrored that in alcohols; and inferring from Bauduin et al. (2005), who noted the greater effect of PPG compared to PEG on lowering the critical micelle concentration of sodium dodecyl sulphate, the propoxy group is more surface active than the ethoxy group, which agrees with the former being more hydrophobic due to the presence of the methyl branch.

Authors have argued structural effects on mass transfer resulting from H-bonding. This includes: the impact of a methyl branch shielding the hydrophilic entity from H-bonding, which decreases H-bonding with water (i.e., inter-molecule H-bonding) and thus increases mass transfer rate (Hacker et al, 2009; Patrick, 2013; Herzberger et al., 2016); and of the role of intra-molecule H-bonding (i.e., between two hydrophilic entities in the same molecule) in reducing inter-molecule H-bonding, which again increases the mass transfer rate (Kuhn, 1952; Knauth and Sabbah, 1990; Dziembowska and Szczodrowska, 1994; Zorębski and Zorębski, 2014). Structural effects on orientation and packing at the interface have been debated for alcohols (Bauer and Pollack, 1935; Sobocinski and Pemberton, 1992; Fukuhara et al., 2014, Fong et al., 2015; Tan and Finch, 2016a, Tan and Finch, 2016c, Jahur et al., 2017), and for polyglycols (Stauffer, 1968; Thurow and Geisen, 1984; Cox et al. 1999; Gélinais et al., 2005; Forgiarini et al., 2010), for example, whether the -O- linkage causes the molecule to lie flat along the interface. Reduced packing because of an inductive effect due to the proximity of a methyl branch enlarging the effective size of the hydrophilic group has also been mooted (Singh and Yadav, 2010). These factors need to be considered in understanding the properties and thus functions of frothers.

2. Quantifying frother functions

To correlate against structural effects, we need quantification of the three frother functions. In this paper, we consider primarily one, the reduction in rise velocity, with some cross-reference to a second, reduction in bubble size. In both cases there now exist sets of quantitative data based on systematic variation in structure of the two main frother classes, alcohols and polyglycols. In bubble size reduction studies, it is observed that the mean bubble size (usually the Sauter mean, D_{32}) decreases to a minimum at a certain transition frother concentration (e.g., Finch and Dobby, 1990), as illustrated in Fig. 2. Cho and Laskowski (2002) interpreted this transition concentration as corresponding to complete suppression of coalescence and introduced the term “critical coalescence concentration” (CCC). This has proved a useful quantification of a frother’s ability to reduce bubble size: the lower the CCC, the more effective the frother. Cho and Laskowski (2002) presented a graphical method of determining CCC (included in Fig. 2), while others have used fitting routines (Nesset et al., 2007, Gomez et al., 2014). Zhang et al. (2012) determined CCC for a range of alcohols and polyglycols (Table 1). Among the findings they showed that CCC decreased for alcohols and polyglycols as alkyl chain length was increased, and for polyglycols as number of PO groups or EO groups was increased.

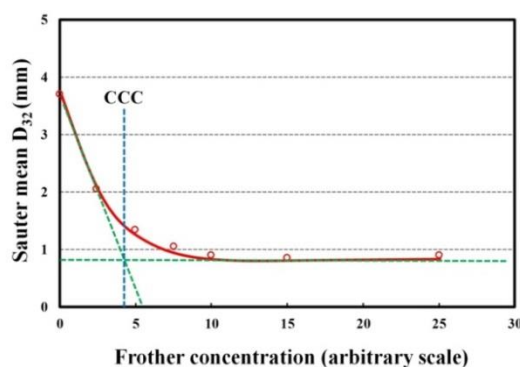


Fig. 2. Reduction in bubble size as a function of frother concentration (included is the CCC estimation procedure of Cho and Laskowski, 2002)

Table 1. CMV¹, CCC² and surface area per molecule (A_{min})³ and standard free energy of adsorption (ΔG_{ads}^0)³ for some alcohols, diols and polyglycols as a function of carbon (n) number. 1. Tan and Finch (2016a; 2016 b); 2. Finch and Zhang, 2014; 3. Fong et al., 2015

Family	Name	$A_{min} \times 10^2$ (nm)	ΔG_{ads}^0 (kJ/mol)	Structure		CMV (mM)	CCC (mM)	
				n	m or l			
Alcohols	1-butanol	29	-11.3	4	---	20	0.85	
	1-pentanol			5	---	2.3	0.29	
	1-hexanol			6	---	0.27	0.11	
	1-heptanol			7	---	0.06	0.072	
Diols	1,2-propanediol			3	---	---	---	
	1,2-butanediol			4	---	20	---	
	1,2-pentanediol			5	---	1.8	---	
	1,2-hexanediol			6	---	0.18	---	
PPG	Propylene glycol	methyl ether		1		---	0.48	
				3	1	3	0.25	
				4		0.5	0.16	
				1		3.5	0.18	
	Dipropylene glycol	propyl ether			3	2	0.14	0.094
					4		0.024	0.066
					1		0.2	0.073
					3	3	0.01	0.045
Tripropylene glycol	butyl ether			4		0.0014	0.029	
				2		20	0.38	
				3	1	6.5	0.22	
				4		1.1	0.12	
PEG	Ethylene glycol	methyl ether		1		25	0.70	
				2		10	0.36	
				3	2	1.8	0.21	
				4		0.4	0.11	
	Diethylene glycol	hexyl ether			6		0.025	0.068
					1		7	0.68
					2	3	1.4	0.34
					4		0.08	0.11
Triethylene glycol	ethyl ether			2		25	0.70	
				3		10	0.36	
				4		0.4	0.11	
				6		0.025	0.068	

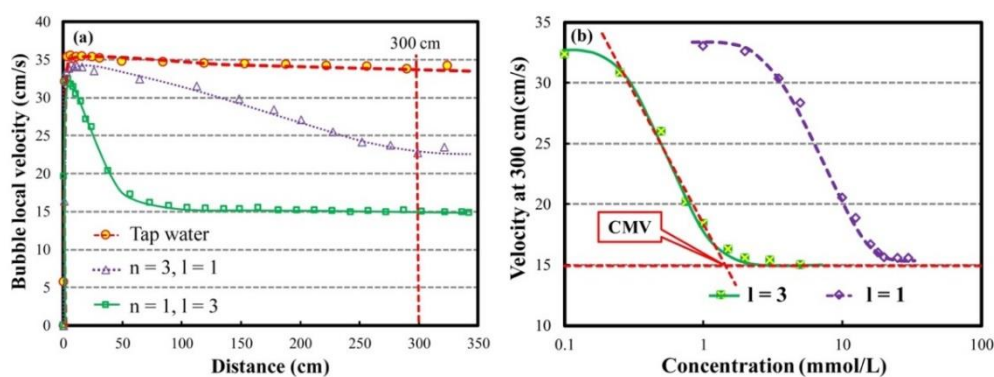


Fig. 3. a) Bubble velocity profiles in the presence of two PEGs at 0.02 mmol/dm³; and b) velocity at 300 cm as a function of concentration for two PEGs ($n = 2$)

In studies related to reduction in bubble rise velocity, Tan and Finch (2016a) introduced the parameter “concentration at minimum velocity” (CMV). To determine, they measured the local velocity of a single rising bubble (ca. 1.45 mm diameter) as a function of distance travelled (bubble velocity profile) and then increased concentration till the minimum velocity at 300 cm was attained, that is, CMV. This size of bubble is strongly affected (slowed down) by presence of surfactant (Clift et al., 1978) and is also a size in the usual range for flotation, ca. 0.5 to 2.5 mm (Finch and Dobby, 1990). Example plots are shown in Fig. 3: a) bubble velocity profile with velocity at 300 cm indicated, and b) bubble velocity at 300 cm as a function of concentration with CMV indicated. Like CCC, we can

interpret that the lower the CMV the more effective the frother, in this case in slowing bubble rise. The CMV has been determined for a range of surfactant structures from the two frother families (Tables 1 and 2) (Tan and Finch, 2016a, 2016b, 2016c, Tan et al., 2016d; Tan et al., 2016e) including for 1, ω -diols (ω is position of second OH with the first OH at position 1). Among the findings Tan and co-workers showed that CMV decreased for alcohols and polyglycols as alkyl chain length increased, and for polyglycols as number of PO groups or EO groups was increased, that is, similar findings as for CCC; in addition, they also showed the significant impact of the relative position of the OH and methyl groups in branched-alcohols. These findings are outlined in more detail below.

Table 2. CMV, A_{\min} and ΔG_{ads}^0 for aliphatic alcohols as a function of methyl and hydroxyl position, and for diols as function of second OH position

Name	Position		CMV (mM)	$A_{\min} \times 10^2$ (nm)	ΔG_{ads}^0 (kJ/mol)
Alcohols	-CH ₃	OH			
Six carbon					
2-methyl-1-pentanol		1	0.23		
2-methyl-2-pentanol	2	2	0.4	38	-12.8
2-methyl-3-pentanol		3	0.65		
3-methyl-1-pentanol		1	0.14		
3-methyl-2-pentanol	3	2	0.37	37	-13.4
3-methyl-3-pentanol		3	0.6	40	-15.4
4-methyl-1-pentanol		1	0.11	32	-13.3
4-methyl-2-pentanol	4	2	0.33	38	-14.1
1-hexanol		1	0.27	29	-14.7
2-hexanol	---	2	0.3	35	-13.5
3-hexanol		3	0.36	35	-13.0
Five carbon					
2-methyl-1-butanol	2	1	1.95		
2-methyl-2-butanol		2	3.5		
3-methyl-1-butanol	3	1	1.25		
3-methyl-2-butanol		2	3.2		
1-pentanol		1	2.3	29	-11.3
2-pentanol	---	2	2.65	34	-10.8
3-pentanol		3	3.05		
Diols	1 st OH	2 nd OH			
Six carbon					
1,2 - hexanediol		1	0.18		
1,5 - hexanediol	1	5	0.4		
1,6 - hexanediol		6	2.5		
Five carbon					
1,2 - pentanediol		1	1.8		
1,4 - pentanediol	1	4	---		
1,5 - pentanediol		5	200		

3. Some correlations for CMV

Fig. 4 shows the dependence of CMV on alkyl chain length for (a) 1-alcohols and 1, 2-diols and (b) polyglycols plotting log CMV vs. carbon n number. It shows a series of self-similar linear plots indicating a significant effect, CMV decreasing by near one-order of magnitude for unit increase in n,

and that PO is more effective than EO in reducing CMV, the more so as alkyl chain length increases.

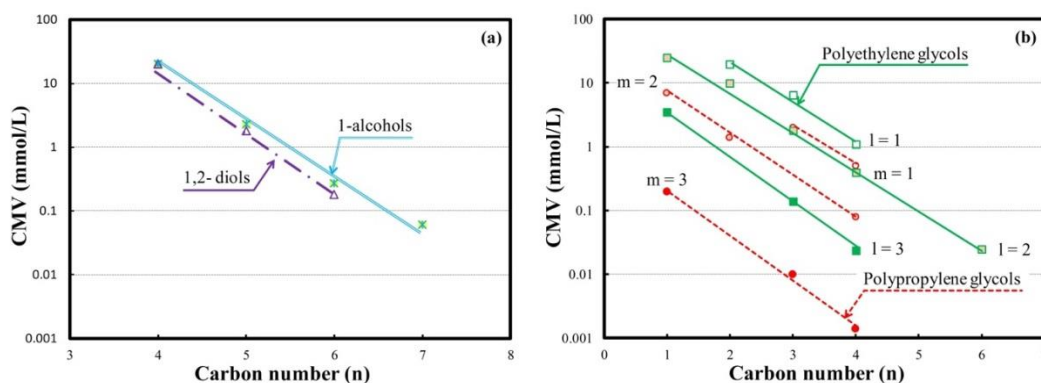


Fig. 4. Effect of alkyl chain length on CMV: (a) for alcohols, and (b) as a function of PO (m) number or EO (l) number in PPG (dashed line) and PEG (full line) families

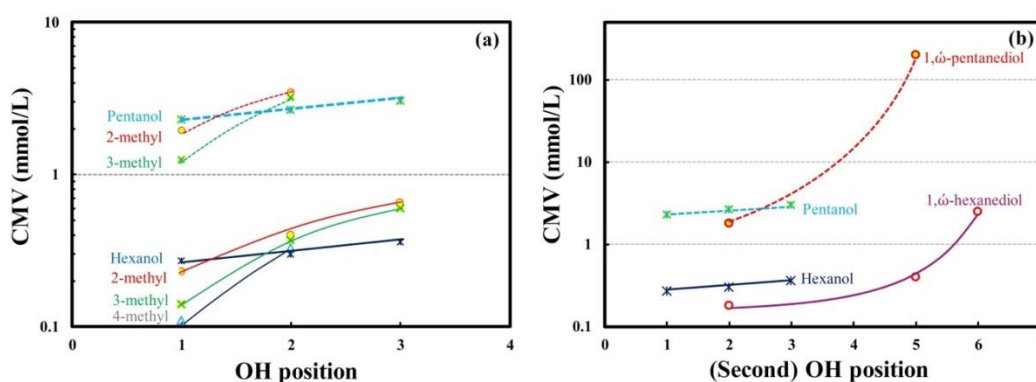


Fig. 5. Effect on CMV of position: (a) OH and methyl branch in alcohols, and (b) second OH in diols (trendline for pentandiol is based on that for hexandiol)

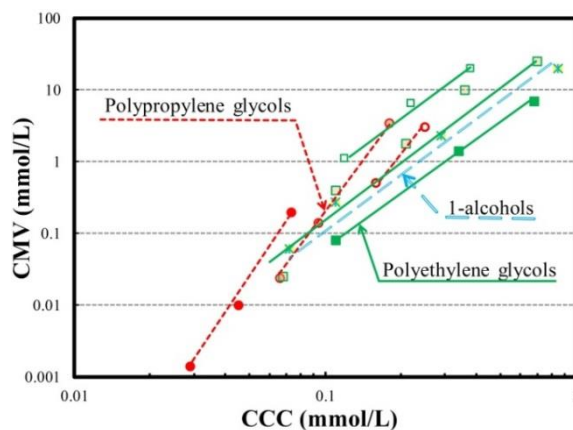


Fig. 6. Relationship between CMV and CCC for 1-alcohols and polyglycols

Figure 5 explores the effect on CMV of (a) the position of OH relative to the methyl group in alcohols, and (b) the position of the second OH in 1, ω-diols compared to the effect of OH position in 1-alcohols. Figure 5a (and b) shows that OH position in straight chain alcohols has a modest and different trend compared to branched alcohols. In branched alcohols, the effect of OH position on lowering CMV is significant and increases as the methyl group moves further away from the OH, that is, the greatest lowering of CMV occurs when OH is in the 1 position with the methyl group as far away as possible (e.g., position 4 in six-carbon alcohols). The effect of OH position in diols is even more notable; as the second OH is moved from position 2 (i.e., the carbon next to the first OH) to the

other terminus the CMV increases significantly, for example, for the five-carbon diol by 2 orders of magnitude.

Figure 6 shows the excellent correlation between CMV and CCC: for 1-alcohols and polyethylene glycols the trends are the same, and for polypropylene glycols the trend is sharper. These correlations indicate that at least in some cases the mechanisms proposed to explain the effect of structure on CMV, that is, the effect on slowing bubble rise, also apply to CCC, that is, the effect on bubble size reduction. In the next section we consider mechanisms.

4. Mechanisms

4.1 Surfactant and the slowing of bubble rise

Surfactant (frother) molecules adsorb and orient at the air/water interface (bubble surface) to minimize contact between the hydrophobic groups and water, leaving the hydrophilic part exposed on the water-side of the interface and the hydrocarbon chain on the air-side. The relative magnitude of hydrophobic to hydrophilic components controls properties such as surface activity, surface concentration and interaction with the environment, for example, through H-bonding (Lum et al., 1999; Fainerman, 2002; Fong et al., 2015).

We now have to consider what occurs after bubble release, that is, under dynamic (time-dependent) conditions. At the moment the bubble detaches, the initially 'clean' surface is progressively 'contaminated' with surfactant as the bubble rises, which is revealed by the decrease in velocity that reflects an increase in drag. The effect is classically explained by the following reasoning (Levich, 1962, Dukhin et al., 1995; Nguyen and Schulze, 2004). Flow of the liquid layer adjacent to the bubble surface transports surfactant to the rear of the bubble, thus creating a surface concentration gradient (Fig. 7). This increase in surface concentration (packing) towards the bubble rear gives rise to a positive gradient in the surface tension in the opposite direction (i.e., surface tension increases towards the front of the bubble). The surface tension gradient (STG) induces flow that opposes the flow of the liquid over the bubble surface thus increasing drag and slowing the bubble rise. The flow induced by STG is known as the Marangoni (or Gibbs-Marangoni) effect. Once dynamic equilibrium is reached, that is, the adsorption rate of surfactant (primarily at the bubble front) equals the desorption rate (primarily from the rear), the bubble attains its minimum (equilibrium or terminal) velocity. For the 1.45 mm diameter bubble used to determine CMV, this velocity is ca. 15 cm/s (Clift et al., 1978; Nguyen and Schulze, 2004). This STG-based mechanism is adopted here – other reasoning is that the hydrophilic groups exposed on the water side of the air/water interface increase the viscosity of the adjacent liquid layer through H-bonding (i.e., increase surface viscosity) (Nguyen and Schulze, 2004); or that the H-bound water increases the apparent mass of the rising bubble (Cappuccitti and Finch, 2008). Regardless, the surfactant properties that control the magnitude of the retarding force will include the following: surface activity, mass transfer rate from bulk to and along the bubble surface, and molecule packing density.

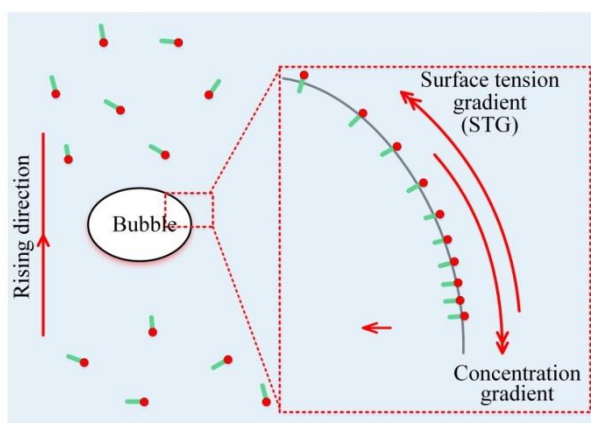


Fig. 7. Illustration of frother transport on bubble surface and development of surface tension gradient

While all these properties can be expected to interact to give rise to the value of CMV (and the other frother functions), in the following we identify cases where one property appears dominant.

4.2 Mass transfer and H-bonding

The following arguments are usually advanced with regard to mass transfer from the bulk but apply equally well to mass transfer along the bubble surface; that is, factors that control mass transfer from the bulk to the surface will also control transport to the bubble rear.

Perhaps the most prominent example where mass transfer appears dominant controlling CMV is the marked effect of the second OH position in 1, ω -diols (Fig. 5b). Mass transfer rate is influenced by the molecule H-bonding with water molecules which acts to slow transport. In the case of diols, there is also opportunity for H-bonding between the two OH groups (i.e., intra-molecule H-bonding) which reduces the H-bonding with water molecules (inter-molecular H-bonding) (Dziembowska and Szczodrowska, 1994; Kuhn, 1952) (Fig. 8a). Intra-molecular H-bonding is greatest when the two OH are closest together (i.e., in 1, 2-diols) and decreases as the second OH moves to the other terminus and thus H-bonding with water (for both OHs) increases. This trend to increased H-bonding with water which slows mass transfer helps explain the increase in CMV as the second OH is moved away from the first (i.e., to 1, 5-pentandiol and 1, 6-hexanediol, Fig. 5b).

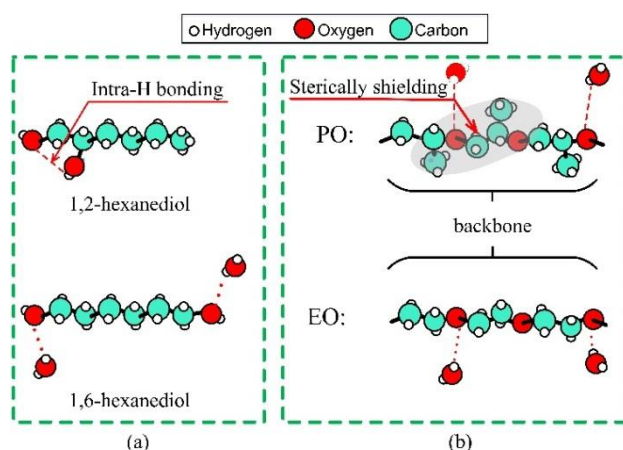


Fig. 8. Illustration of H-bonding effect on mass transfer rate for: (a) diols and (b) PO- vs EO-polyglycols

An H-bonding effect on mass transfer may also contribute to the greater ability of PO- vs. EO-polyglycols (PPG vs. PEG) to lower CMV (Fig. 4b). The difference between EO and PO is the latter has a methyl branch. This acts to 'shield' the polar -O- reducing H-bonding with water thus permitting the PPG to have higher mass transfer rate than the PEG (Hacker et al, 2009, Patrick, 2013; Herzberger et al., 2016) (Fig. 8b) and thus, in this instance, greater ability to reduce CMV.

4.3 Surface concentration and molecule packing

Molecule orientation and packing at the air/water interface strongly affect surface properties (van Duynhoven et al., 2005). In the present context, the greater the packing density (surface concentration) at the bubble rear, it can be argued, the greater the STG, and thus the greater the drag slowing bubble rise resulting in a lower CMV. This orientation/packing effect is illustrated for alcohols (Fig. 9). Fig. 9a shows that the more vertical orientation (in regard to the bubble surface) of 1, 2-hexandiol compared to 1, 6-hexanediol allows for denser packing, which corresponds to the lower CMV of the 1, 2-hexandiol (Fig. 5b). This packing effect and the mass transfer argument presented above combine to give the marked effect of position of the second OH in 1, ω -diols.

Figure 9b compares two straight chain alcohols, 1-hexanol and 3-hexanol, and again the more vertical orientation of the former enables higher packing density (at the bubble rear) which gives a higher STG and thus corresponds to the lower CMV of 1-hexanol (Figs. 5a, 5b). The effect of position of the OH in the straight chain alcohols, however, is notably less than for the branched chain alcohols (Fig. 5a). Although packing is shown to be less for 3-hexanol than 1-hexanol the surface is well covered due to the orientation of the hydrocarbon chain which may mitigate the effect of packing on

STG. For the branched chain alcohols (Fig. 9b) the chain is shown remaining vertical as the methyl branch position is changed: as the methyl group approaches the OH (2-methyl-1-pentanol) the effect is to 'wedge' the molecules further apart compared to 4-methyl-1-pentanol, which does correspond to the lower CMV of the latter. Compared to 3-hexanol the hydrophobic coverage may be less with 4-methyl-1-pentanol, which might contribute to the more marked effect on CMV with the branched alcohols compared to the straight chain alcohols. An additional feature in the branched alcohols is the effect of the proximity of the methyl group to the OH; the closer to the OH the greater the 'inductive' effect which acts to increase the size of the electron cloud (sphere of influence) around the OH (see dashed arrow in Fig. 5), that is, increases the area the OH effectively occupies and lowers packing density (Singh and Yadav, 2010). This inductive effect may further strengthen the impact of the relative position of methyl to OH in the branched alcohols.

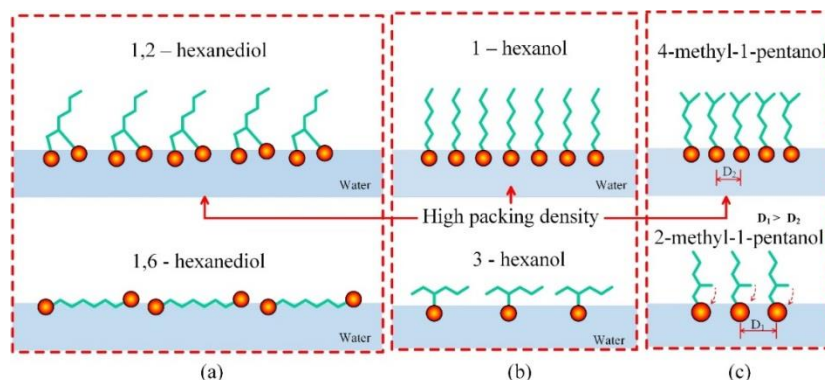


Fig. 9. Effect of orientation on packing density: (a) second OH position in diols; (b) OH position in alcohols; (c) methyl branch position in branched alcohols

Data in support of these suggested orientation/packing arrangements for alcohols comes from recent work of Fong et al. (2015). From equilibrium surface tension measurements, they calculated the molecule cross-sectional area at monolayer coverage (i.e., the value at close packing, or minimum possible area, A_{\min}), as recorded in Tables 1 and 2. For the 1-alcohols A_{\min} is the same (29×10^{-2} nm), as expected as all orient vertically, and moving the OH to the centre increases A_{\min} (e.g., for 3-hexanol to 35×10^{-2} nm) as the molecule's hydrophobic chain adopts a more parallel arrangement (with respect to the bubble surface). The branched chain alcohols all have higher A_{\min} compared to the 1-alcohols (up to 40×10^{-2} nm for 3-methyl-3-pentanol), as anticipated, and in at least one case, comparing 4-methyl-1-pentanol ($A_{\min} = 32 \times 10^{-2}$ nm) to 4-methyl-2-pentanol $A_{\min} = 38 \times 10^{-2}$ nm), there is an effect on the area that corresponds to the strong effect on CMV (Fig. 5a).

4.4 Surface activity

Surface activity is the result of some of the factors already considered, such as relative magnitude of hydrophobic to hydrophilic groups, packing density, and interaction with the environment. The advantage is surface activity can be measured. From Fong et al. (2015), values of ΔG_{ads}° (ΔG_2° in the original paper) are recorded in Tables 1 and 2 for the structures examined here.

Figure 10a shows the dependence of CMV on ΔG_{ads}° (as the absolute value) for alcohols, where x stands for position of either the methyl group or OH group. The expectation is that as ΔG_{ads}° increases (negatively), the magnitude of STG will increase and the CMV decrease. The trends fall into three groups. For group 1, role of chain length in straight chain alcohols regardless of the position of OH (i.e., the 1-alcohols and 2-alcohols), this expected trend is most evident. For group 2, the straight chain alcohols when position of OH is altered (x -pentanol and x -hexanol) and the one example of branched alcohol when position of the methyl group is changed for a fixed position of OH (x -methyl-2-pentanol), we identify the same, but weaker trend. For group 3, where the OH position is changed for a fixed position of the methyl group (3-methyl- x -pentanol and 4-methyl- x -pentanol), interestingly, the trend reverses.

This 'weakening to reversal' of the trend is mirrored in the trends in CMV against the area per molecule, A_{\min} (Fig. 10b). For group 1, the A_{\min} for 1-alcohols is constant independent of chain length, and for the 2-alcohols, while A_{\min} is larger (reflecting the orientation, Fig. 9b), the subsequent effect of chain length is negligible. In this regard A_{\min} , it is argued, plays no role modifying the effect of ΔG_{ads}° for group 1. For group 2 there is now a change in A_{\min} , all three members giving a similar weak trend (similar slope). Finally, for group 3, there is now a strong effect of A_{\min} on CMV. Putting these observations together, it seems that the impact of surface activity is moderated by the role of packing.

As a summary, it is evident that several properties need to be considered to explain the effect of structure on CMV, and that metrics based on equilibrium conditions, such as ΔG_{ads}° , need modifying to apply to the dynamic conditions under which frothers perform.

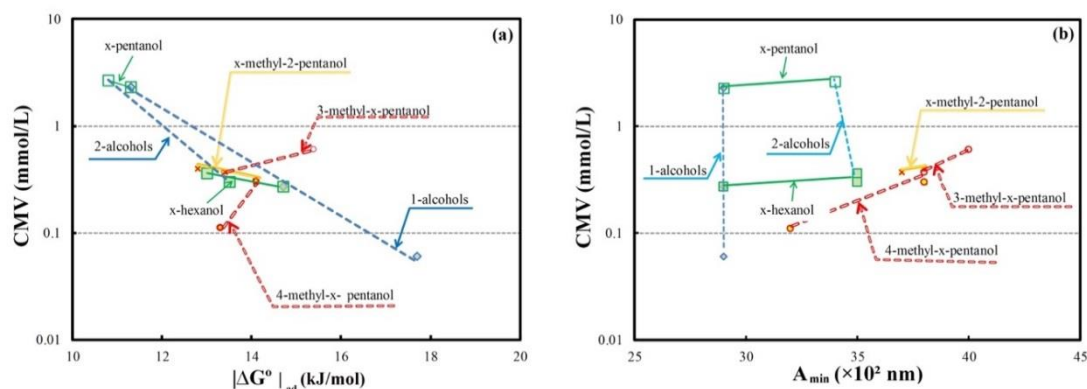


Fig. 10. Log CMV as a function of: (a) standard free energy of adsorption, and (b) minimum surface area per molecule

5. Conclusions

Reviewing data from systematic studies on two frother families, alcohols and polyglycols, has identified correlations between molecular structure and the slowing of bubble rise as measured by the concentration at minimum velocity, CMV. Examining mechanisms based on the role of surface tension gradient (STG) in controlling drag on the rising bubble, shows that the following at least need to be incorporated: the role of H-bonding in mass transfer along the bubble surface, packing density at the bubble rear, and surface activity, the latter using recent data for the standard free energy of adsorption.

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