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Determination of Critical Coalescence Concentration and Bubble Size for Surfactants Used as Flotation Frothers

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ABSTRACT: The paper presents a correlation between the critical coalescence concentration and hydrophilic−lipophilic balance/molecular weight ratio for surfactants used as flotation frothers. The correlation is based on experimental data published in literature. The obtained empirical equation allows one to accurately predict the critical coalescence concentration based only on the chemical structure of the frother. It was found that another empirical equation, based on one adjustable parameter called the frother concentration constant, can be used to predict the Sauter mean bubble size d_{32} for different flotation frothers.

1. INTRODUCTION

Frothers play a crucial role in mineral flotation. The influence of frothers on the bubble size and flotation process has been studied by many authors.[1−5] Frothers reduce bubble size and prevent bubble coalescence and stabilize the froth. The surfactants used as flotation frothers are characterized by different parameters. Foaming ability is described by the dynamic foamability index (DFI)[6,7] and dynamic stability factor.[8] The ability to prevent bubble coalescence can be characterized by the critical coalescence concentration (CCC).[1] The relation between DFI and CCC allows classification of frothers into selective and powerful.[9,10]

The influence of frother concentration on bubble size, expressed as the Sauter mean diameter d_{32}, is presented in Figure 1. According to Figure 1, as Cho and Laskowski[1] noted,

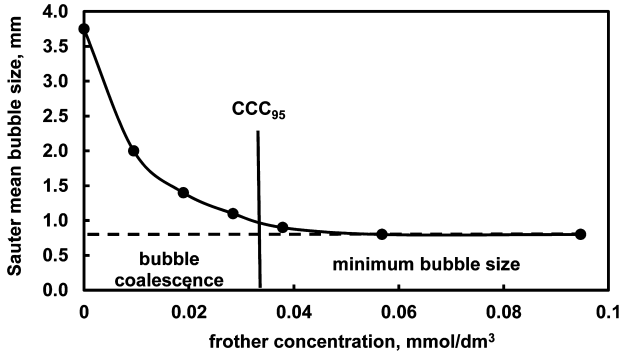

Figure 1. Effect of commercial frother DF250 concentration on Sauter mean bubble size d_{32}. Data are from Finch et al.[4] CCC_{95} denotes 95% Sauter mean bubble size reduction compared to mean bubble size in water only.

the Sauter mean bubble size decreases with frother concentration and coalescence is prevented at the critical coalescence concentration (CCC). This trend is observed for all flotation frothers providing different values of CCC. The critical coalescence concentration is very useful, though difficult to estimate. It has different values depending on the definition of CCC.[4,11] CCC_x indicates CCC level for mean bubble size reduction in comparison to bubble size in water only: $CCC_x = (d_{max} - d_{min})(1 - x/100) + d_{min}$. CCC_0 means that no frother is used and bubbles reach the maximum size (d_{max}); CCC_{50} indicates that only 50% of bubble size is reduced; and CCC_{100} is where bubble coalescence is completely prevented and the bubble size is minimum (d_{min}).

The properties of each surfactant can be characterized by the hydrophilic−lipophilic balance (HLB). Its value depends on the chemical groups in the considered molecule[12,13] and can be estimated from the following formula:

$$\mathrm{HLB} = 7 + 1.3(\mathrm{O}) + 1.9(\mathrm{OH}) - 0.475(\mathrm{C}_x\mathrm{H}_y) \quad (1)$$

where O and OH are numbers of hydrophilic oxygen and hydroxyl functional groups, respectively. In eq 1 C_xH_y stands for numbers of lipophilic (or hydrophobic) −CH, $-CH_2-$, CH_3-, and =CH− groups. Table 1 shows structural properties of three selected frother families: aliphatic alcohols (C_n), poly(propylene glycol) alkyl ethers (C_nP_m), and poly(propylene glycol)s (P_m).

Table 1. Frothers with Number of Lipophilic and Hydrophilic Functional Groups

		no. of functional groups		
frother family	chemical formula	C_xH_y	O	OH
aliphatic alcohols, C_n	$C_nH_{2n+1}OH$	n	0	1
poly(propylene glycol) alkyl ethers, C_nP_m	$C_nH_{2n+1}(OC_3H_6)_mOH$	$n + 3m$	m	1
poly(propylene glycol)s, P_m	$H(OC_3H_6)_mOH$	$3m$	$m - 1$	2

A relationship between the critical coalescence concentration (CCC), hydrophilic−lipophilic balance (HLB), and molecular weight (MW) was studied by Laskowski et al.[9] and recently by Zhang et al.[5] However, no general correlation between HLB and CCC was given. Zhang et al.[5] showed that each frother family exhibits a relationship between HLB and CCC, which depends on the number of alkyl (n) and propylene oxide (m) groups. In this case there was no apparent relationship between CCC, HLB, and MW.

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In this paper, a correlation between the critical coalescence concentration, hydrophilic−lipophilic balance, and molecular weight for different flotation frothers, based on experimental data published in literature, was studied. The obtained equation was compared with experimental data and allowed one to predict the critical coalescence concentration for surfactants used as flotation frothers. A different equation was used to predict a relationship between Sauter mean bubble size d_{32} and frother concentration C based only on one adjustable parameter.

Table 2. Frother Properties[a]

	n	m	HLB	MW (g/mol)	CCC_{95} (mmol/dm^3)
Aliphatic Alcohols C_n					
1-propanol	3		7.48	60	3.933
1-butanol	4		7	74	0.851
1-pentanol	5		6.53	88	0.284
1-hexanol	6		6.05	102	0.108
1-heptanol	7		5.58	116	0.069
1-octanol	8		5.1	130	0.062
2-propanol	3		7.48	60	5.117
2-butanol	4		7	74	1.041
2-pentanol	5		6.53	88	0.341
2-hexanol	6		6.05	102	0.108
2-heptanol	7		5.58	116	0.078
2-octanol	8		5.1	130	0.062
3-pentanol	5		6.53	88	0.466
3-hexanol	6		6.05	102	0.127
Propylene Glycol Ethers C_nP_m					
propylene glycol methyl ether	1	1	8.28	90	0.489
propylene glycol propyl ether	3	1	7.33	118	0.246
propylene glycol butyl ether	4	1	6.85	132	0.159
di(propylene glycol) methyl ether	1	2	8.13	148	0.176
di(propylene glycol) propyl ether	3	2	7.18	176	0.091
di(propylene glycol) butyl ether	4	2	6.7	190	0.063
tri(propylene glycol) methyl ether	1	3	7.98	206	0.073
tri(propylene glycol) propyl ether	3	3	7.03	234	0.047
tri(propylene glycol) butyl ether	4	3	6.55	248	0.028
Poly(propylene glycol)s P_m					
di(propylene glycol)		2	9.25	134	0.396
tri(propylene glycol)		3	9.125	192	0.172
tetra(propylene glycol)		4	9	250	0.088
poly(propylene glycol) 425		7	8.625	425	0.014
poly(propylene glycol) 725		12	8	725	0.010
poly(propylene glycol) 1000		17	7.375	1000	0.008
Commercial Frothers					
FX120-01	6		6.05	102	0.108
DowFroth 250 DF250	1	4	7.83	264	0.038
DowFroth 1021 DF1021	1	6.7	7.48	420	0.014
FX160-05	3	2.5	7.11	207	0.072
FX160-01	1	3.8	7.86	251	0.048
F150		7	8.625	425	0.014
F160	4	2.5	6.63	217	0.037

[a]Data from Zhang et al.[5].

2. CRITICAL COALESCENCE CONCENTRATION VERSUS HYDROPHILIC−LIPOPHILIC BALANCE/MOLECULAR WEIGHT RATIO

Table 2 shows properties of aliphatic alcohols, poly(propylene glycol) alkyl ethers, poly(propylene glycol)s, and commercial frothers characterized by number of alkyl (n) and polypropylene (m) groups, calculated values of HLB, and experimental CCC_{95} values of Zhang et al.[5] The experiments were carried out in a 0.8 m^3 mechanical flotation cell. CCC_{95} indicates that 95% of the Sauter mean bubble size is reduced in comparison to bubble size in water only. It can be seen that HLB values decrease with increasing number of lipophilic groups, and for all frothers considered in this work, HLB values are higher than 5.1. Frothers with lower values of HLB and CCC are more hydrophobic because they are less effective in reducing the hydrophobic force, which is an attractive force in bubble coalescence.[14] On the other hand, Laskowski et al.[9] noted that a powerful frother produces more stable foam and has low values of CCC. A decrease in HLB reduces CCC value. According to Zhang et al.,[5] this decrease can be modeled by two adjustable parameters, which depend on frother family and are constant for each family. They found that the influence of molecular weight on CCC exists only for aliphatic alcohols.

In this work the reviewed experimental data of CCC_{95} shown in Table 2 are plotted again, this time as a CCC_{95} versus HLB/MW relationship (Figure 2). Figure 2 shows a strong correlation between critical coalescence concentration and the HLB/MW ratio. The line with the best fit to experimental points by a nonlinear least-squares regression by use of Sigma Plot software package was found for one adjustable parameter A, and has the form:

$$CCC_{95} = \frac{B(\mathrm{HLB/MW})(A - 100)}{A - D(\mathrm{HLB/MW})} \tag{2a}$$

where B and D are constants depending on the maximum values of CCC_{95} and HLB/MW and are defined as

$$B = \frac{(CCC_{95})_{max}}{(\mathrm{HLB/MW})_{max}} = \frac{5.1}{0.125} = 40.8 \tag{2b}$$

$$D = \frac{100}{(\mathrm{HLB/MW})_{max}} = \frac{100}{0.125} = 800 \tag{2c}$$

For all frothers considered in this work (Table 2, Figure 2), parameter A was equal to 105.14 with determination coefficient R^2

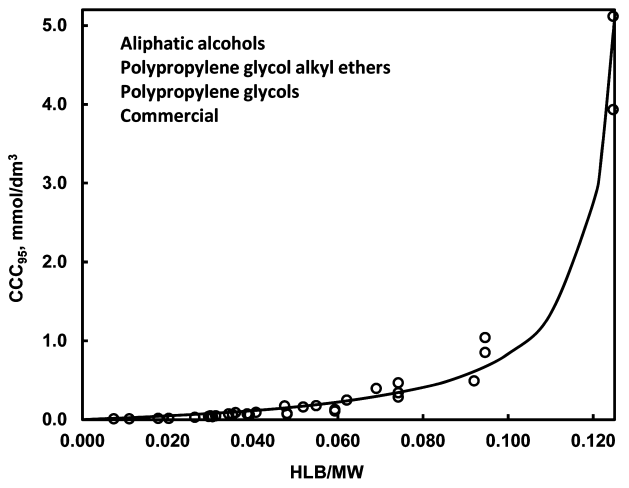

Figure 2. Replotted data of Zhang et al.[5] to show the CCC_{95} vs HLB/MW correlation (eq 3, determination coefficient R^2 = 0.97).

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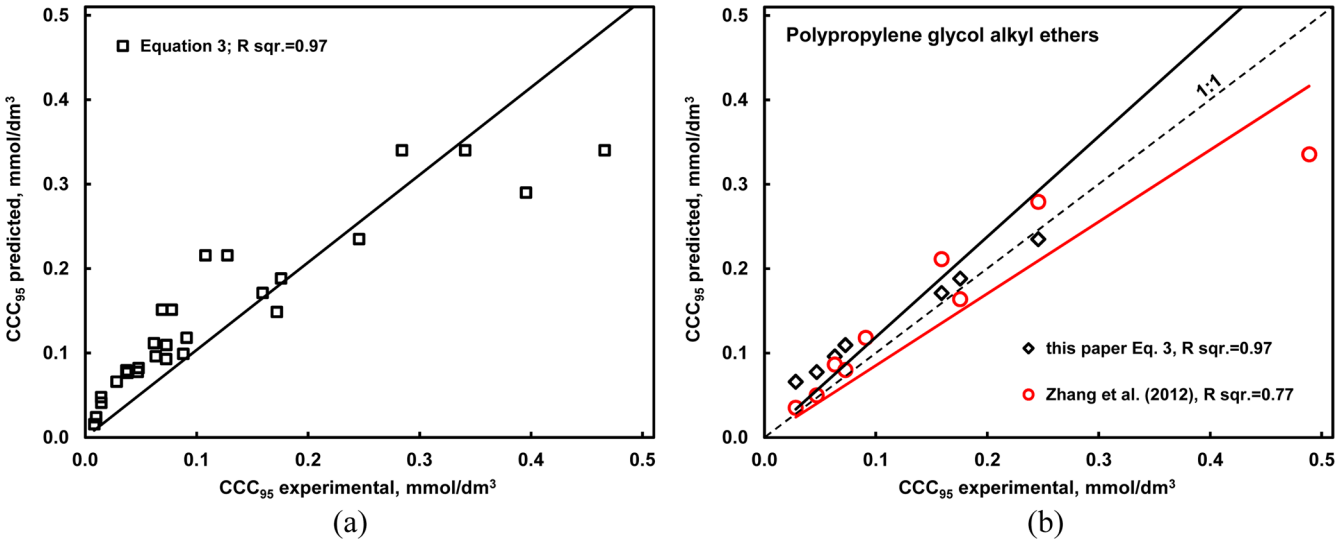

Figure 3. Comparison of experimental and predicted values of CCC_{95} for (a) flotation frothers and (b) poly(propylene glycol) alkyl ethers.

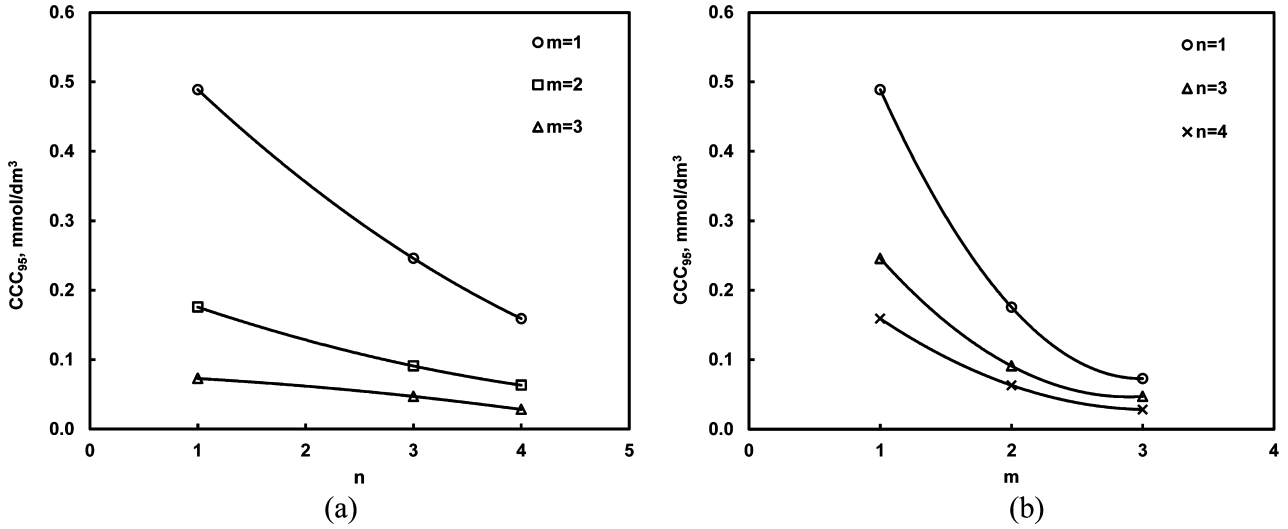

Figure 4. Effect of number of alkyl (n) and propylene oxide (m) groups per molecule on CCC_{95} for poly(propylene glycol) alkyl ethers.

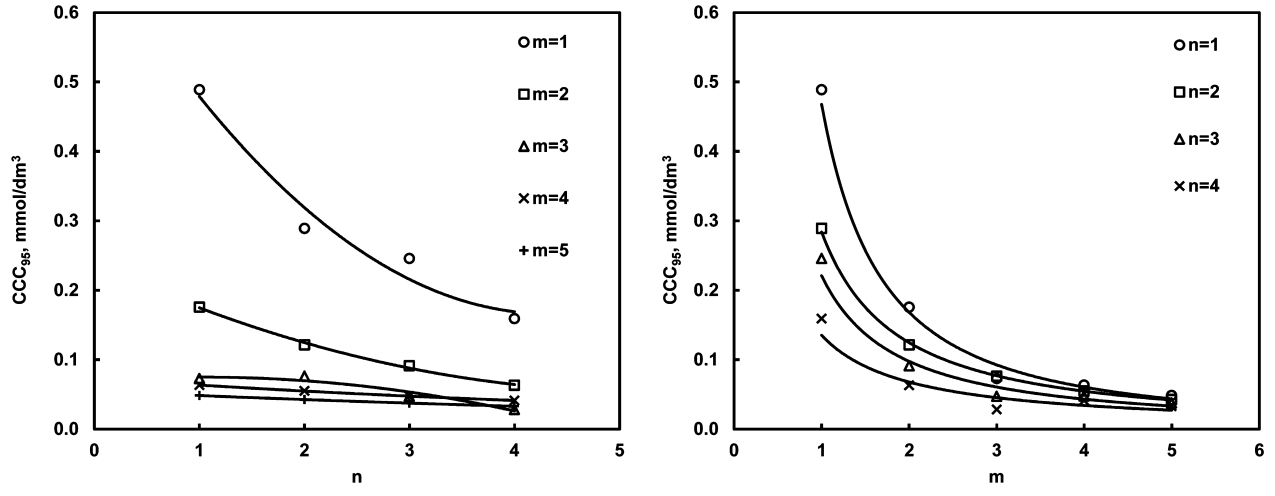

Figure 5. Model fitting for CCC_{95} versus number of alkyl n (left) and propylene oxide m (right) groups per molecule.

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of 0.97. The final equation for CCC_{95} versus HLB/MW ratio, obtained by substitution of eqs 2b and 2c into eq 2a, is

$$CCC_{95} = \frac{209.71(HLB/MW)}{105.14 - 800(HLB/MW)} \quad (3)$$

The proposed equation (eq 3) allows one to predict the values of critical coalesce concentration CCC_{95} based only on the chemical structure of the frother, that is, hydrophilic−lipophilic balance and molecular weight. Another empirical model proposed by Zhang et al.[5] is complex and is based on numbers of alkyl (n) and propylene oxide (m) groups:

$$CCC = [(4.74 \times 10^{-17}) \exp(-3.497n) + (1.956 \times 10^{-19}) \exp(-0.001452n)] \exp\left[\left(\frac{6.985n + 4.814}{1.455n}\right)\left(-0.149m + \frac{5.158n + 29.9}{3.152 + n}\right)\right] \quad (4)$$

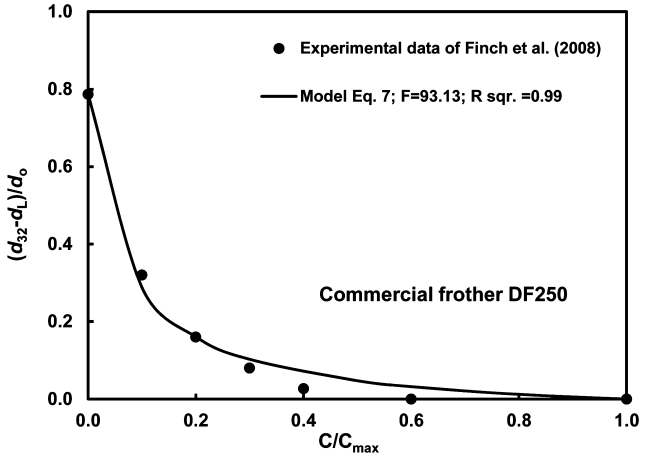

Figure 6. Normalized curve for commercial frother DowFroth 250 (DF250, C_1P_4).

A comparison of the experimental data of Zhang et al.[5] and values of CCC_{95} predicted in this work for poly(propylene glycol) alkyl ethers C_nP_m is given in Figure 3 as an example. From Figure 3b it can be seen that the model proposed in this work (eq 3) gives a much better fit to the data, with determination coefficient $R^2 = 0.97$, in comparison to the model proposed by Zhang et al.[5] (eq 4), where $R^2 = 0.77$.

The data of Zhang et al.[5] can also be used to show the influence of number of alkyl (n) and propylene oxide (m) groups on the critical coalescence concentration. Figure 4 shows that, for poly(propylene glycol) alkyl ethers, CCC_{95} decreases with increasing number of both alkyl (n) and propylene oxide (m) groups. This was also observed by Zhang et al.[5] They proposed an empirical equation (eq 4) that fits the data with $R^2 = 0.77$ (Figure 3b) for n = 1, 3, 4 and m = 1, 2, 3. The correlation proposed in this work, given by eq 3, also allows one to predict

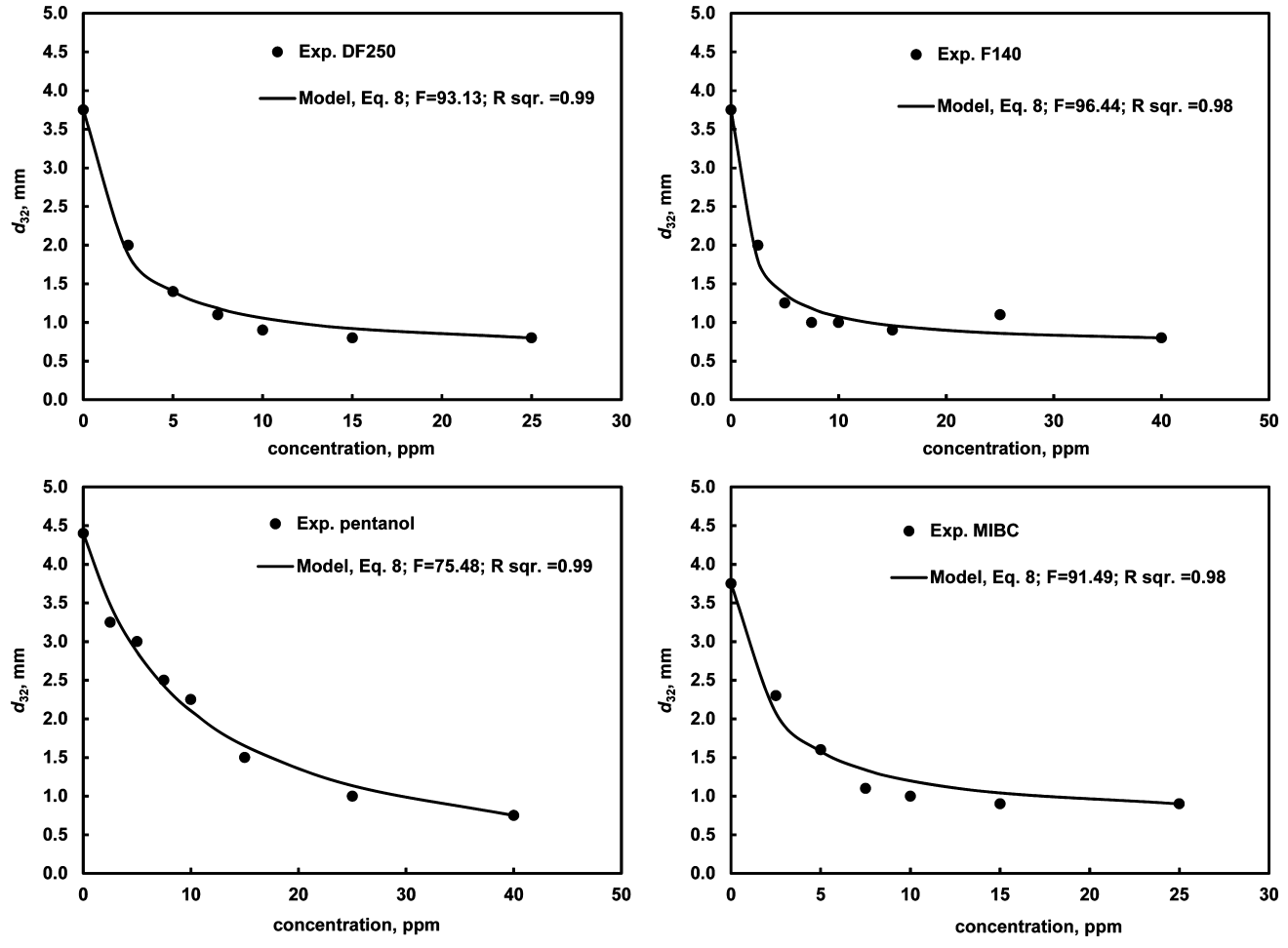

Figure 7. Comparison of experimental[4] and predicted (eq 8) data for tested frothers.

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values of CCC_{95} for all alkyl (n) and propylene oxide (m) groups. The values of CCC_{95} for $n = 2$ and $m = 4$ and 5, which have been unknown, now can be estimated. Figure 5 shows the predicted values for poly(propylene glycol) alkyl ethers $C_nH_{2n+1}(OC_3H_6)_mOH$ with $n = 2$ and $m = 4$, 5, which accurately fit the pattern given in Figure 4. It confirms that the model proposed in this work is general for all flotation frothers and can be used to provide information about the critical coalescence concentration, based only on chemical structure, in the form of HLB/MW ratio.

3. BUBBLE SIZE IN RELATION TO FROTHER CONCENTRATION

The influence of commercial frother DF250 concentration C on bubble size, defined as Sauter mean diameter d_{32}, is presented in Figure 1. The d_{32} versus C relationship can be plotted with experimental data as well as predicted from different models. The empirical model for Sauter mean bubble size prediction based on concentration and the critical coalescence concentration of frother was developed by Finch and co-workers.[4,5,11] Their model is based on frother concentration C, initial d_0 ($=d_{max}$) and minimum d_L ($=d_{min}$) bubble size, and constant B, which has no physical meaning. The Sauter mean bubble size d_{32} can be calculated from the following equation:

$$d_{32} = d_L + (d_0 - d_L)\exp(-BC) \quad (5)$$

where d_L can be calculated from an empirical equation:

$$d_L = -0.072\mathrm{HLB} + 1.43 \quad (6)$$

For commercial DowFroth 250 frother (DF250, C_1P_4), d_L is close to 1 mm for HLB = 7.83. The calculated d_L value is similar to that shown in Figure 1.

An examination of the data of Finch and co-workers[4,15] for different flotation frothers revealed that, to relate bubble size d_{32} and frother concentration C, it is useful to plot the normalized bubble size function $(d_{32} - d_L)/d_0$ versus normalized frother concentration C/C_{max} term, where C_{max} stands for the maximum concentration of frother. All flotation frothers considered in this work follow a certain pattern. The new curve for commercial frother DF250 is given in Figure 6 as an example. The line fits well to experimental points. Nonlinear least-squares regression by use of Sigma Plot software package for one adjustable parameter F was found in the form

$$\frac{d_{32} - d_L}{d_0} = \left(1 - \frac{d_L}{d_0}\right)\frac{[1 - (C/C_{max})](F - 100)}{[F - 100(C/C_{max}) - 100]} \quad (7)$$

where parameter F, applied for relating d_{32} and C, can be called the empirical frother concentration constant. This constant is independent of frother concentration and can be used to predict the Sauter mean bubble size d_{32}. The maximum value of $(d_{32} - d_L)/d_0$ occurs for $C/C_{max} = 0$ and is equal to $(1 - d_L/d_0)$. Now we can rearrange eq 7 to be used for prediction of the bubble size, defined as the Sauter mean diameter d_{32}, and the trend of d_{32} versus C line:

$$d_{32} = (d_0 - d_L)\frac{[1 - (C/C_{max})](F - 100)}{[F - 100(C/C_{max}) - 100]} + d_L \quad (8)$$

A comparison of experimental d_{32} values with those predicted from eq 8 for commercial frothers DF250, F140 (polyglycol), pentanol (1-pentanol), and MIBC (methyl isobutyl carbinol) is given in Figure 7 as an example. For instance, the DF250 frother concentration constant is 93.13 and provides a very high determination coefficient, $R^2 = 0.99$. For all of the flotation frothers reviewed in this work, the determination coefficients were greater than 0.97.

4. CONCLUSIONS

Based on analysis of literature experimental data for surfactants used as flotation frothers, the following conclusions can be drawn.

(1) For flotation frothers there is a strong correlation between the critical coalescence concentration and ratio of hydrophilic–lipophilic balance and molecular weight. This correlation can be described by an empirical model. The model given by eq 3 allows one to predict the critical coalescence concentration from the chemical structure of the frother. Excellent agreement is observed between the determined and experimental values of CCC_{95}.

(2) It was found that a new relationship between normalized bubble size $(d_{32} - d_L)/d_0$ and normalized frother concentration C/C_{max} can be used to model the influence of frother concentration on Sauter mean bubble size d_{32}. The obtained model given by eq 7 is based on one adjustable parameter called the frother concentration constant. It is used to predict the Sauer mean bubble size d_{32} for any flotation frothers.

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Notes

The authors declare no competing financial interest.

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