

## Article

# Correlations for Easy Calculation of the Critical Coalescence Concentration (CCC) of Simple Frothers

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**Abstract:** Can the critical coalescence concentration (CCC) of the flotation frothers be predictable? What is the relation between their molecular structure and their CCC values? A literature survey found specific correlations between the hydrophilic-lipophilic balances (HLB) and HLB/Mw (where Mw stands for the molecular mass) of homologue series of frothers and their CCC values, but the results are invalid when the molecule’s functional groups change. For this reason, 37 frothers with known values of CCC were analyzed. The CCC values of seven frothers were determined, and the rest were taken from the literature. The frothers were subdivided in homologue series with an increasing number of the carbon atoms with an account for the type and the location of the functional group, thus deriving three types of correlations  $\ln CCC = f(HLB)$  applicable for: (i) alcohols; (ii) propylene glycols alkyl ethers and propylene glycols; (iii) ethylene glycols alkyl ethers. The average accuracy of these correlations between CCC and HLB is 93%.

**Keywords:** frother; critical coalescence concentration (CCC); foam; molecular geometry

## 1. Introduction

It is well known that the surface activity of the frothers in their aqueous solutions depends mostly on their molecular structure. Hence, their surface tension isotherms [1,2], critical micelle concentration [1–4], foaminess [5–9], foam durability [10–16], and foam production [17], also depends on their molecular structure. Indeed, frothers start inhibiting the coalescence of bubbles at very small concentrations, at which they are unable to lower the surface tension [18]. For this reason, the dynamic foamability index (DFI) introduced by Malysa et al. [19,20] was preferred as a definite criterion for the strength of the frothers under dynamic conditions, like those found in the flotation reactors. Another well-preferred parameter similar to DFI, but more accurate than the dynamic foamability index, is the critical coalescence concentrations (CCC) introduced by Laskowski et al. [21–23]. Generally, CCC is the minimal concentration required to prevent the coalescence of the bubbles, but because the coalescence is a stochastic process. A well-accepted definition of CCC is the frother concentration, at which 50% of the bubbles, passing through a porous frit, do not coalesce, and thus give rise to pneumatic foam. The values of CCC are important for the proper choice of flotation frothers. Therefore, the CCC values

of many frothers were measured [18,24–43]. Meanwhile, currently, new formulations of frothers and collectors often emerge according to the specific needs of the mining industry. Hence, a demand for faster determination of the CCC values of the frothers appears. Szyszkla et al. [44] report that higher molar mass of the frother correlates with lower values of CCC. Zhang et al. [37] established a correlation between the CCC values and the number of Propoxy groups and carbon atoms in the main chain of Propylene glycol alkyl ethers ( $C_n(C_3H_6O)_mOH$ ), but their correlation is very complicated and has an accuracy about 45%. Furthermore, Kowalczyk [39] established a more general correlation between CCC and HLB/Mw of alcohols, Propylene glycol alkyl ethers, and Propylene glycols, but our estimate showed again an accuracy of about 45%. A possible reason for such a disagreement could be sought in the lack of account for the specific molecular structure of the different frothers. Furthermore, Szyszkla [31,45] reports a strong correlation between CCC values, molar mass, and HLB as defined by Davies [46], but these findings are just indicative because she only analyzed a series of 4 frothers. There have been no attempts in the literature to produce a more accurate account of the frother's molecular structure.

The quantitative structure–property/activity relationship (QSPR/QSAR) is a contemporary semi-empirical powerful method for predicting the properties (QSPR) [47–53] and activities (QSAR) [54,55] of different systems (frothers, bio-molecules, liquid systems, etc.), such as the critical micelle concentration (CMC), the hydrophilic-lipophilic balance (HLB), the cloud point, the solubility, the toxicity, the biological activity, and the vapor pressure, etc. They operate with a number of molecular descriptors, calculated by quantum-chemical software programs. Thus calculated, they are variables multiplied by unknown fitting coefficients within linear or nonlinear regression procedure operating with experimentally determined property (for QSPR) or activity (for QSAR) of series of substances with known molecular geometry. Once the unknown coefficients are determined, the properties or activities of many other substances can be calculated by imputing their molecular descriptors into the already build procedure. The output parameter of the procedure is the property (or activity) of the substance of interest with a certain mathematical accuracy. In such a way, the long and meticulous experiments on the determination of the properties and activities of many substances can be avoided along with the associated expenses. It is worth noting that none of the above works is devoted to the calculation of the CCC values of the frothers. To our knowledge, only Szyszkla et al. [31,44] and Kowalczyk [39] related the CCC values of some frothers with their molecular structure, mostly with their molecular mass and the HLB values as defined by Davies [46]. Thus, we are motivated to develop a procedure that can calculate the CCC values of the frothers based on their molecular structure. The molecular descriptor, which we use in the present study, is the HLB values defined by Davies [46]. To study more a detailed relation between the molecular structure of the frothers and their CCC values, we collected literature on experimentally determined CCC values [18,24–43] of a series of frothers with subsequent change in their molecular structure. There was a subsequent increase in the number of methylene groups in the main chain of primary alcohols, secondary alcohols, tertiary alcohols, and a branched alcohol, and propoxy and ethoxy frothers. In addition to this, we carried out the experiments to determine the CCC values of selected frothers, which are of significant interest to the mining industry and analyzed the relation between their CCC values and their molecular structure. Thus, we established the relative effect of the number of methylene groups, the position of hydroxyl (OH) group on the main chain and the number of propoxy and ethoxy groups on the CCC values of the frother. Hence, we call upon further investigation on the relationship between the CCC values of the frothers and their molecular structure.

## 2. Materials and Methods

### 2.1. Description of the Frothers

To study the dependence between the molecular structure of the frother and its CCC value, we collected the CCC values of the following series of frothers as presented in Table 1.

**Table 1.** Frothers, molecular formula, hydrophilic-lipophilic balance (HLB), critical coalescence concentration (CCC), and sources.

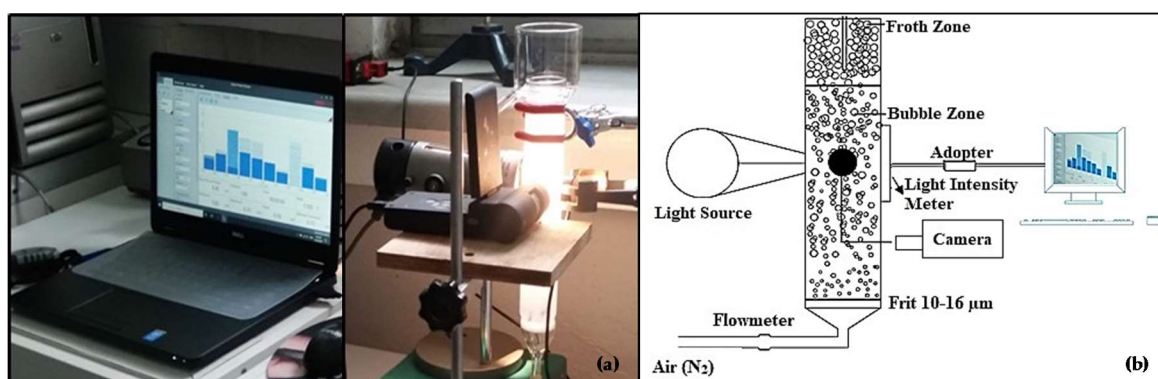
Frother	Molecular Formula	HLB	CCC, mol/L	Reference
1-Propanol	C <sub>3</sub> H <sub>7</sub> OH	7.48	$3.93 \times 10^{-3}$	[37]
1-Butanol	C <sub>4</sub> H <sub>9</sub> OH	7.00	$8.50 \times 10^{-4}$	[37]
1-Pentanol	C <sub>5</sub> H <sub>11</sub> OH	6.53	$2.84 \times 10^{-4}$	[37]
1-Hexanol	C <sub>6</sub> H <sub>13</sub> OH	6.05	$7.90 \times 10^{-5}$	[37]
1-Heptanol	C <sub>7</sub> H <sub>15</sub> OH	5.58	$5.52 \times 10^{-5}$	[37]
1-Octanol	C <sub>8</sub> H <sub>17</sub> OH	5.10	$6.20 \times 10^{-5}$	[37]
2-Propanol	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	7.48	$5.11 \times 10^{-3}$	[37]
2-Butanol	C <sub>2</sub> H <sub>5</sub> CH(OH)CH <sub>3</sub>	7.00	$1.04 \times 10^{-3}$	[37]
2-Pentanol	C <sub>3</sub> H <sub>7</sub> CH(OH)CH <sub>3</sub>	6.53	$3.40 \times 10^{-4}$	[37]
2-Hexanol	C <sub>4</sub> H <sub>9</sub> CH(OH)CH <sub>3</sub>	6.05	$1.08 \times 10^{-4}$	[37]
2-Heptanol	C <sub>5</sub> H <sub>11</sub> CH(OH)CH <sub>3</sub>	5.58	$7.76 \times 10^{-5}$	[37]
2-Octanol	C <sub>6</sub> H <sub>13</sub> CH(OH)CH <sub>3</sub>	5.10	$6.14 \times 10^{-5}$	[37]
MIBC	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH(OH)CH <sub>3</sub>	6.53	$9.78 \times 10^{-5}$	Present study
3-Pentanol	C <sub>2</sub> H <sub>5</sub> CH(OH)C <sub>2</sub> H <sub>5</sub>	6.53	$4.65 \times 10^{-4}$	[37]
3-Hexanol	C <sub>3</sub> H <sub>7</sub> CH(OH)C <sub>2</sub> H <sub>5</sub>	6.05	$1.27 \times 10^{-4}$	[37]
2-Ethyl 1-Hexanol	C <sub>4</sub> H <sub>9</sub> CH(C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> OH	5.10	$1.23 \times 10^{-4}$	[56]
Propylene Glycol Methyl Ether	CH <sub>3</sub> O(C <sub>3</sub> H <sub>6</sub> O)H	8.30	$5.19 \times 10^{-4}$	[37]
Propylene Glycol Propyl Ether	C <sub>3</sub> H <sub>7</sub> O(C <sub>3</sub> H <sub>6</sub> O)H	7.35	$2.45 \times 10^{-4}$	[37]
Propylene Glycol Butyl Ether	C <sub>4</sub> H <sub>9</sub> O(C <sub>3</sub> H <sub>6</sub> O)H	6.88	$1.59 \times 10^{-4}$	[37]
Dipropylene Glycol	HO(C <sub>3</sub> H <sub>6</sub> O) <sub>2</sub> H	9.25	$3.95 \times 10^{-4}$	[37]
Dipropylene Glycol Methyl Ether	CH <sub>3</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>2</sub> H	8.18	$1.69 \times 10^{-4}$	[37]
Dipropylene Glycol Propyl Ether	C <sub>3</sub> H <sub>7</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>2</sub> H	7.23	$9.08 \times 10^{-5}$	[37]
BDPG	C <sub>4</sub> H <sub>9</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>2</sub> H	6.75	$6.31 \times 10^{-5}$	Present study
PPG200	HO(C <sub>3</sub> H <sub>6</sub> O) <sub>3</sub> H	10.55	$7.03 \times 10^{-4}$	Present study
Dowfroth 200	CH <sub>3</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>3</sub> H	8.05	$1.01 \times 10^{-4}$	[26]
Tri(Propylene Glycol) Propyl Ether	C <sub>3</sub> H <sub>7</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>3</sub> H	7.10	$4.69 \times 10^{-5}$	[37]
BTPG	C <sub>4</sub> H <sub>9</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>3</sub> H	6.63	$2.82 \times 10^{-5}$	Present study
Tetrapropylene Glycol	HO(C <sub>3</sub> H <sub>6</sub> O) <sub>4</sub> H	9.00	$8.79 \times 10^{-5}$	[37]
Dowfroth 250	CH <sub>3</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>4</sub> H	7.93	$3.30 \times 10^{-5}$	[27]
PPG400	HO(C <sub>3</sub> H <sub>6</sub> O) <sub>6</sub> H + HO(C <sub>3</sub> H <sub>6</sub> O) <sub>7</sub> H	8.69	$9.52 \times 10^{-6}$	Present study
PPG600	HO(C <sub>3</sub> H <sub>6</sub> O) <sub>10</sub> H	8.25	$5.00 \times 10^{-6}$	Present study
Dowfroth 1012	CH <sub>3</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>6</sub> H	7.55	$1.66 \times 10^{-5}$	[27]
Ethylene Glycol Butyl Ether	C <sub>4</sub> H <sub>9</sub> O(C <sub>2</sub> H <sub>4</sub> O)H	7.35	$1.19 \times 10^{-3}$	[31]
BDEG	C <sub>4</sub> H <sub>9</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>2</sub> H	7.70	$8.4 \times 10^{-4}$	[31]
BTEG	C <sub>4</sub> H <sub>9</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>3</sub> H	8.05	$5.10 \times 10^{-4}$	Present study
Triethylene Glycol Methyl Ether	CH <sub>3</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>3</sub> H	9.48	$6.80 \times 10^{-4}$	[25]
Diethoxy Hexanol	HO(C <sub>2</sub> H <sub>4</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>12</sub> OH	6.75	$3.10 \times 10^{-5}$	[41]

## 2.2. Materials

The chemicals (BASF, Germany) used in this study were namely polypropylene glycols (PPG 200, 400, and 600), tri propylene glycol (BTPG), triethylene glycol (BTEG), dipropylene glycol (BDPG), and Methyl isobutyl carbinol (MIBC). All the measurements were conducted at constant room temperature:  $23 \pm 1$  °C. All glassware was rinsed with ethyl alcohol (99% purity, MERCK) and washed with distillation water, followed by steam cleaning and drying in a clean oven. To ensure that the frothers were dispersed in solutions, each frother solution was stirred at 500 rpm for 4 min.

## 2.3. Experimental Conditions

The bubble coalescence measurements for the frothers were carried out as a function of frother concentration (ppm) using a 4 cm × 20 cm micro-flotation cell having 10–16 µm pore diameter frit. Nitrogen was used as the gas in the experiments, and the experiments were carried out at an nitrogen volume of 50 cm<sup>3</sup>/min (Figure 1). In the measurements, a light was passed through the column, and the light intensity of the portion (non-absorbed) leaving the column was measured by the adapter (Thorlabs, Newton, NJ, USA). The measurements started with no light absorbed by the solution, which meant the bubble coalescence occurred in the system until no light was received. The critical coalescence concentration for the frothers was determined at 50% values of the bubble coalescence. The detailed information about the measurements is given in reference [57].



**Figure 1.** (a) Experimental set-up of bubble coalescence measurement; (b) Schematic representation of bubble coalescence measurements [56].

### 3. Results and Discussion

The dependence between the CCC values of the frothers and their HLB values as defined by Davies [57], was studied following the approach of Szyszka et al. [31,44] and Kovalszuk [39], however in the present case we applied this approach on a number of significantly different types of frothers. As mentioned above, the CCC values of 30 frothers were taken from the literature [25–27,31,37,41] and we measured the CCC values of 7 frothers, which are of particular interest to the mining industry. The calculated HLB value of each frother following the formula introduced by Davies [57] is as follows:

$$\text{HLB} = 7 + \sum_{i=1}^m H_i - 0.475n \quad (1)$$

where  $m$  is the number of hydrophilic groups in the molecule,  $H_i$  is the value if  $i$ th hydrophilic group (see Table 2) and  $n$  is the number of lipophilic groups in the molecule ( $-\text{CH}-$ ,  $-\text{CH}_2-$ ,  $\text{CH}_3-$ ,  $=\text{CH}-$ ).

**Table 2.** Types of hydrophilic groups and their corresponding values.

Hydrophilic Groups	Group Value
$-\text{SO}_4^- \text{Na}^+$	38.7
$-\text{COO}^- \text{K}^+$	21.1
$-\text{COO}^- \text{Na}^+$	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
Ester (free)	2.4
$-\text{COOH}$	2.1
Hydroxyl (free)	1.9
$-\text{O}-$	1.3
Hydroxyl (sorbitan ring)	0.5

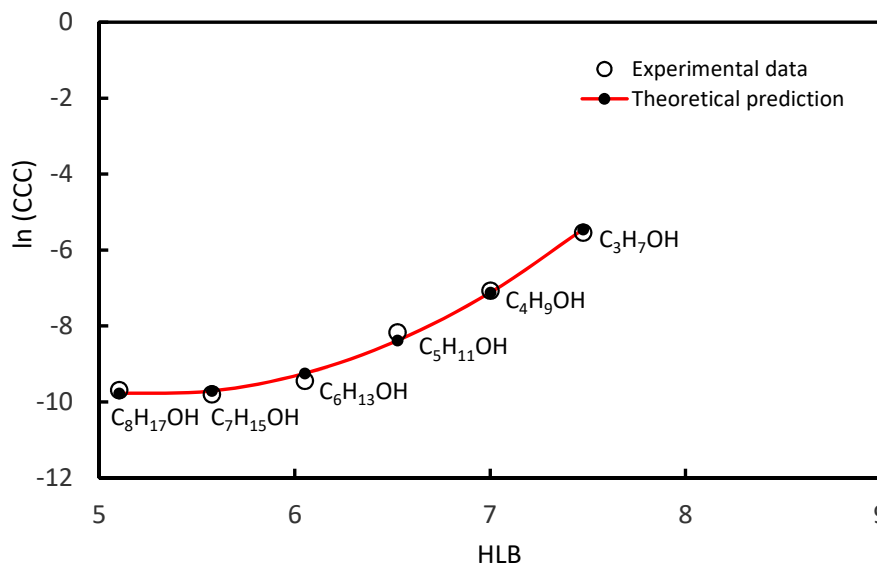
#### 3.1. CCC Values of Homologue Series of Primary, Secondary Alcohols, and Tertiary Alcohols

CCC values of series of primary, secondary alcohols, tertiary alcohols [37], and branched alcohol were analyzed with regard to their HLB values and molecular structure. We found the following dependence of the CCC values and the HLB values:

$$\ln \text{CCC} = a + b\text{HLB} + c\text{HLB}^2 - 0.19(1 - S) + n_{\text{CBr}}\xi_1, \quad (2)$$

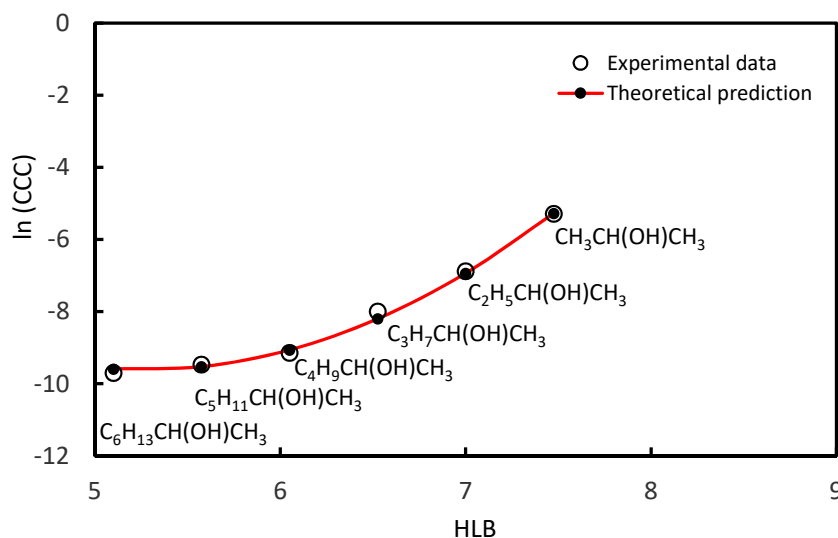
where HLB is the hydrophilic/lipophilic balance of the organic molecule,  $a = 14.695$ ,  $b = -9.3133$ ,  $c = 0.8852$ ,  $S$  is the position of the OH group in the main chain,  $n_{\text{CBr}}$  is number of C-atoms branched from the main chain,  $\xi_1$  is contribution from the branched C-atoms to the CCC values:  $\xi_1 = 1.4 n_{\text{CBr}} - 2.4$ .

The first set of experimental data  $\ln(\text{CCC})$  values for the series  $\text{C}_3\text{H}_7\text{OH}$ – $\text{C}_8\text{H}_{17}\text{OH}$  versus HLB) and their corresponding theoretical values (see Equation (2)) is presented in Figure 2. One can see that when the hydrocarbon chain of the alcohols increases, both its HLB value and  $\ln(\text{CCC})$  decrease. It is well known that the smaller values of HLB correspond to the larger surface activity of the frothers and the related smaller values of CCC. Yet, when the number of the carbon atom in the main chain is larger than 6 ( $\text{C}_7\text{H}_{15}\text{OH}$ ,  $\text{C}_8\text{H}_{17}\text{OH}$ , etc.) the CCC value practically does not depend on the length of the hydrocarbon chain anymore ( $\text{CCC}(\text{C}_7\text{H}_{15}\text{OH}) = 5.52 \times 10^{-5} \text{ mol/L}$ ,  $\text{CCC}(\text{C}_8\text{H}_{17}\text{OH}) = 6.20 \times 10^{-5} \text{ mol/L}$ ). This means that  $6.2 \times 10^{-5} \text{ mol/L}$ – $6.5 \times 10^{-5} \text{ mol/L}$  is the limit of CCC values, which the primary alcohols can achieve by increasing the hydrocarbon chain. Moreover, one can see as well that the experimental and the theoretical values of CCC are in good agreement.



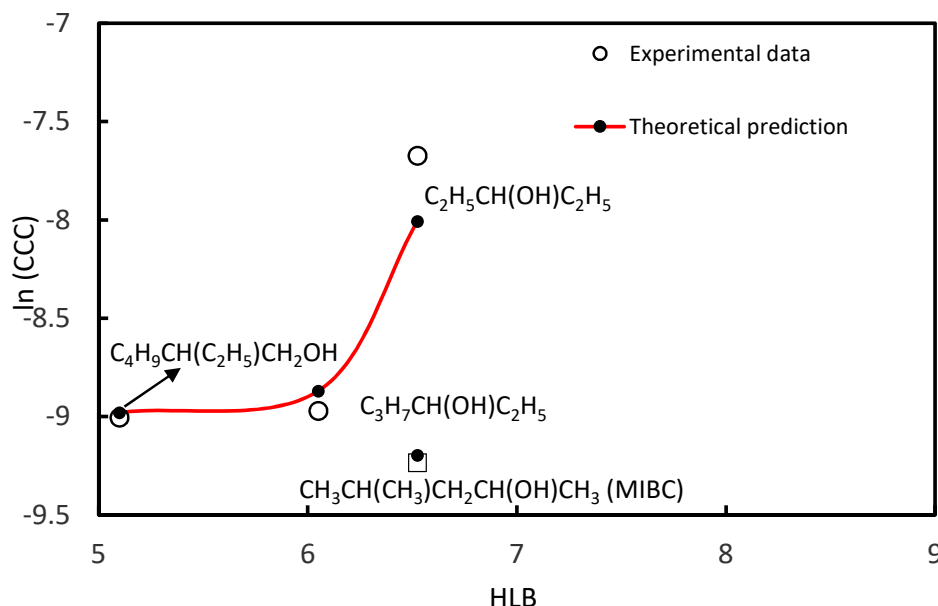
**Figure 2.** Experimental [37] and theoretical (see Equation (2)) values of  $\ln(\text{CCC})$  versus HLB values of homologue series of primary alcohols  $\text{C}_3\text{H}_7\text{OH}$ – $\text{C}_8\text{H}_{17}\text{OH}$ .

The experimental and the theoretical values of CCC for homologue series of the secondary alcohols  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ – $\text{C}_6\text{H}_{13}\text{CH}(\text{OH})\text{CH}_3$  versus their HLB values are presented in Figure 3. The values of CCC in this particular case is slightly higher as compared to the CCC values of the primary alcohols. Otherwise, the dependence here is the same as in the case of the primary alcohols.



**Figure 3.** Experimental [37] and theoretical (see Equation (2)) values of  $\ln(\text{CCC})$  versus HLB values of homologue series of secondary alcohols  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ – $\text{C}_6\text{H}_{13}\text{CH}(\text{OH})\text{CH}_3$ .

Figure 4 presents the experimental and theoretical values of  $C_2H_5CH(OH)C_2H_5$ ,  $C_3H_7CH(OH)C_2H_5$ ,  $C_4H_9CH(C_2H_5)CH_2OH$ , and Methyl isobutyl carbinol (MIBC,  $CH_3CH(CH_3)CH_2CH(OH)CH_3$ ). One can see here that the limiting CCC value at  $n > 6$ , is different from the above mentioned case of normal primary and secondary alcohols  $CCC = 1.23 \times 10^{-4}$  mol/L, while MIBC ( $CH_3CH(CH_3)CH_2CH(OH)CH_3$ ) rather follows the dependence given in Figure 3. One can see as well that the agreement between the experimental and the theoretical values (obtained using Equation (2)) is satisfactory.



**Figure 4.** Experimental [37] and theoretical (see Equation (2)) values of  $\ln(CCC)$  versus HLB values of the tertiary alcohols  $C_2H_5CH(OH)C_2H_5$ ,  $C_3H_7CH(OH)C_2H_5$  [38],  $C_4H_9CH(C_2H_5)CH_2OH$  [56] and MIBC (produced in this study).

### 3.2. CCC Values of Propoxy Frothers

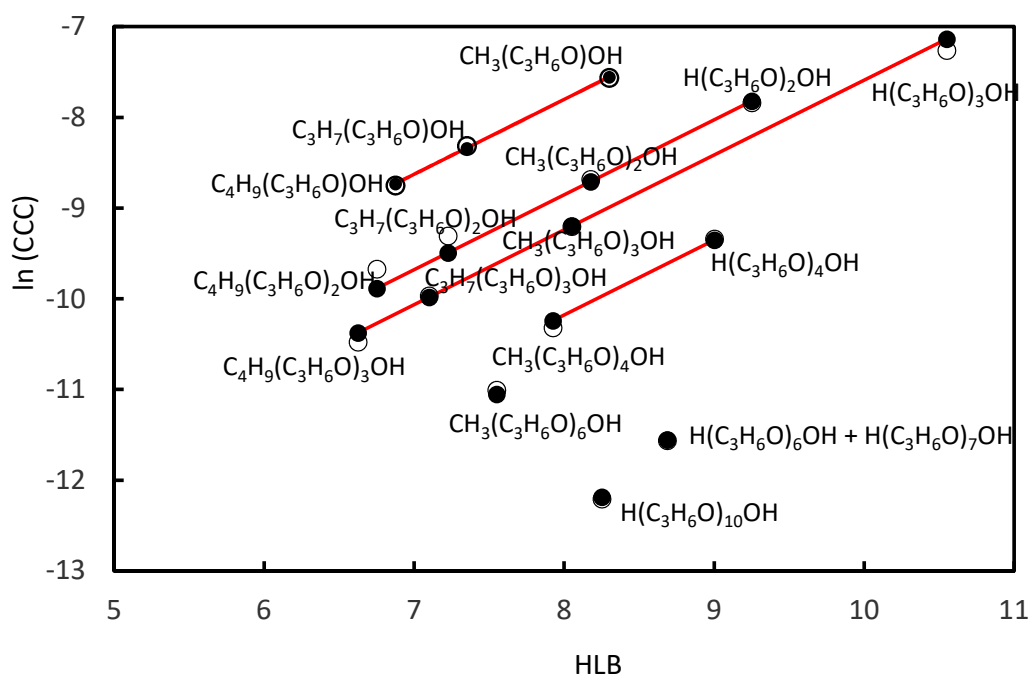
The experimental values of CCC of Propoxy frothers were taken from the literature [27,37] and some of them were obtained in the present work. The following empirical relation between the

$$\ln CCC = a + bHLB + (1 - \xi)cor(1), \quad (3)$$

where  $a = -14.404$ ,  $b = 0.8252$ ,  $cor = 0.9$ ,  $\xi$ —Propoxy contribution to the CCC values depending on the number of the Propoxy groups.

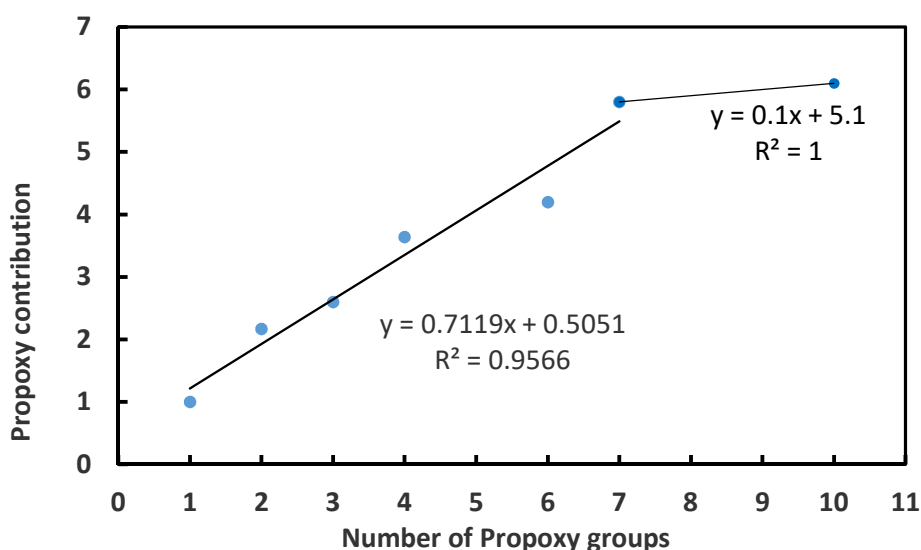
Figure 5 presents  $\ln(CCC)$  versus HLB dependence of different groups of Propoxy frothers. Each group represents the increasing number of carbon atoms in the main chain of the frother molecule. The different groups differ by the number of Propoxy groups in the main chain. One can see that all the dependencies between  $\ln(CCC)$  and the HLB values are linear in the range of  $CH_3$ – $C_4H_9$ . We suppose that a limiting CCC value with longer alkyl chains is possible, similar to the Figures 2–4. The increase of the number of carbon atoms in the main chain results in a decrease of both the HLB value and  $\ln(CCC)$  value. This is expected because the frother molecules in such a way become more hydrophobic. The increase of the number of Propoxy groups ( $C_3H_6O$ ) in molecules with the same number of carbon atoms in the main chain causes a slight decrease in the HLB values and a strong decrease in the CCC values of the frothers. We have to note here that the above dependencies fall in the range of  $CH_3$ – $C_4H_9$  alkyl groups of the frothers. As mentioned above a limiting value of the CCC requires the presence of a sufficient length of hydrocarbon chains. If this is real then the limiting value of CCC should decrease with increasing the number of Propoxy ( $C_3H_6O$ ) groups in the molecule. In Equation (1) the parameter  $\xi$  denotes the contribution of the Propoxy groups to the CCC values of the frother. This parameter depends on the number of the Propoxy ( $C_3H_6O$ ) groups of the molecule.





**Figure 5.**  $\ln(\text{CCC})$  versus HLB of Propoxy frothers of the types  $(\text{C}_n\text{H}_{2n+1}(\text{C}_3\text{H}_6\text{O})\text{OH})$ ,  $(\text{H}(\text{C}_3\text{H}_6\text{O})_2\text{OH})$ ,  $\text{C}_n\text{H}_{2n+1}(\text{C}_3\text{H}_6\text{O})_2\text{OH}$ ,  $(\text{H}(\text{C}_3\text{H}_6\text{O})_3\text{OH})$ ,  $\text{C}_n\text{H}_{2n+1}(\text{C}_3\text{H}_6\text{O})_3\text{OH}$ ,  $(\text{H}(\text{C}_3\text{H}_6\text{O})_4\text{OH})$ ,  $\text{CH}_3(\text{C}_3\text{H}_6\text{O})_4\text{OH}$ ,  $\text{CH}_3(\text{C}_3\text{H}_6\text{O})_6\text{OH}$ ,  $\text{H}(\text{C}_3\text{H}_6\text{O})_6\text{OH} + \text{H}(\text{C}_3\text{H}_6\text{O})_7\text{OH}$ ,  $\text{H}(\text{C}_3\text{H}_6\text{O})_{10}\text{OH}$  [27,37]; empty dots represent the experimental values, while the full dots correspond the theoretical values.

The dependence of the Propoxy  $(\text{C}_3\text{H}_6\text{O})$  contribution  $\xi$  to  $\ln(\text{CCC})$  of the frother is depicted in Figure 6. A brief look at Equation (1) and Figure 6 indicate that the parameter  $\xi$  decreases the value of  $\ln(\text{CCC})$  as far as in all of the cases  $\xi > 1$  (see Equation (1)). One can see as well that in the range of  $(\text{C}_3\text{H}_6\text{O})-(\text{C}_3\text{H}_6\text{O})_7$  the slope of the linear dependence is  $b = 0.71129$ , which means that it is less than unity, i.e., the contribution is always a number smaller than the number of the Propoxy groups  $(\text{C}_3\text{H}_6\text{O})_n$  in the molecule. One can see the existence of limiting value of  $\xi$  and  $(\text{C}_3\text{H}_6\text{O})_{n>7}$ . One can also see the good agreement between the experimental and the theoretical (see Equation (1)) values.



**Figure 6.** Propoxy contribution  $\xi$  versus number of Propoxy  $(\text{C}_3\text{H}_6\text{O})$  groups in the molecule.

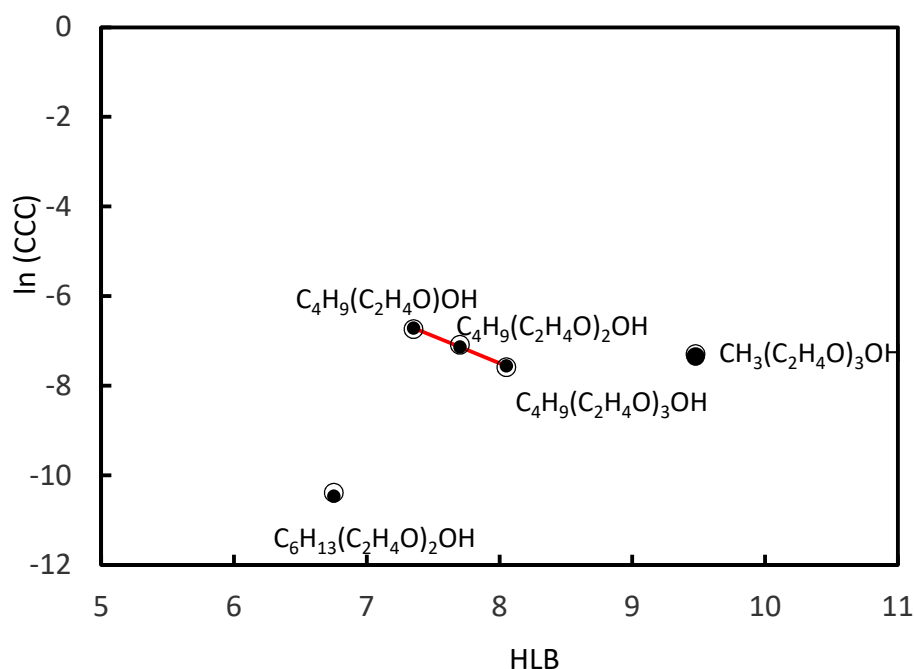
### 3.3. CCC Values of Ethoxy Frothers

The following dependence between  $\ln(\text{CCC})$  and HLB for the Ethoxy frothers was established:

$$\ln \text{CCC} = a + b(\text{HLB} - \xi_2), \quad (4)$$

where  $a = 2.1875$ ,  $b = -1.2104$ , and  $\xi_2$  is the contribution of the ethoxy ( $\text{C}_2\text{H}_4\text{O}$ ) groups to  $\ln(\text{CCC})$  values of the ethoxy frothers.

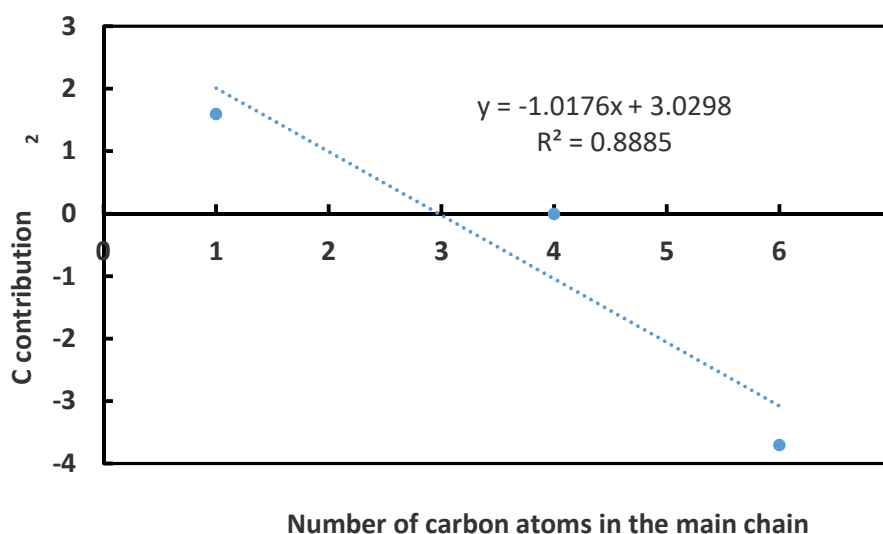
Figure 7 presents the experimental and theoretical dependence of the  $\ln(\text{CCC})$  values on the HLB values of the ethoxy frothers. The experimental data about the Ethoxy frothers (Figure 7) are significantly less than the experimental data of the Propoxy frothers (Figure 5). Nevertheless, we succeeded to establish the dependence of Equation (4). One can see in Figure 7, that increasing the Ethoxy groups ( $\text{C}_2\text{H}_4\text{O}$ ) increases the HLB number, but decreases  $\ln(\text{CCC})$  value, which is unexpected. The molecules become more hydrophilic and at the same time, have lower CCC values, which correspond to larger surface activity. Equation (4) contains the unknown parameter  $\xi_2$ , which is the contribution of the ethoxy ( $\text{C}_2\text{H}_4\text{O}$ ) groups to  $\ln(\text{CCC})$  values of the ethoxy frothers.



**Figure 7.**  $\ln(\text{CCC})$  versus HLB of Ethoxy frothers—full circles—experimental values, empty circles represent the theoretical values; empty dots represent the experimental values, while the full dots correspond to the theoretical values.

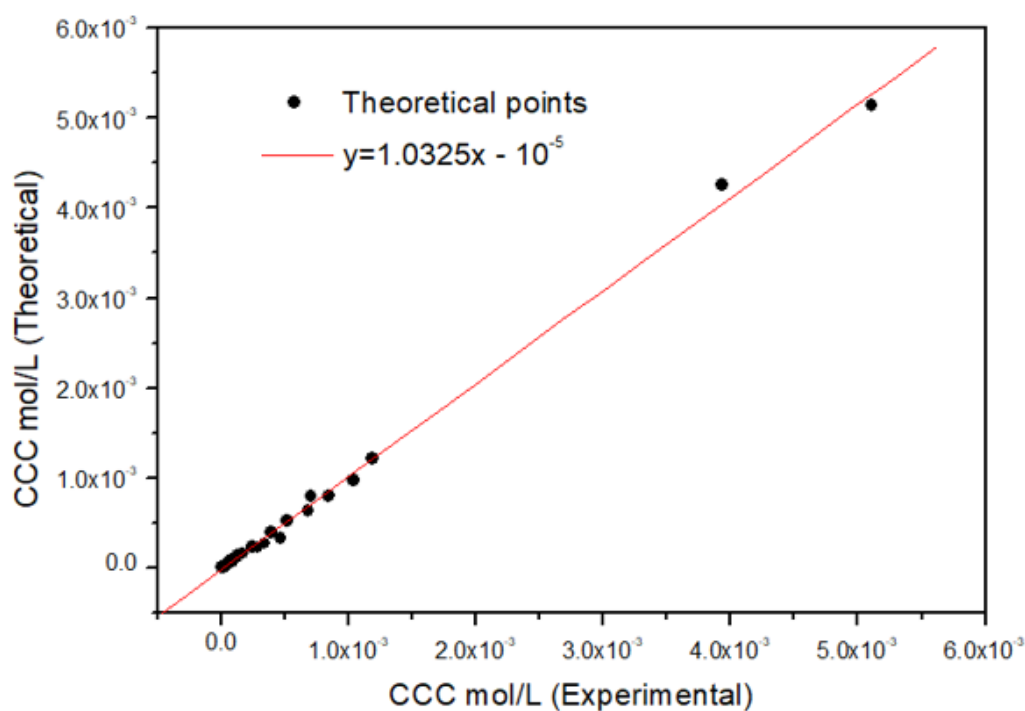
Figure 8 presents the Ethoxy contribution  $\xi_2$  versus the number of Ethoxy ( $\text{C}_2\text{H}_4\text{O}$ ) groups in the molecule of the Ethoxy frothers. In contrast to the case of the Propoxy frothers, (see Figure 6) the slope in Figure 8 is negative, which correlates well with the negative slope in Figure 7. Otherwise, here, similar to the Propoxy frothers, the Ethoxy groups contribute to lower values of the CCC values. Similar to Figure 5, the agreement between experimental and theoretical values (see Equation (4)) for the Ethoxy frothers is good.





**Figure 8.** Ethoxy contribution  $\xi_2$  versus the number of Ethoxy ( $C_2H_4O$ ) groups in the molecule.

Figure 9 presents the experimental versus the theoretical values (see Equations (2)–(4)) of all the 37 frothers analyzed in the present study. One can see that the slope in Figure 9 is close to 1. Our analysis showed 7% average error in calculating the values of the frothers following the theoretical empirical equations described above (see Equations (2)–(4)). Indeed, we suggested 3 equations: one for the alcohol frothers (Equation (2)), one for the Propoxy frothers (Equation (3)), and one for the Ethoxy frothers (Equation (4)) instead of one general equation encompassing all of the classes of frothers with various molecular structures. We certainly know that such a description is possible within the QSPR method, but with another molecular descriptor (not the HLB value).



**Figure 9.** Theoretical versus experimental values of the critical coalescence concentration (CCC).

#### 4. Conclusions

The approach of Szyszka et al. [31,44] and Kovalszuk [39], to obtain a correlation between the CCC values, the HLB values of the frothers and their molecular mass. To our knowledge, this is the first study to establish a relation between the CCC value and the molecular structure of the frother. They applied their approach to particular cases of homologue series of frothers and established that it is difficult to switch between frothers belonging to different homologue series. Following a similar approach, we established empirical equations on a number of homologue series of frothers. The CCC values of many of them were taken from the literature [25–27,31,37,41] while the CCC value of some particular frothers, which are of special interest in the mining industry was measured in our laboratories. We conveniently established the dependence between  $\ln(\text{CCC})$  values and the HLB value of the frothers in the form of three empirical equations:

- For the homologue series of alcohol frothers, the position of the hydroxyl group (OH) on the main chain of the frother's molecule and the branched alkyl groups attached to the main chain of the was accounted for;
- For the homologue series of Propoxy frothers, the number of the Propoxy ( $\text{C}_3\text{H}_6\text{O}$ ) groups in the main chain of the molecule of the frother was taken into account;
- For the homologue series of Ethoxy frothers, the number of the Ethoxy ( $\text{C}_2\text{H}_4\text{O}$ ) groups in the main chain of the molecule of the frother was considered.

Therefore, the approach of Szyszka et al. [31,44] and Kovalszuk [39] was further extended in the present study. We must confess that our approach, even though it is similar to that of Szyszka et al. [31,44] and Kovalszuk [39] is still limited, because it contains 3 equations of different particular homologue series, instead of one general equation that encompasses all of the homologues series of the different frothers. Moreover, we recognize that such an approach should be applied to a significantly larger amount of frothers (not only 37) with various molecular geometries. Finally, with this work, we call upon the further development of this approach in the literature by other authors.

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