On the frother’s strength and its performance

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ABSTRACT

It is a common rule that the strength of the frother is assessed by either its dynamic foamability index (DFI) or its critical coalescence concentration (CCC). The smaller the value of CCC the stronger the frother is. This general rule (CCC rule) however is superficial although being well accepted. Yet, there are critical questions about the performance of the frothers on the bubbles:

1. Are the Gibbs elasticities stemming from the different frothers equally efficient in inhibiting the bubble coalescence?
2. How the Gibbs elasticity control the mean bubble diameter for every specific frother?
3. How the CCC value of the frothers and the mean bubble diameter are related?

This work raises these questions and suggests a rule based on the Gibbs elasticity performance (Gibbs elasticity rule). The performances of seven frothers (PPG 200, PPG 400, PPG 600, BDPG, BTPG, BTEG, and MIBC), whose surface tension isotherms, CCC values, bubble fraction coalescence, and Sauter mean bubble diameter vs. frother concentration were previously studied, were analyzed According to the CCC rule, these frothers follow the order of increasing strength: MIBC < BTEG < BDPG < PPG 200 < BTPG < PPG 600 < PPG 400. The Gibbs elasticity rule questions what will be the bubble fraction coalescence at a certain fixed value of the Gibbs elasticity of a frother? The above mentioned frothers according to this rule follow the series of PPG 400 < BTPG < BDPG < MIBC < BTEG < PPG 200. Surprisingly, it was established that PPG 600 exhibits abnormal behavior, thus significantly inhibiting the bubble coalescence in a different way, not related to the Gibbs elasticity. For this reason, PPG 600 in the above series was not included. Moreover, correlations between the mean bubble diameter, the Gibbs elasticity, and the CCC value were established. Additionally, a new dimensionless parameter was developed. It estimates the strength of a frother \( \approx \ln(\zeta_{\text{CCC}}/\alpha_0) \). A surprising correlation between the CCC values of 21 frothers and their \( \zeta \) values was developed. Moreover, it was established a correlation allowing us to calculate the bubble fraction coalescence vs. the frother concentration if the CCC value is known.

1. Introduction

The aqueous solutions of the frothers can be characterized by their ability to generate initial foam volume (foamability) and the durability of the already generated foam (Exerowa and Kruglyakov, 1997). For this reason, the authors studied the foamability (Bikerman, 1938; Petkova et al., 2020; Pugh, 2002; Rosen and Solash, 1969; Rosen and Zhu, 1988) and the foam stability (Andersson and Paul, 1982; Aveyard and Clint, 1996; Barber and Hartland, 1975; Exerowa and Kruglyakov, 1997; Umstatter, 1947; Varade et al., 2011; Weaire and Phelan, 1996) separately. While the foam durability and the foamability of the frothers in aqueous solutions are properties of the same system, they are unified by introducing a new value called “foam production” (Karakashev et al., 2012). However, these properties of the foam systems are valid for static foams – after the generation of the foam, the latter one is left to decay with the time. The distinction between foamability and foam durability
becomes indifferent in the case of pneumatic foam (e.g. refs. (Davidson and Harrison, 1966; Grace and Harrison, 1969; Karakashev et al., 2013)). This is the case of the flotation froths, where researchers utilize either the dynamic foaming index (DFI) (Czarniecki et al., 1982; Malysha et al., 1978) or the critical coalescence concentration (CCC) (Cho and Laskowski, 2002; Laskowski, 2003; Laskowski et al., 2003) of the frothers. Both values regard unstable pneumatic foams (froths). The different frothers have their specific CCC values, which depend on the content and the geometry of the frother’s molecule (Karakashev et al., 2020). The CCC value of the frothers were originally defined as the critical concentration, above which the bubbles practically do not coalesce anymore (Cho and Laskowski, 2002). The latter were determined by means of optical visualization. So far as good, the latter definition of the CCC value is just rough estimation. Our colleagues from Istanbul Technical University developed significantly more precise procedures determining the bubble fraction coalescence (BFC) versus the frother concentration (Guven et al., 2020). They defined the CCC value as the frother concentration, at which 50% of the bubbles coalesce. It is well known that the frothers inhibit the coalescence of the bubbles by means of the Gibbs elasticity of the adsorption layers. The latter one is expressed by the ability of the bubbles to counteract local deformations, which emerge during their coalescence. The Gibbs elasticity \( E_g \) increases with the increase of the fraction of the occupied area \( \theta \) by the frother on the air/water interface. This introduces the first sight of the frother’s performance over the bubble’s surface. Yet, the dependence of different frothers on \( E_g \) vs. \( \theta \) and the role of frother’s molecule should be questioned to understand the general performance of the frothers at the air/water interface. Another important question is if frothers with equal values of the Gibbs elasticity of their adsorption layers inhibit the bubble coalescence equally or differently? If the latter is true, this means that the Gibbs elasticities stemming from different frothers may have different effectiveness. Whether the achievement of 50% bubble fraction coalescence of one frother requires a smaller value of Gibbs elasticity \( E_g \) compared to another frother? If such differences exist, the Gibbs elasticities of some frothers will be more effective than the Gibbs elasticities of other frothers. Malysha (Malysha, 1992) was the first to introduce the term effective Gibbs elasticity, which he related with the dilatational elasticity of the foam lamella at the characteristic relaxation time of the adsorption layer under lack of equilibrium. He related the effective Gibbs elasticity with the retention time of the foam and the number of the carbon atoms in the hydrocarbon chain of the homologue series of alkanols. Hence, it appeared that the effective Gibbs elasticity is related to the molecular structure and the characteristic adsorption time. The idea, which we follow with this work is the same, but it is based on another very precise experiment - BFC versus frother concentration.

Furthermore, the dependence of the bubble fraction coalescence on the frother concentration is a well-accepted criterion for the strength of the frother, but the same dependence about the frother concentration is a well-accepted criterion for the strength of the frother and also the CCC value of the frothers. Be it the molecular structure and the characteristic adsorption time. The idea, which we follow with this work is the same, but it is based on another very precise experiment - BFC versus frother concentration.

2. Experimental data and procedures

The surface tension isotherms of polypropylene glycols (PPG 200, 400, and 600), Butyl tri propylene glycol (BTPG), Butyl triethylene glycol (BTEG), Butyl dipropylene glycol (BDPG), and methyl isobutyl carbinol (MIBC) were determined in our previous work (Batjargal et al., 2021; Guven et al., 2020) by means of automatic tensiometer/goniometer (model 290, Ramé – Hart Instruments Co., USA). The solutions were prepared from deionized (DI) water and the surface tension versus time for each particular concentration of every frother was demined for 3 h at a constant temperature of 20 °C. The equilibrium value of the surface tension for each one of the concentrations was determined from these kinetic curves. The frothers were obtained by BASF and are designed for flotation use. Their purity is >99%

Also, our experimental data on bubble fraction coalescence (BFC) and Sauter mean bubble diameter versus frother concentration dependencies, and the Sauter mean bubble diameter versus the air/flow rate at different sizes of the pores of the porous frit, published in the literature (Batjargal et al., 2021; Guven et al., 2020) were used. A special optical system containing a glass column with a porous frit was used for this aim. The frother solution was poured into the column and nitrogen through a porous frit was sparged through the solution with a controlled gas rate, thus allowing the formation of froth cap. The BFC curves were determined employing a special light - detector system very precisely, while the size of the bubbles were determined optically by continuous monitoring.

These seven frothers are called Group 1 in this work and make a detailed study on their performance on the surfaces of the bubbles. Moreover, it was taken into consideration another group of fourteen frothers, called here Group 2, whose CCC was taken from the literature (Zhang et al., 2012). The surface tension isotherms of six of them were measured in the present study, while these of the rest of them were taken from the literature. These are Dowfroth 250 (DF250), Dowfroth 200 (DF200), Dowfroth 1012 (DF 1012) (Laskowski, 2004), Polyoglic Olephrep F-507 (Corona-Arroyo et al., 2015), \( \alpha \)-terpinine, 2 - ethyl hexanol (Gupta et al., 2007), and Heptanol and Octanol. The surface tension isotherms of Dipropylene glycol (DPG), Tripropylene glycol (TPG), PPG 425, Methyl propoxy ether (PM), Di-propoxy methyl ether (DPM) and Tri-propoxy methyl ether (TPM) were determined in the present study using profile analysis tensiometry. The surface tension isotherms of the frothers from Groups 1 and 2 were processed using the adsorption model of Ivanov (Ivanov et al., 2010; Slavchov et al., 2014), which is based on the Helfand-Frish-Lebowitz 2D equation of state (Helfand et al., 1961) of moving discs in a plane using Baxter sticky potential (Baxter, 1969). The model consists of the following adsorption isotherm and equation of state:

\[
K_C = \frac{\theta}{(1 - \theta)} \left( \frac{2}{1 + R_p} \right) \exp \left[ \frac{\theta(4 - 3\theta)}{\sigma} \right] \frac{2}{1 + R_p} \\
\sigma = \sigma_0 - \frac{2RT}{(1 - \theta)} \frac{1}{1 + R_p} \\
R_p = \sqrt{1 + 16\theta^2 \frac{\sigma}{1 - \theta}}
\]

where \( K_C \) is the equilibrium adsorption constant of the frother, \( C \) is its bulk concentration, \( \theta \) is its fraction of the occupied area on the bubble surface, \( \Gamma_{\text{is}} \) is its maximal adsorption, \( \beta \) is the interaction parameter, \( \sigma \) is the equilibrium surface tension of the frother solution, \( \sigma_0 \) is a cohesion constant, whose value is close to the surface tension of the water at temperature \( T \) and \( R \) is gas constant. The application of the set of Eq. (1) to the surface tension isotherms of the above mentioned frothers gives their adsorption parameters \( K_C \), its cross-sectional area on the air/water interface \( \sigma_0 \), the interaction parameter \( \beta \). The adsorption parameters of the frothers from Group 1 and their corresponding CCC values were determined in ref. (Guven et al., 2020). The adsorption
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3. Results and discussion

3.1. Effectiveness of the Gibbs elasticity of different frothers

The analysis hereafter begins with the frothers from Group 1. Experimental data on their bubble performance are used... Fig. 1 shows the dependence of the Gibbs elasticity $E_g$ on the fraction of the surface occupation $\theta$ on the air/water interface by the frothers from Group 1.

The Gibbs elasticities curves in Fig. 1 were calculated using Eq. (2).

\[ E_g = -2 \theta \frac{d \sigma}{d \theta} = 4 \Gamma_s R T \theta \left[ R_\theta (1 - \theta^2) - \theta^2 (1 - 16 \theta^2) + 8 \theta \theta^2 \right] R_\theta \]

\[ = \sqrt{1 - \theta^2 + 16 \theta^2} \frac{1}{1 - \theta} \]

(2)

One can see that the maximal adsorption of each frother $\Gamma_s (1/\theta_0)$, related to the cross-sectional area of the molecule on the air/water interface, is responsible for the strength of the dependence $E_g$ vs. $\theta$. Hence, smaller frother molecules promote higher values of $E_g$ and vice versa. It will be presented hereafter in detail the $E_g$ vs. $\theta$ dependence of the frothers from Group 1 along with their individual $E_g$ values for achieving 50% bubble fraction coalescence (BFC). Such dependence will provide information about the strength of the frothers and the effectiveness of their individual Gibbs elasticities. If the frothers inhibit the bubble coalescence differently at equal Gibbs elasticity, this means that each one of them possesses certain effectiveness of the Gibbs elasticity, depending on the molecule's geometry. Yet, the inhibition of bubble coalescence is possible due to another reason (e.g., formation of 2D net (Malcolm Andrew et al., 2006)) except to the Gibbs elasticity. Another useful relation is the dependence of the bubble mean diameter on the Gibbs elasticity under equal conditions of the different frothers. Moreover, in this work a new parameter, called frother's strength parameter is defined. It estimates the strength of each frother:

\[ \zeta = \ln \left( \frac{K_{\text{CC}}}{\alpha_0} \right) \]

(3)

where $L_{CH}$ is the length of one methylene group ($L_{CH} = 1.26 \text{ Å}$). The larger the value of $\zeta$, the stronger the frother is and vice versa. The frother's strength parameter $\zeta$ shows how strong is the propensity of the frother to adsorb on the air/water interface. It will be further shown the correlation between the values of CCC of the frothers and their $\zeta$ values.

Table 1 presents the molecular weights, the adsorption parameters, the CCC values, and the frother's strength parameter $\zeta$ values of the frothers from Groups 1 and 2.

Table 1

| Frothers | Molecular Weight (g/mol) | $K_e$ (m) | $\alpha_0$ (Å²) | $\Gamma_s$ (mol/m²) | $\rho$ | CCC (mol/L) | $\zeta$ |
|----------|-------------------------|----------|-----------------|-------------------|------|-------------|------|
| PPG 600  | 540 – 660               | 5.00 x 10^-4 | 166.00          | 1.00 x 10^-6     | 0.68 | 5.00 x 10^-6 | 10.54 |
| PPG 400  | 360 – 440               | 5.00 x 10^-4 | 49.28           | 3.37 x 10^-6     | 0.00 | 9.52 x 10^-6 | 11.76 |
| BTPG     | 243.36                  | 9.72 x 10^-6 | 23.00           | 7.22 x 10^-6     | 0.00 | 2.01 x 10^-5 | 8.58  |
| PDG      | 190.28                  | 2.46 x 10^-6 | 19.96           | 8.32 x 10^-6     | 0.00 | 8.93 x 10^-5 | 7.35  |
| MBC      | 102.17                  | 1.17 x 10^-7 | 12.39           | 1.34 x 10^-5     | 0.00 | 9.70 x 10^-5 | 6.90  |
| Polyglycol FS07 | 425.00              | 7.53 x 10^-7 | 9.93            | 1.67 x 10^-5     | 0.00 | 9.78 x 10^-5 | 7.30  |
| DF200    | 206.29                  | 1.70 x 10^-6 | 44.27           | 3.75 x 10^-6     | 0.00 | 8.90 x 10^-5 | 6.18  |
| DF250    | 264.37                  | 2.50 x 10^-6 | 85.14           | 1.95 x 10^-6     | 4.88 | 3.30 x 10^-5 | 7.03  |
| DF1002   | 397.95                  | 1.00 x 10^-4 | 98.40           | 1.69 x 10^-6     | 6.97 | 1.50 x 10^-5 | 9.46  |
| 2Ethyl Hexanol | 130.00              | 1.00 x 10^-4 | 62.69           | 2.65 x 10^-6     | 0.00 | 2.00 x 10^-5 | 9.91  |
| a - Terpineol | 148.00                | 1.03 x 10^-5 | 32.59           | 5.10 x 10^-6     | 0.00 | 2.31 x 10^-5 | 8.29  |
| Heptanol  | 116.88                  | 3.12 x 10^-6 | 14.04           | 1.18 x 10^-6     | 0.73 | 5.52 x 10^-5 | 7.94  |
| Octanol   | 130.23                  | 4.09 x 10^-6 | 19.39           | 8.56 x 10^-6     | 0.00 | 6.20 x 10^-5 | 7.88  |
| DPG      | 134.14                  | 3.30 x 10^-6 | 10.11           | 1.64 x 10^-6     | 0.00 | 4.04 x 10^-5 | 3.72  |
| TPM      | 192.25                  | 1.25 x 10^-7 | 19.82           | 8.38 x 10^-6     | 0.00 | 1.75 x 10^-4 | 4.57  |
| PPG425   | 425                    | 6.03 x 10^-4 | 21.97           | 7.56 x 10^-6     | 0.00 | 1.40 x 10^-5 | 12.75 |
| PM       | 90.12                   | 2.78 x 10^-6 | 13.00           | 1.28 x 10^-6     | 0.00 | 4.74 x 10^-4 | 3.29  |
| DM       | 148.20                  | 1.03 x 10^-7 | 19.06           | 8.71 x 10^-6     | 0.00 | 1.67 x 10^-5 | 4.22  |
| TPM      | 192.25                  | 8.82 x 10^-7 | 31.29           | 5.31 x 10^-6     | 0.00 | 7.00 x 10^-5 | 5.87  |
It is evident that the cross-sectional area of the frother’s molecule \( \alpha \) on the air/water interface is related to the effectiveness of the Gibbs elasticity. Surprisingly, PPG 200 made an exclusion because it has the most effective Gibbs elasticity, and at the same time it has \( \alpha \) value close to some of the preceding frothers in the series (\( \alpha_0 = 21.85 \text{ Å}^2 \)). Another exclusion is PPG 600, which has the largest molecule from the group (\( \alpha_0 = 166 \text{ Å}^2 \)), and whose \( \zeta \) value at 50% BFC is close to BDPG and BTPG. The PPG frothers have another way to stabilize the froths except for the Gibbs elasticity. Such a way could be the formation of a 2D net at the air/water interface, which can significantly increase the surface viscosity of the air/water interface similar to the system in ref. (Malcolm Andrew et al., 2006).

Fig. 2 presents the bubble fraction coalescence (BFC) versus the Gibbs elasticity \( \zeta \) of frothers from Group 1. One can see that in all of the cases the increase of the Gibbs elasticity causes a decrease of the BFC values, but the more effective frothers start a significant decrease of the BFC from the very beginning of the increase of their \( \zeta \) values. Such is the case of PPG 200. As the most effective frother, it’s BFC curve dropped prior to those of the other frothers, with the increase of the Gibbs elasticity. This means that smaller Gibbs elasticity values are required to achieve good BFC performance. One can see as well that the BFC curves of BTEG and MIBC (practically coinciding) dropped a little bit prior to those of BDPG and BTPG (practically coinciding) with the increase of the \( \zeta \) value. This means that the Gibbs elasticity of BTEG and MIBC is a little bit more effective than that of BDPG and BTPG. Finally, the BFC curve of PPG 400 dropped substantially after the other frothers with the increase of \( \zeta \) indicating that PPG 400 has the least effective Gibbs elasticity. Moreover, one can see as well that at small values of the Gibbs elasticities the BFC curves of BTEG, MIBC, BDPG, and BTPG practically coincide. Therefore, the effectiveness of the Gibbs elasticity increases with the increase of its value. Surprisingly, the BFC curve of PPG 600 dropped sharply with a significantly larger decrement than those of the other frothers with the increase of the Gibbs elasticity. This is an indication of abnormal behavior of this frother, showing an additional way to stabilize the froth. Most probably, the PPG 600 molecules form a 2D net on the air/water interface and lead to a substantial increase in the surface viscosity of the bubbles. This is the second mechanism of froth stabilization, which occurs rarely with the surface-active species.

The effectiveness of the Gibbs elasticity, which was suggested here is the Gibbs elasticity values of the frothers, which are required to achieve 10% BFC. The reason to choose 10% BFC, but not 50% BFC (related with the CCC value) is that the \( \zeta \) values of the frothers are mostly distanced at 10% BFC. The frother with the most effective Gibbs elasticity, as seen in Fig. 2, is PPG 200, which has \( \zeta = 2.6 \times 10^{-4} \text{ N/m} \) to achieve 10% BFC. Therefore, it was assumed the value of \( \zeta = 10^{-4} \text{ N/m} \) (to achieve 10% BFC) as an upper limit, corresponding to 100% effectiveness of the Gibbs elasticity (EGE). Therefore, it was calculated the EGE values of the frothers from Group 1 using the following simple formula:

\[
\ln\left(\frac{10^{-1}}{100}\right) = \ln\left(\frac{\zeta_{PG 600}}{\zeta_{PG 400}}\right) = EGE = x
\]

(4)

Table 2 presents the frothers from Group 1 and their corresponding cross-sectional areas on the air/water interface \( \alpha_0 \) the EGE values, and the frother’s strength parameter \( \zeta \). It is evident that small difference of the cross-sectional areas \( \alpha_0 \) of the frothers’ molecules on the air/water interface (see the pairs (BTPG and BDPG) and (BTEG and MIBC) in Table 2) correspond to practically the same effectiveness of their Gibbs elasticities. One can see in Table 2 that PPG 400 has the smallest EGE value (25.27%) corresponding to \( \alpha_0 = 49.28 \text{ Å}^2 \). BTPG and BDPG have smaller molecules with close to each other sizes (\( \alpha_0 = 23 \text{ Å}^2 \) and \( \alpha_0 = 19.96 \text{ Å}^2 \)) and have identical EGE values (40.24%). Similarly, BTEG and MIBC have smaller molecules with close to each other sizes (\( \alpha_0 = 12.39 \text{ Å}^2 \) and \( \alpha_0 = 9.93 \text{ Å}^2 \)) and have identical EGE values (45.60%). Finally, and surprisingly, PPG 200 has larger molecules (\( \alpha_0 = 21.85 \text{ Å}^2 \)), but it has the largest EGE value (64.62 %). This could be due to the secondary froth stabilization mechanism involved except the Gibbs elasticity.

Fig. 3 shows the dependence of the EGE value on the cross-sectional area of the frother’s molecules at the air/water interface \( \alpha_0 \). One can see that the EGE versus \( \alpha_0 \) dependence is linear, but PPG 200 makes an exclusion most probably due to taking part in the secondary stabilization mechanism. As mentioned above, PPG 600 is another frother with abnormal behavior stabilizing the froth in a way, which cannot be explained with the Gibbs elasticity. Most probably this could be due to the formation of 2D net between the propylene segments of the different molecules by

Table 2

| Frothers       | PPG 400 | BTPG | BDPG | BTEG | MIBC | PPG 200 | PPG 600 |
|----------------|--------|------|------|------|------|--------|--------|
| \( \alpha_0 \) Å² | 49.28  | 23.00 | 19.96| 12.39| 9.93 | 21.85  | 166    |
| EGE, %         | 25.27  | 40.24| 45.60| 45.60| 64.62| N/A    |        |
| \( \zeta \)    | 11.76  | 8.58 | 7.35 | 6.90 | 7.30 | 5.34   | 10.54  |
means of hydrogen bonds. Hence, the surface tension isotherm of PPG 600 is presented in Fig. 4. One can see the abnormal abrupt drop of the surface tension from $\sigma = 70.54 \text{ mN/m}$ at $10^{-7} \text{ mol/L}$ to $\sigma = 64.46 \text{ mN/m}$ at $5 \times 10^{-7} \text{ mol/L}$ (see Fig. 4). Such a drop of the surface tension is unusual and cannot be seen with the conventional surfactants. Therefore, it can certainly be stated from our observations in Figs. 2 and 4 that PPG 600 exhibits a surface state on the air/water interface, making the bubbles additionally more difficult to coalesce. Most possibly, the formation of 2D net at the air/water interface is probably responsible but requires independent measurements.

The bubble fraction coalescence (BFC) versus the frother concentration dependance is an adequate way to assess the performance of the frothers, as it enables the possibility to conduct the above mentioned analysis. Yet, another important dynamic parameter is the Sauter mean bubble diameter. There were exploited the experimental data about the Sauter mean bubble diameter at 50 ppm of the frothers from Group 1 published by ref. (Batjargal et al., 2021). Hence, their molar concentrations and the related values of the Gibbs elasticities were recalculated. Fig. 5 shows the Sauter mean bubble diameter versus Gibbs elasticity at 50 ppm frothers from Group 1, air flow rate 50 ml/min, and frit pore size: 10–16 $\mu$m.

PFG 400 has the largest value of the Gibbs elasticity producing larger bubbles than PPG 600. This is in line with our above mentioned analysis showing the least effective Gibbs elasticity of PPG 400 (EGE = 25.27%). It produces smaller bubbles than PPG 200, BDPG, BTPG, BTEG, and MIBC because of its high surface activity causing the largest value of the Gibbs elasticity from the whole series of Group 1, corresponding to smaller bubble fraction coalescence (BFC) than those of PPG 200, BDPG, BTPG, BTEG, and MIBC. Nevertheless, PFG 400 exhibits the worst effective Gibbs elasticity in the whole series of frothers from Group 1.

Furthermore, Fig. 6 shows the correlation between the Sauter mean bubble diameter at 50 ppm frothers from Group 1 and their CCC values at air flow rate 50 ml/min, and frit pore size: 10–16 $\mu$m.

The general trend shows an increase of the Sauter mean bubble diameter with the increase of the CCC values, but a divergence in the cases of MIBC, BDPG, and BTEG indicating an upper limit of the Sauter mean bubble diameter above a certain CCC value (above $6 \times 10^{-5} \text{ mol/L}$) can be seen.

### 3.2. Frother’s strength and its performance

It was described here above the effectiveness of the Gibbs elasticity of the different frothers from Group 1, thus ordering them in a series of increasing effectiveness as shown in Table 2. Yet, the effectiveness of the Gibbs elasticity is only one of the sides of the coin. The other one is the surface activity of the frothers, as some frothers are more surface-active than others. The CCC values of the frothers are the result of the combined effect of the Gibbs elasticity effectiveness and their surface activity. Indeed, the CCC value of the frothers regards pneumatic froths, which are continually fed by new portions of bubbles in contrast to the static foams, which are characterized by foamability and foam durability. It is well known that the surface activity of the frothers is described by their adsorption parameters, contained in their adsorption isotherm and equation of state (see Eq. (1)) – the equilibrium adsorption constant $K_s$, the maximal adsorption $\Gamma_{\infty}$ (or cross-sectional area per molecule $a_0$) and the interaction parameter $\beta$. The analysis shows that the CCC values of the frothers corresponding to 50% bubble fraction coalescence (50% BFC) stem from the contributions of the Gibbs elasticity (mostly affected by $a_0$) and the surface activity (affected by both $\alpha_0$ and $K_s$). The cross-sectional area $a_0$ rules out the effectiveness of the Gibbs elasticity (EGE) (see Fig. 3), while both $a_0$ and $K_s$ rule out the value of $E_G$ at a certain concentration of the frothers. Therefore, small values of $E_G$ and large value of $K_s$ favor both high EGE value and large value of the Gibbs elasticity at a certain concentration of the frothers and vice versa. Yet, there are many frothers with both large values of $K_s$ and $a_0$ and vice versa. Such frothers should have mediocre surface activity,
the frothers from Group 1.

Fig. 7. The Gibbs elasticity $E_g$ versus the frothers strength $\zeta$ at $10^{-5}$ mol/L frother from Group 1.

thus promoting either higher EGE value and low value of the Gibbs elasticity or lower EGE value and higher value of the Gibbs elasticity. The very surface activity of the frother stems from the joined contribution of $K_s$ and $\alpha_p$ parameters. Hence, the surface activity of the frothers and their CCC values should be best correlated. Surface activity should be well correlated with the Gibbs elasticity as well because the latter one is the driver of froth stabilization. Yet, any other factors, which can stabilize the froth like the hydrophobic particles, or the formation of 2D net on the air/water interface are not excluded. Therefore, the adsorption parameters to build up such dimensionless parameter showing the surface activity as given by Eq. (3) were used. This parameter is called frother’s strength (see Tables 1 and 2). The values of the strength of the frothers from Groups 1 and 2 are presented in Table 1. One can see that the strength parameter is a parameter, whose value lies between the numbers 5 and 12 (for frothers from Groups 1 and 2). The weakest frothers have $\zeta$ close to 5, while the strongest frothers have $\zeta$ close to 12. Fig. 7 shows the dependence of the Gibbs elasticity $E_g$ versus the strength parameter $\zeta$ of the frothers from Group 1 at $10^{-4}$ mol/L. One can see that the Gibbs elasticity increases with the increase of the frother’s strength and the increment of this dependence increase significantly for frothers with $\zeta > 7.35$.

Another important question is whether the frothers strength $\zeta$ affects the effectiveness of the Gibbs elasticity (EGE). Fig. 8 shows this dependence for the frothers from Group 1. One can see that the increase of the frothers strength $\zeta$ causes a decrease in the effectiveness of the Gibbs elasticity (EGE), i.e. the more surface active frothers have less effective Gibbs elasticities and vice versa. Though surprising, this dependence is general, as far as frothers with similar molecular sizes exist. But, different values of $\zeta$ can have identical EGE values. Such an example is the two pairs of frothers (BTEG and MIBC) and (BDPG and BTPG).

Furthermore, the frothers from Group 1 can be ordered in a series of increasing strength $\zeta$ as follows:

\[ \text{PPG 200 (} \zeta = 5.34) < \text{BTEG (} \zeta = 6.9) < \text{MIBC (} \zeta = 7.30) \approx \text{BDPG (} \zeta = 7.35) < \text{BTPG (} \zeta = 8.58) < \text{PPG 600 (} \zeta = 10.54) < \text{PPG 400 (} \zeta = 11.76) \]

To estimate more properly the frothers performance one need to compare the above series with the series of the frothers in decreasing CCC value:

\[ \text{MIBC (9.87x10^{-5} mol/L) } \approx \text{BTEG (9.70x10^{-5} mol/L) > BDPG (8.93x10^{-5} mol/L) > PPG 200 (5.73x10^{-5} mol/L) > BTPG (2.01x10^{-5} mol/L) > PPG 400 (9.52x10^{-6} mol/L) > PPG 600 (5.00x10^{-6} mol/L) } \]

One can see in Fig. 8 that PPG 200 has both the smallest strength ($\zeta = 5.34$) and the highest Gibbs elasticity effectiveness (EGE = 64.62%). Hence, it is in the middle of the CCC series (CCC = 5.73x10^{-5} mol/L). As the highest EGE value of PPG 200 is not compatible with the smallest molecule (see Fig. 3) from the whole Group 1 of frothers, one can envisage that this highest EGE value is due to occurring of a second froth stabilizing mechanism, which could be some islands of 2D structures of PPG 200 molecules, which could increase the surface viscosity of the air/water interface. Furthermore, BTEG ($\zeta = 6.9$) and MIBC ($\zeta = 7.30$) are the next members of increasing frothers’ strength series, but they have practically the same EGE values (EGE = 45.60%). Their molecules are the smallest ones from the whole Group 1 ($\alpha_p = 12.39 \text{ Å}^2$, $\alpha_p = 9.93 \text{ Å}^2$). Therefore, their CCC values are practically the same and the largest one from the whole series (CCC = 9.87x10^{-5} mol/L, CCC = 9.70x10^{-5} mol/L). The next member of increasing frother’s strength is BDPG ($\zeta = 7.35$), which practically coincides with that of MIBC ($\zeta = 7.30$), and both exhibit EGE values smaller and close to each other (40.24% and 45.60%) than PPG 200. The CCC value of BDPG is 8.93x10^{-5} mol/L. This value is close to the values of MIBC (9.87x10^{-5} mol/L) and BTEG (9.70x10^{-5} mol/L). Hence, these similarities in the frother’s strength values, EGE values and CCC values reveal that MIBC, BTEG, and BDPG have practically identical performance on the surface of the bubbles and inhibit the bubble coalescence practically identically. Furthermore, the next member of increasing strength is BTPG ($\zeta = 8.58$) who has practically the same EGE value of BDPG (EGE = 40.25%), and similar molecule size (BTPG $\alpha_p = 23.00 \text{ Å}^2$ and BDPG $\alpha_p = 19.96 \text{ Å}^2$). One can see in Fig. 7 that at $\zeta > 7.35$ the increment of the Gibbs elasticity increases with the increase of the value of $\zeta$. So, with the same EGE value as BDPG but an increased value of $\zeta$ above 7.35 it gives a significantly higher value of the Gibbs elasticity (see Fig. 7), which causes a smaller value of CCC (2.01x10^{-5} mol/L). Furthermore, the next two members with increasing strength are PPG 600 ($\zeta = 10.54$) and PPG 400 ($\zeta = 11.76$). PPG 400 has the smallest EGE value (EGE = 25.27%) and at the same time it has the largest strength ($\zeta = 11.76$) from the whole Group 1 of frothers (opposite to PPG 200). Therefore, its CCC value (9.52x10^{-6} mol/L) is smaller than the preceding frothers in the series (2.01x10^{-5} mol/L, 5.73x10^{-5} mol/L). Nevertheless, the CCC value of PPG 600 (5.00x10^{-6} mol/L) is significantly smaller than that of PPG 400 (9.52x10^{-6} mol/L). This could be due to the enormously high effectiveness of the Gibbs elasticity in the case of PPG 600 or activation of a second froth stabilizing mechanism like the formation of 2D surface net on the air/water interface. Moreover, the increase of the increment of the Gibbs elasticity value versus the frother’s strength at $\zeta > 7.35$ could be due to the formation of larger or smaller aggregates of molecules, held each other by the hydrogen bonds between the propylene segments. Such formation of aggregates should emerge even in the case of PPG 200. The latter contains 3 propylene segments as the molecule of BTPG. So, with 3 and more propylene segments, the molecules can form aggregates due to intermolecular hydrogen bonds and the size of these aggregates depends on the number of the propylene segments. Of course, this opinion of ours based on pure analysis remains a hypothesis until being proved. Overall, one could
order the frothers from Group 1 in the following order of increasing performance at the same molar concentration:

\[ \text{MIBC} \approx \text{BTEG} \approx \text{BDPG} < \text{PPG 200} < \text{BTPG} < \text{PPG 400} < \text{PPG 600} \]

Furthermore, the data from ref. (Batjargal et al., 2021) on the Sauter mean bubble diameter at 50 ppm frother concentration from Group 1 as a function of the air flow rate, as depicted in Fig. 8 were used. The molar concentration of each frother and consequently, its Gibbs elasticity were calculated. First of all, contrary to the observations in the literature for other frothers (Gorain et al., 1995; Grau et al., 2005), the Sauter mean bubble diameter decreases with increasing the air flow rate. This should be due to the ultrafast adsorption of PPG 200, BTEG, BDPG and BTPG, and MIBC. PPG 400 and PPG 600 reach a minimum beyond which the Sauter mean diameter of the bubbles increases with the increase of the air flow rate. These two frothers possibly use the second mechanism for froth stabilization, except the Gibbs elasticity, and adsorb significantly slower on the bubbles than the other frothers. As can be seen in Fig. 9 that BTEG (\(E_g = 1.03 \times 10^{-3} \text{ N/m}, \ EGE = 45.60\%\)) produces the largest bubbles whereas BDPG (\(E_g = 2.79 \times 10^{-3} \text{ N/m}, \ EGE = 40.24\%\)) produces smaller bubbles. Furthermore, PPG 200 (\(E_g = 3.94 \times 10^{-4} \text{ N/m}, \ EGE = 64.62\%\)), produces smaller bubbles than BDPG due to its highest EGE value from the whole Group 1 of frothers. MIBC (\(E_g = 2.50 \times 10^{-4} \text{ N/m}, \ EGE = 45.6\%\)) produces smaller bubbles than PPG 200 (\(E_g = 3.93 \times 10^{-4} \text{ N/m}, \ EGE = 64.62\%\) and BDPG (\(E_g = 2.79 \times 10^{-3} \text{ N/m}, \ EGE = 40.24\%\)). BTPG (\(E_g = 7.95 \times 10^{-3} \text{ N/m}, \ EGE = 40.24\%\)) produces smaller bubbles than MIBC (\(E_g = 2.50 \times 10^{-3} \text{ N/m}, \ EGE = 45.6\%\)). PPG 400 (\(E_g = 6.13 \times 10^{-2} \text{ N/m}, \ EGE = 25.27\%\)) produces smaller bubbles than BTPG (\(E_g = 7.95 \times 10^{-3} \text{ N/m}, \ EGE = 40.24\%\)). PPG 600 (\(E_g = 2.54 \times 10^{-2} \text{ N/m}\)) produces the smallest bubbles from the whole Group 1.

As mentioned before, one can find this frother special due to its abnormal behavior with an evident second mechanism for froth stabilization. For this reason, it was not classified with our EGE classification. Fig. 10 shows the Sauter mean bubble diameter (SMD) at 50 ppm of each frother and air flow rate 50 ml/min, and 10 μm–16 μm pores of the porous frit and the corresponding \(E_g\) and EGE values of each frother. It is curious to note that the porous frit has pores with sizes in the range of 10 μm–16 μm, while SMD of the bubbles is in the range of 190 μm to 350 μm. This means that the bubbles undergo significant coalescence on the bottom of the porous frit, thus becoming significantly bigger. The frothers inhibit mostly the coalescence of this secondary population of bubbles.

Another important point is the relation between the frother’s strength parameter and its CCC values. To find such a dependence the experimental data on the CCC values and the surface tension isotherm of Groups 1 and 2, thus including overall 21 frothers were used. The surface tension isotherms of these frothers were processed by means of the

![Fig. 9. Sauter mean bubble diameter at 50 ppm frothers from Group 1 versus the air flow rate (Batjargal et al., 2021) at frit pore size 10 μm–16 μm.](image_url)

![Fig. 10. Sauter mean diameter (SMD) of the bubbles at 50 ppm of each frother at air flow rate = 50 ml/min, and the \(E_g\) and EGE values of each frother from Group 1 (Batjargal et al., 2021).](image_url)
model of Ivanov (see Eq. (1)), thus calculating their strength parameter \( \zeta \), which are presented in Table 1. Fig. 11 shows the dependence of the CCC values of the frothers from Groups 1 and 2 versus their strength parameter \( \zeta \). One can see in Fig. 11, that in the range of \( \zeta = 12.76 \) to \( \zeta = 8.3 \), containing strong frothers (PPG 400, PPG 425, PPG 600, 2-ethyl hexanol, DF 1102, BTPG, \( \alpha \) - Terpeniol) the CCC values are scattered around a certain average value of \( \text{CCC} = 1.45 \times 10^{-5} \text{ mol/L} \) and this average value does not depend on the strength \( \zeta \) of the frother. This means that there is a low limit of the CCC value of the strong frothers – at \( \zeta > 8.35 \) the CCC value of the frothers practically does not change but is scattered around this low limit. In the range of \( 5 < \zeta < 8.3 \) the CCC dependence on the frothers strength \( \zeta \) has a bell shape. The CCC value increases from \( \text{CCC} = 1.45 \times 10^{-5} \text{ mol/L} \) to \( \text{CCC} = 10^{-4} \text{ mol/L} \) with the decrease of the \( \zeta \) value from \( \zeta = 8.3 \) to \( \zeta = 7 \) (DF 250, Heptanol, Octanol, BDPG, MIBC, BTEG). At a lower value of the strength parameter \( 5 < \zeta < 7 \), which represents weaker frothers, the CCC value decreases to the previous low level of the CCC value (DF 200, PPG 200, TPM, and F 507). This could be related to the higher efficiency of their Gibbs elasticity. At \( \zeta < 5 \) one can see strong increase in the value of CCC with the further decrease of the \( \zeta \) value (DPM, TPG, DPG, and PM) up to \( \text{CCC} = 4.74 \times 10^{-4} \text{ mol/L} \) (at \( \zeta = 3.29 \), PM). Hence, it was found out two overall dependencies of the CCC values on strength parameter \( \zeta \) - bell shape dependence in the range of 12.76 to 5 and straight-line dependence at \( \zeta < 5 \). This result is surprising and the reason for the two dependencies of the CCC values on the \( \zeta \) parameter should be studied more detailed. Table Curve software was exploited to find out an equation capable of describing this experimental dependence in the range of \( \zeta = 12.76 \) to \( \zeta = 5 \).
5 and found out that it can be described by means of the Beta distribution Beta($a, b, c, d, f$) (equation No 8055 in the table curve list).

\[
CCC = a + b \left( \frac{\zeta - c + \Delta m}{\Delta n} \right)^{-1} \left( 1 - \frac{\zeta + \Delta m}{n} \right)^{m-1} ; m = \frac{e - 1}{e + f - 2} \text{.} \tag{5}
\]

The numerical coefficients in Eq. (5) are the following: $a = 1.45 \times 10^{-5}$, $b = 8.95 \times 10^{-5}$, $c = 6.62$, $d = 3.05$, $e = 1.53$, $f = 1.66$. It should be noted that the frothers from Groups 1 and 2 are with molecular weights > 90. Frothers with molecular weight smaller than 90, for example butanol, propanol, etc were not analyzed. It was taken into consideration mostly the commercial frothers, used in the mining industry.

### 3.3. Correlations for easy calculation of the bubble fraction coalescence vs. The frothers concentration at known CCC value

The CCC values of the frothers regard their concentration, at which they achieve 50% bubble fraction coalescence (50% BFC). What about the concentrations for achieving other BFC (10%, 30%, 70%...)? The BFC curves of the frothers from Group 1 published in ref. (Batjargal et al., 2021) were used. It was found out the following correlation between the BFC and the frothers concentration:

\[
\text{BFC} = a + b \ln \left( \frac{C}{\text{CCC}} \right) + c \left[ \ln \left( \frac{C}{\text{CCC}} \right) \right]^2 + d \left[ \ln \left( \frac{C}{\text{CCC}} \right) \right]^3 \tag{6}
\]

where CCC is the critical coalescence concentration, $C$ is the frother’s concentration, and $a, b, c, d$ are coefficients, calculated by means of the formula in Eq. (6). This correlation was used resulting in the following theoretical curves with good coincidence with the experimental points, as shown in Fig. 12:

The correlation between the BFC and the froth concentration at the known value of CCC shows that such a correlation can be made for other frothers if the CCC value is known.

![Fig. 12. (continued).](image-url)
4. Conclusion

The following conclusions were made after careful analysis of the frother’s performance:

1. The Gibbs elasticity, generated by the frothers, is the main driver for the inhibition of the bubble coalescence;
2. Different frothers with the same value of the Gibbs elasticity inhibit the bubble coalescence differently i.e. identical values of the Gibbs elasticity from different frothers correspond to different bubble fraction coalescence (BFC) values; Hence, a new value “Effectiveness of the Gibbs elasticity” was introduced;
3. The effectiveness of the Gibbs elasticity (the EGE value) has a trend of overall decrease with the increase of the cross-sectional area of the frothers’ molecules at the air/water interface \( \sigma_0 \) (size of the molecules);
4. PPG 600 and PPG 200 have a second mechanism for froth stabilization except for the Gibbs elasticity; Probably they form a 2D net of the air/water interface;
5. The Sauter mean diameter (SMD) of the bubbles has an overall trend of decrease with the increase of the Gibbs elasticity. A minimum of SMD of the bubbles was established with PPG 600, beyond which it increases with PPG 400. This could be due to the second froth stabilization mechanism of PPG 600, which is evident;
6. The Sauter mean diameter (SMD) of the bubbles has an overall trend of increase with the increase of the CCC values of the frothers until reaching the plateau around which the CCC values of the frothers are scattered; This is an indication of an upper limit in the SMD of the bubbles with the increase of the CCC values;
7. It was formulated a new parameter called “frother strength \( \zeta \)”, which is based on its adsorption parameters; The frother strength \( \zeta \) is a value showing the surface activity of the frothers;
8. The effectiveness of the Gibbs elasticity (the EGE value) has an overall trend of decrease with the increase of the frother strength \( \zeta \);
9. There were established two basic correlations between the CCC values of the frothers from Groups 1 and 2 and their strength parameter \( \zeta \); For more details look at the text.
10. It was established a correlation between the bubble fraction coalescence (BFC) of the frothers and their concentration at the known CCC value. If one knows the CCC value of a certain frother he can easily calculate the BFC versus frother concentration dependence.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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