

Article

The Performance of Carbonate-Modified Nonionic Surfactants in Microplastic Flotation

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Abstract: For a group of nonionic surfactants with polar head groups synthesized by the copolymerization of ethylene oxide and carbon dioxide, the potential for their application in the foam flotation of microplastic particles was investigated. Their performance was compared to conventional that of nonionic surfactants and correlated with their adsorption behavior at the water–air surface through the maximum-bubble-pressure technique. The carbonate content of the surfactant head groups increased the biodegradability of the surfactants and affected their foaming properties and their performance in the flotation process. Since the inserted carbonate units increased the hydrophilicity of the whole surfactant but decreased the polarity of their headgroups, the number of carbonate units can be considered as an independent tuning parameter for adjusting these surfactants to a particular application. With this feature, the countercurrent trends of the two most important performance indicators, namely the removal rate and enrichment factor, can be resolved.

Keywords: surface tension; adsorption; foam; foam stability; flotation; carbonate-modified nonionic surfactants



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1. Introduction

Understanding surfactants' adsorption properties is important for many different applications. The adsorption of surface-active molecules must stabilize newly formed interfaces in order for gases, liquids, or solids to be dispersed in a continuous phase [1]. In processes such as foam formation [2,3], the emulsification of oils [4–6], or the wetting of paper or textiles [7] only fractions of a second are available for this adsorption process. The performances of different surfactants in these applications is governed by the rate of the adsorption process rather than by the equilibrium surface tension [8,9]. A direct investigation into the influence of the surfactant properties on their performance is rather difficult due to the complexity of such dispersion processes, which are characterized by strong influences on the material properties and fluid-dynamic conditions within the applied devices. Any choice of surfactant for recipe optimization can only be based on empirical evidence. The measurement of the dynamic surface tension of a surfactant solution is frequently used as the central parameter for determining the effect of a surfactant's molecular structure on its transport and adsorption behavior [10,11].

For other applications, the contact angle of a surfactant solution on the flat surface of a relevant solid material is taken as an indicator of the interactions of the materials and their wetting behavior. The contact angle of the liquid at the solid surface is a consequence of the ratio of the interfacial tensions of the three involved phases according to Young's Equation (1) [12].

$$\cos \theta = \frac{\sigma_{SG} - \sigma_{LS}}{\sigma_{LG}} \quad (1)$$

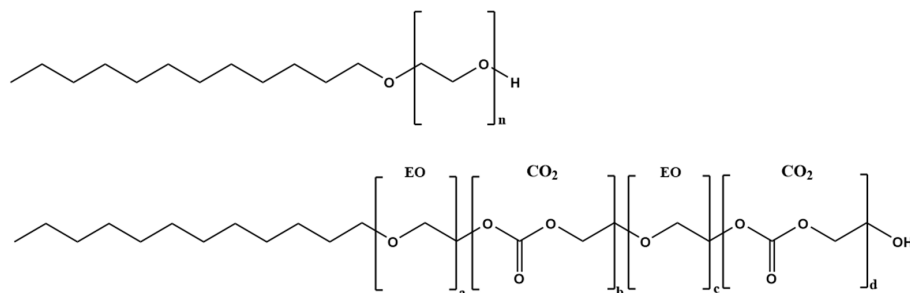
with θ being the contact angle and σ_{SG} , σ_{LS} , and σ_{LG} being the interfacial tensions at the solid–gas, liquid–solid, and liquid–gas interfaces, respectively. The typical ranges of contact angles describe non-wetting, partial, or complete wetting.

It is common knowledge that the degree of ethoxylation has a significant impact on the performances of nonionic surfactants in a variety of applications. The hydrophilicity of these surfactant molecules rises with the number of ethylene oxide groups, resulting in modifications to numerous distinctive properties, such as the critical micelle concentration (CMC), cloud point, and packing parameter. The hydrophilic–lipophilic balance (HLB) values of various surfactants are frequently used to illustrate this [13]. Additionally, at a given concentration, the rate of surface-tension reduction increases with the number of ethylene oxide (EO) units in a series of these surfactants [14]. The observed changes in the rate of surface-tension reduction cannot easily be attributed to one of the molecular properties because the molecular weight, CMC, and aggregation number change as the number of EO units increases. If the variation in the degree of ethoxylation is not sufficient for adjusting the adsorption behavior of a surfactant in a particular application, the ethylene-oxide units can be partly or completely replaced by propylene oxide [15]. This results in more hydrophobic but still surface-active molecules. The froth flotation of minerals is an important application field for propylene-oxide-based surfactants. Their essential function is surface-tension reduction for gas-bubble stabilization in the flotation foam and, simultaneously, the wetting of the particles to be transferred out of the dispersion into the foam [16]. A variety of so-called frothers is available with different chain lengths of propylene oxide chain bound to alkyl chains of different lengths between 4 and 10 C-atoms [17]. A key parameter for the performance of these frothers is the critical coalescence concentration, which stabilizes the minimal size of air bubbles and prevents their coalescence. This concentration is found at the adsorption isotherm of the compound at the water–air surface, close to the critical micelle concentration (CMC) if the surfactants can form micelles. Since propylene-oxide-based surfactants exhibit no good biodegradability [18], there is a need for alternatives with better biodegradability while retaining the same performance in the separation processes, since otherwise, the separation efficiency could decrease and operation costs increase [19]. Polyethercarbonates, as headgroups of surface-active molecules, could represent such an alternative. The polarity of these groups can be tuned by their carbonate content, which increases the biodegradability substantially [20–22].

As hydrophilic building blocks, traditional nonionic surfactants contain an EO chain of a certain length (distribution). However, one way to tune surfactant properties and, consequently, systematically tune the dynamic surface properties discussed above, is to modify this EO block by incorporating additional units other than EO. This question is interesting because recently available surfactants allow a portion of the EO to be replaced by CO₂, which is both fundamentally interesting and relevant in the context of using sustainable-resource CO₂ rather than gasoline-based EO. We recently conducted research on the phase behavior, CMC, and micellar structures found in surfactants with an increasing head group of carbonate units [23]. This study investigated two sets of nonionic surfactants to learn more about their surface-active properties and the key parameter for a high rate of surface-tension reduction. The effect of the degree of ethoxylation was examined in a series of alkyl ethoxylates with varying numbers of EO groups. The hydrophilic head groups of the second series of nonionic surfactants were made up of two building units: CO₂ and ethylene oxide. These surfactants have different fractions of carbonate despite having roughly the same molecular weight, which affects how they interact with the solvents and the interface. The question in this study is whether a combination of the two headgroup building blocks, EO and CO₂, provides a further degree of freedom for the design of surfactants with specialized properties for specific applications.

A process that has the potential to yield polycarbonates with good degradability is the copolymerization of CO₂ with epoxides. The copolymerization of CO₂ and epoxides has been developed by numerous businesses all over the world as a result of the recent development of catalytic systems, which are either heterogeneous or homogeneous. The

development of a method for using CO₂ as a C1 building block for polymer synthesis was the focus of previous studies. Zinc hexacyanocobaltate (DMC) was developed by Gürtler et al. as a catalyst to produce polyether carbonate polyols from multifunctional alcohol as a starting point [24]. Naturally, one might anticipate that such nonionic surfactants with carbonate in their hydrophilic head group would resemble the traditional C_iEO_j surfactants in their properties for low CO₂ levels, but that with rising carbonate content, their properties might gradually deviate (Scheme 1).



Scheme 1. Molecular structure of carbonate-modified nonionic surfactants.

We observed that carbonate units contribute to the hydrophilicity of carbonate-modified surfactants in a previous investigation of their HLB values. The phase-inversion temperature (PIT)-shift method yielded HLB values that were significantly higher than those of the carbonate-free analogs, despite the fact that the carbonate unit introduced a hydrophobic effect on the surface-active properties, as evidenced by the reduction in the CMC [23]. The obtained HLB values of 11 to 15 suggest that they could be used for detergents and other purposes [25]. Nevertheless, carbonate modification has little effect on surfactants' dynamic behavior.

The sparging test is a common method to check surfactants' foaming ability [26]. Through a porous plate, air enters a glass-column-enclosed surfactant solution in this device. A stable foam is formed if the surfactant is able to adsorb at the air–water interface within the residence time of the bubbles in the surfactant solution. Until the surfactant solution is depleted, the generated foam volume follows the injected air volume. The foam volume is reduced by bubble coalescence and drainage. The maximum possible foam volume, an essential performance parameter in a foam-generation agent, is determined by the relationship between the rate of foam formation and the rate of foam collapse. Figure 1 depicts a schematic representation of the results of a relevant test.

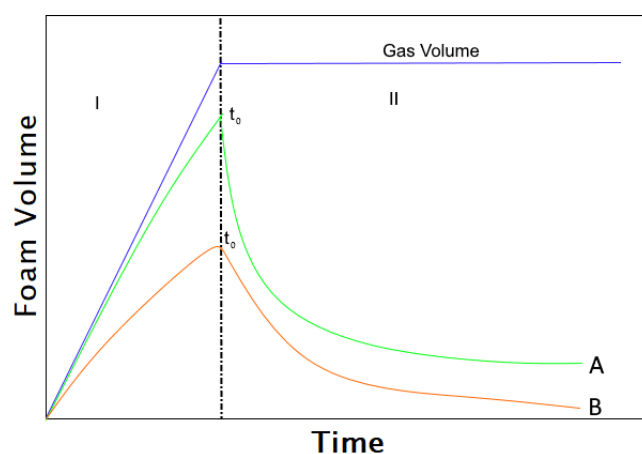


Figure 1. A schematic representation of sparging-test results. During the first period (I), the foam volume grew when air is injected. The foam decay was further monitored after the gas flow was stopped (period II). While Curve B demonstrates a weaker performance, Curve A depicts the performance of a surfactant with high foamability and foam stability.

The dependency of the foam height, H , on time is described in Equation (2):

$$\left(\frac{dH}{dt}\right)_{growth} = \frac{j_g}{1 - \varepsilon} - \left(\frac{dH}{dt}\right)_{collapse} \quad (2)$$

where ε is the foam's volumetric liquid fraction and j_g is the superficial gas velocity.

The surfactant's ideal behavior would imply that the gas flow essentially controls its volume and that it quantitatively stabilizes the injected gas's bubbles. A sparging test [26] was used in this study to alter the bubble lifetime within a sub-second range, providing a challenging situation for the tested surfactants. In the same setup, flotation experiments are possible if dispersions of particles are filled into the column and the gas flow is maintained continuously. The dispersed particles were removed from the liquid phase by the rising gas bubble and concentrated in the formed foam, which was collected and analyzed for the performance of the surfactant in this experiment. The objective of this combination of experiments was to obtain an insight into the influence of CO₂ modification on the adsorption behavior of the new surfactants at the solid–liquid surfaces.

Among various sources of aqueous contamination, plastics, as difficult-to-degrade materials, can persist in the environment for up to a century; they have therefore aroused universal concern in the last decade [27,28]. This concern is due to the high production and wide consumption of plastics (359 million tons in 2018) in most aspects of human activities without proper treatment. In addition, only about 9% of plastics are recycled, while 12% are incinerated and 79% are discharged into the environment [29,30]. After their useful lifespan and disposal by methods other than recycling, plastic products undergo gradual fragmentation into microplastics (MPs) through weathering, photolysis, abrasion, and mechanical and microbial decomposition. The small size of MPs prevents their recovery with current technologies. Although there are several technologies with high treatment efficiency, many of them do not have economic or environmental viability. Many treatment methods generate hazardous substances as by-products or decompose contaminants into other toxic pollutants. An alternative treatment technology that allows the removal of contaminants without any changes in the chemical structure is flotation. Although it has been used in other areas of the industry, its use in wastewater treatment has received great interest from scientists. One of the modifications of the flotation method to achieve high removal efficiency involves employing foams based on their surface activity [31]. Surfactants act as modifiers of the gas-bubble surface and facilitate the adsorption of contaminants onto this surface. Hence, among the various kinds of flotation technologies, foam flotation is an emerging technique that has high potential due to its high throughput and selectivity, the simplicity of its equipment and design, its low operational costs, and low levels of sludge generation. Since the environmental hazards of conventional surfactants restrict their utilization, highly degradable CO₂-modified surfactants could be good substitutes in wastewater treatment processes [32].

The research questions in this contribution are as follows:

1. Are carbonate-modified nonionic surfactants suitable for flotation applications?
2. Which carbonate content is beneficial for such applications?
3. Which properties of these surfactants in solutions could be key descriptors for selection and optimization?

2. Materials and Methods

2.1. Chemicals

Entries 1–6 in Table 1 are nonionic surfactants produced by Sasol, Germany, which are commercially available. The supplier's product information provided the characterization data.

Table 1. Characteristic data of nonionic surfactants with different lengths of hydrophilic EO head groups but the same hydrophobic chain mixture of C₁₂ and C₁₄. All surfactants were supplied by Sasol, Germany.

No.	Surfactant	Name	Specification		
			CMC (mmol/L)	σ_{eq} (mN/m) (at 0.01 g/L)	HLB (–)
1	C ₁₃ EO ₄	Marlipal O13/40	0.069	35.5	9.4
2	C ₁₃ EO ₅	Marlipal O13/50	0.076	37.5	10.5
3	C ₁₃ EO ₆	Marlipal O13/60	0.079	38.5	11.4
4	C ₁₃ EO ₇	Marlipal O13/70	0.081	39.0	12.1
5	C ₁₃ EO ₈	Marlipal O13/80	0.085	40.5	12.8
6	C ₁₃ EO ₁₀	Marlipal O13/100	0.116	43.5	13.7

Covestro AG produced a group of newly developed carbonate-modified nonionic surfactants (listed in Table 2) by copolymerizing ethylene oxide with CO₂ using a bimetallic catalyst and dodecanol as the starter. A description of the solvent-less synthesis was published in [24,25]. At the end of the copolymerization, the catalyst was removed by filtration, and the remaining monomer and the by-product ethylene carbonate by degassing. The characterization was performed without further purification of the surface-active products.

Table 2. Summarized data of Mn, Mw, CO₂ content, CP, and HLB values for all surfactants with the carbonate-modified head groups. Reprinted with permission from Ref. [25] 2023, Elsevier.

No.	Surfactant	Mn (g/mol)	CO ₂ (%)	CP (°C)	HLB (–)
7	C ₁₂ (CO ₂) _{3.1} EO _{8.2} -OH	680.2	19.64	69.0	14.3
8	C ₁₂ (CO ₂) _{1.5} EO _{11.5} -OH	762.4	8.84	85.0	14.9
9	C ₁₂ (CO ₂) _{1.3} EO _{11.4} -OH	744.0	7.76	88.0	14.4
10	C ₁₂ (CO ₂) _{0.6} EO _{13.3} -OH	792.0	3.32	>100	16.5

Polyethylene terephthalate (PET) particles 300 µm in diameter (supplier: Goodfellow/Sigma Aldrich, St. Louis, MI, USA) were used as a model substance for microplastic (MP) contamination. Flotation experiments were performed with 150 mg of PET particles dispersed in 200 mL of surfactant solution with a standard concentration of 100 µmol/L. For all investigated surfactants, this concentration was slightly above the critical micelle concentration.

2.2. Methods

2.2.1. Tensiometry: Method of Maximum Bubble Pressure

A Krüss (BP50) bubble-pressure tensiometer was used to measure the dynamic surface tension of aqueous surfactant solutions at 25 °C. The measurements were carried out with various surface ages ranging from 10 to 16,000 ms.

Equation (3), where r is the inner radius of the capillary, p is the pressure inside the bubble, and ρg is the solution's density and gravity, was used to calculate the surface tension σ_t from the pressure inside the bubbles. The measured pressure correction for buoyancy and hydrostatic pressure was as follows:

$$\sigma_t = \frac{r[p_{max} - (h - \frac{2}{3}r)\rho g]}{2} \quad (3)$$

2.2.2. Contact Angle

A DataPhysics OCA 20 video-based optical contact-angle measuring system with automated droplet shape analysis using the Young equation was used to investigate the wetting behavior of aqueous surfactant solutions at planar surfaces of various solid materials. Using a standard test protocol, solutions containing 1.0 g/L of nonionic surfactant were tested on a polished PET surface to compare modified and unmodified surfactants.

2.2.3. Foaming Test

A double-walled glass tube with a height of 20 cm and an inner diameter of 4 cm was used to conduct a sparging test. A liquid layer of approximately 2.5 cm was formed when 30 mL of surfactant solutions were poured into it. A mass-flow controller adjusted the rate of air introduction (from 5 to 20 mL/min) through a sinter plate with pore sizes ranging 40 to 100 μm (Figure 2a). The estimated sizes of the produced air bubbles were between 300 and 500 μm . An estimated lifetime of approximately 0.5 s was given for a rising velocity of approximately 40 mm/s. Surfactant adsorption is required to achieve sufficiently low surface tension for effective foam formation. During a 30-min period of constant gas flow, the foam volume was monitored. Subsequently, the stability of the foam was monitored without further gas supply. The apparatus was carefully dried with nitrogen and rinsed twice with acetone and distilled water before each experiment.

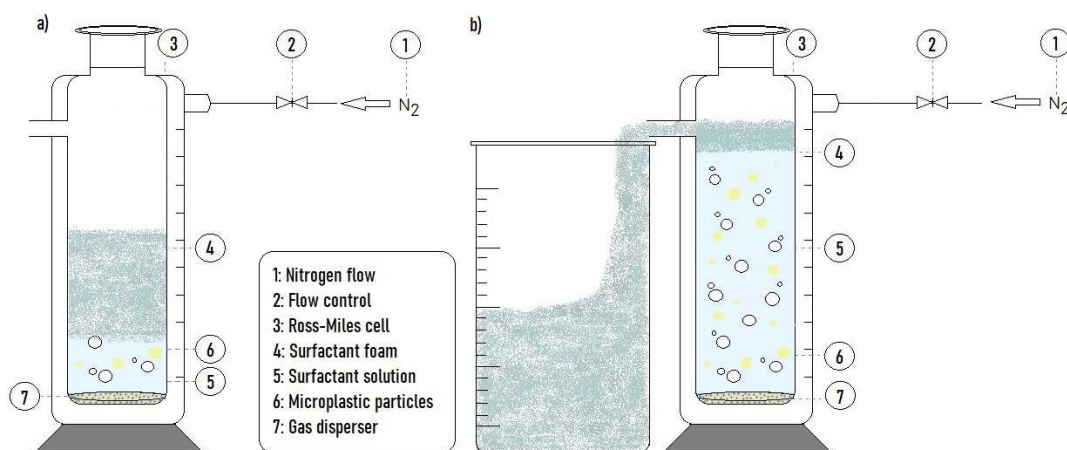


Figure 2. (a) Scheme for a sparging-test cell with a height of 20 cm and an ID of 4 cm. (b) Scheme of operation of sparging-test cell for flotation experiments. Typical conditions for the experiment: surfactant solution of 30 mL, 5–10 mL/min gas flow rate.

The foamability FA of the surfactants is expressed as the volume V of foam produced from the volume of injected gas:

$$FA = V_{\text{foam}}/V_{\text{gas}} \quad (4)$$

where V_{foam} is the observed foam volume and V_{gas} is the injected-gas volume. The stability is expressed with the half-life time of the foam volume ($t_{1/2}$) recorded after stopping the gas supply.

2.2.4. Flotation Experiments

The parameters of the flotation tests in the applied device were optimized in a previous study. The effects of the operation conditions on the test results are discussed in detail in [16]. The optimal test conditions for an analysis of the performance of the surfactants were transferred to this study. For flotation experiments, the column described above was filled with 200 mL of surfactant solutions, in which 150 mg of PET particles were dispersed before the experiments for 10 min (Figure 2b). With this amount of liquid, the cylinder was filled to about 95% of its volume. The volume of foam remaining in the column was

negligible compared to the foam in the collection vessel. The gas-flow rate through the sinter plate with pore sizes ranging from 40 to 100 μm was chosen for all experiments to be 10.4 mL N_2/min . The foam collected at the column outlet was stored for about 2 h, awaiting the collapse of the foam. The PET particles were filtered, washed, and dried. The weight was determined together with the filter paper with a known weight.

The removal of PET particles, R , was calculated using Equation (5) [18]:

$$R = 100\% \times \left(1 - \frac{m_R}{m_F}\right) \quad (5)$$

where m_R (in mg) is the mass of PET particles in the residual solution in the column after 30 min of the flotation experiment and m_F (in mg) is the mass of PET particles in the initial feed solution.

The enrichment factor (EF) was calculated using Equation (6) [18]:

$$EF = \frac{C_{foam}}{C_F} \quad (6)$$

where C_{foam} (in $\text{mg}\cdot\text{L}^{-1}$) is the PET particles' concentration in the collected foam after 30 min and C_F (in $\text{mg}\cdot\text{L}^{-1}$) is the PET particles' concentration in the initial feed solution. The volume of water that was removed during the flotation from the feed was considered for the calculation of the concentration.

3. Results

3.1. Flotation

The flotation of PET microplastic particles with diameters of 300 μm was performed in the above-described flotation cell with an initial concentration of PET particles of 750 mg/L and a surfactant concentration of 100 $\mu\text{mol}/\text{L}$. This microplastic concentration represents the situation in highly contaminated water. All the tests showed a similar course, as depicted in Figure 3. Differences were observed in the initial slopes of the curves and the removal rates at which the individual curves leveled off. For a comparison of the performance of the investigated surfactants, the removal rate at 30 min (Figure 4A) and at the end of the flotation (Figure 4C) was chosen as a representative operational condition. The endpoint of the flotation was taken when no further foam was generated by the gas injection. In addition to the removal of microplastic particles that was achieved by the addition of further surfactants (expressed as a % of the initial concentration), their enrichment in the foam was a performance indicator for the surfactants (Figure 4B,D). For the nonionic surfactant that consisted only of an ethoxylated headgroup, the opposite trend occurred, where better removal with an increasing degree of ethoxylation, but decreasing enrichment factors, is observed. This was caused by the more stable foams that were formed with the greater number of hydrophilic headgroups, which enabled the more efficient transport of the PET particles. At the same time, the increased number of hydrophilic headgroups carried more water with the foam, suppressing the enrichment factors for the same experiments.

The surfactants with headgroups from ethylene oxide and CO_2 showed no clear trend in their performance, although the presented results are also arranged along with the increasing HLB values of the surfactants. For these surfactants, a stronger increase in removal was observed between 30 min and the endpoint of the flotation, indicating a slower but more efficient flotation process. Both the removal rate and the enrichment factor showed similar trends to those seen for the ethoxylates, albeit less pronounced. In addition to the increasing hydrophilicity, further properties seemed to have controlled their performance. For the identification of these surfactant properties, the physicochemical properties of the investigated surfactants were analyzed and correlated with these performance data.

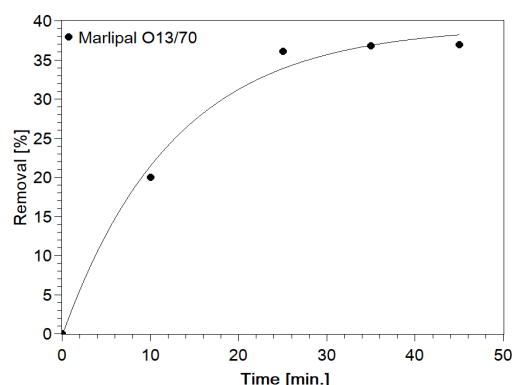


Figure 3. Flotation experiment with PET microplastic particles. Initial conc.: 750 mg/L. Gas-flow rate: 10.4 mL N₂/min.

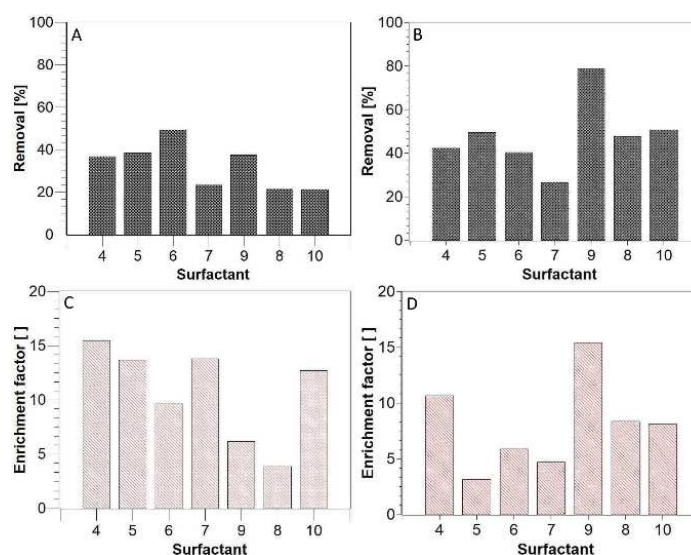


Figure 4. Flotation results of conventional and carbonate-modified nonionic surfactants (surfactant numbers are shown in Table 1). Conditions: 300 μ m PET particles. Initial conc.: 750 mg/L. Gas-flow rate: 10.4 mL N₂/min and a surfactant conc. of 100 μ mol/L. (A) Removal after flotation time 30 min, (B) removal after completed flotation (about 2 to 4 h), (C) enrichment factor after 30 min, (D) enrichment factor after completed flotation.

3.2. Equilibrium Surface Activity and Micellization

The CMC, surface tension at the CMC (σ_{CMC}), and headgroup area a_0 derived from these experiments are summarized in Table 3. The surface-active properties of the carbonate-modified surfactants were reported previously [33]. The critical micelle concentration CMC, which varied between the unmodified surfactants and those with the highest carbonate content by a factor of about three, was where the carbonate modification exerted its greatest influence [23]. Yada et al. observed a similar pattern for the substitution of propylene oxide for ethylene oxide, which also resulted in surfactants that were slightly less hydrophilic [15]. From the slope of the surface-tension reduction as a function of the concentration, the headgroup area per surfactant molecule was determined via the analysis of Gibb's isotherm, and the values are given in Table 3. For the CO₂-modified C₁₂ surfactants, the values were in the range of 0.55–1.07 nm², which were in very good agreement with the value of 0.66 nm² reported for the pure C₁₂E₈ at 25 °C. For C₁₂(CO₂)_{3.1}EO_{8.2}OH only, a lower value, of 0.55 nm², was determined, which indicates an essentially lower tendency towards hydration with an increasing number of CO₂ units. This observation is supported by the investigation of the HLB values of these surfactants, according to which a CO₂ unit contributed less to the HLB value than the EO group. This reduced hydration of the surfactant head groups

resulted in a closer packing of the molecules at the interfaces, allowing stronger interactions with hydrophobic materials, as will be shown in the following section. More details of the adsorption analysis are given in [23].

Table 3. Summarized data of the surface-tension measurements of the CO₂-modified nonionic surfactants Adapted with permission from Ref. [23], 2023, Elsevier.

No.	Surfactants	CMC (mmol/L)	σ_{CMC} (mN/m)	a_0 (nm ²)
7	C ₁₂ (CO ₂) _{3.1} EO _{8.2} -OH	0.053	34.4	0.55
8	C ₁₂ (CO ₂) _{1.5} EO _{11.5} -OH	0.091	35.9	0.65
9	C ₁₂ (CO ₂) _{1.3} EO _{11.4} -OH	0.099	36.5	0.67
10	C ₁₂ (CO ₂) _{0.6} EO _{13.3} -OH	0.118	35.9	0.69
11	C ₁₂ (CO ₂) ₀ EO _{14.0} -OH	0.175	40.1	1.07

3.3. Wetting of Solid Surfaces

Contact-angle measurements on a flat PET substrate with aqueous solutions containing 1.0 g/L of surfactant were used to investigate the adsorption at the solid–liquid interface. This was significantly higher than the CMC of any of the surfactants. Consequently, the equilibrium surface tensions of the corresponding solutions determined the surface tensions of all the solutions. The surface tension of the solution on the solid surfaces should be reflected in the contact angle of the solutions, as predicted by Young’s equation. The strong variation in the contact angles among the group of carbonate-modified surfactants shown in Table 4 indicates the strong impact of the carbonate modification on these surfactants’ adsorption properties, which was significantly different from the reference surfactant, C₁₃EO₈. A much weaker effect would have been expected among a group of conventional nonionic surfactants with varying degrees of ethoxylation. This could suggest that the surfactant can also adsorb to medium-polarity surfaces with the head group rather than the hydrophilic tail because of the carbonate modification of the head groups. Carbonate-modified surfactants have significantly higher surface energy for the solid–liquid interface, according to Young’s equation. Compared to the ethoxylated surfactants, this increase cannot only be attributed to the increasing hydrophilicity, but also to a contribution of the carbonate groups to the interactions at the solid–liquid interface.

Table 4. Surface tension (σ) and contact angles (θ) of 1 g/L surfactants solution at a PET surface.

Surfactant Solution	σ (L/g) (mN/m)	θ (PET) (°)	σ (L/s) * (mN/m)
H ₂ O	72.0	65.6	14.3
C ₁₃ EO ₇	39.0	32.0	11.7
C ₁₃ EO ₈	40.5	34.1	16.9
C ₁₃ EO ₁₀	43.5	49.5	16.6
C ₁₂ (CO ₂) _{3.1} EO _{8.2} OH	34.4	48.1	21.0
C ₁₂ (CO ₂) _{1.5} EO _{11.5} OH	35.9	51.0	21.4
C ₁₂ (CO ₂) _{1.3} EO _{11.4} OH	36.5	60.5	26.0
C ₁₂ (CO ₂) _{0.6} EO _{13.3} OH	35.9	62.0	27.2
C ₁₂ (CO ₂) ₀ EO ₁₄ OH	40.1	52.9	19.8

Note(s): * Calculated by Young’s equation (Equation (1)).

3.4. Foaming Behavior

The surfactant properties’ impact on the carbonate-modified surfactants’ application potential was investigated by examining their foaming behavior. For this comparison, the

foaming kinetics in a sparging cell were examined (Figure 5). The carbonate-modified surfactants were tested, and the foam formed exactly in line with the volume of the injected gas. All the surfactants, as shown by these curves, had sufficiently high diffusion coefficients to stabilize the gas bubbles almost immediately after they were injected. Even the limited lifespan in the selected configuration was sufficient to ensure that all of the injected air was fully absorbed by the produced foam. The bubble coalescence and drainage did not result in a loss of foam volume. The foam volume slowly decreased without further gas injection. Interestingly, the C_{12} surfactants generally exhibited higher foam stability when compared to the representative example of the reference surfactant ($C_{13}EO_8$), but this was true regardless of the carbonate content.

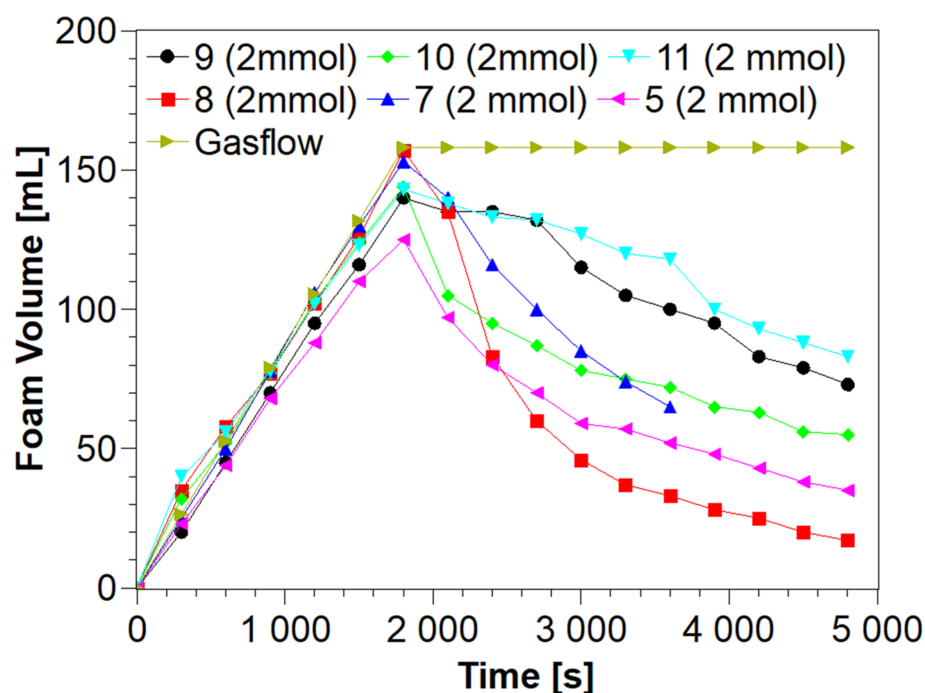


Figure 5. A sparging-test comparison of nonionic surfactants modified with carbonate (surfactant numbers are shown in Table 1). Conditions of the experiment: 30 mL of a solution containing 2 mmol/L surfactant and 5.6 mL of air per minute.

The foamability and half-life times of the produced foams were determined from the foam volumes and they are summarized in Table 5 for a quantitative discussion of the sparging tests. All the carbonate-modified surfactants exhibited very similar levels of foamability at a high level, but there were significant differences in their stabilities. Hydrophilicity, or the increase in the size of the head group, was essential for the stability to rise. The carbonate modification resulted in slight decreases in stability at headgroup sizes, which were comparable (entries 10 and 11). All the modified surfactants had better foam stability than the commercial reference surfactant, $C_{13}EO_8$, indicating that CO_2 could potentially replace some of the ethylene oxide in surfactant synthesis. Table 5 also includes some of the characteristic properties of the substances that were investigated for a discussion of the physical parameters that controlled the stability of the foam.

Table 5. Quantification of the foaming behavior of the carbonate-modified nonionic surfactants for a correlation with their physical properties Adapted with permission from Ref. [20], 2023, Elsevier. The CMC and headgroup area a_0 were obtained from the static-surface-tension data. The FA was calculated from Equation (4).

No.	Surfactants	CMC (mmol/L)	a_0 (nm ²)	D_{mono} (m ² /s)	FA (–)	$t_{1/2}(\text{foam})$ (s)
7	C ₁₂ (CO ₂) _{3.1} EO _{8.2} -OH	0.0529	0.43	$8.0 \cdot 10^{-9}$	0.97	1400
8	C ₁₂ (CO ₂) _{1.5} EO _{11.5} -OH	0.0914	0.57	$3.5 \cdot 10^{-9}$	0.99	1000
9	C ₁₂ (CO ₂) _{1.3} EO _{11.5} -OH	0.0985	0.59	$4.5 \cdot 10^{-9}$	0.96	3500
10	C ₁₂ (CO ₂) _{0.6} EO _{13.3} -OH	0.1177	0.65	$5.0 \cdot 10^{-9}$	0.91	2300
11	C ₁₂ (CO ₂) ₀ EO _{14.0} -OH	0.1750	1.07	$8.0 \cdot 10^{-9}$	0.90	3600
5	C ₁₃ EO ₈	0.0800	-	$4.0 \cdot 10^{-9}$	0.80	1400

4. Discussion

For the efficient removal of particles from dispersions by foam flotation, the formation of stable gas bubbles is important, since these can strongly attach to the solid particle and transport them using their buoyant force to the surface of the liquid and into a stable form. With this foam, particles can be removed from residual liquid. The formation of gas bubbles, as well as the bubble–particle aggregates, is strongly affected by the additives in this process. These surface-active compounds reduce the gas–liquid interfacial tensions and stabilize the rising bubbles, as well as the resulting foam. For this purpose, surfactants that adsorb quickly and strongly to the g/L surface are beneficial. Fast adsorption is favored at a low molecular weight, while strong adsorption is achieved by larger molecules with well-balanced hydrophilic head groups and hydrophobic tails. At the same time, the wetting of the liquid at the surface of the solid particle is controlled by the same surfactants. In this case, the most favorable situation is partial wetting, which allows a strong attachment of the particles to the bubbles and a good attachment of the buoyant force to the particle.

Higher contact angles in the range between 30 and 120° are favorable for this purpose [19]. The selection of surfactant for efficient adsorption at two different surfaces, in general, represents a compromise, especially if the adsorption properties of the surfactants can only be modified by a single tuning parameter, such as the alkyl-chain lengths of ionic surfactants or the degree of ethoxylation of nonionic surfactants.

To demonstrate the importance of the wetting behavior of the surfactant solution to the efficiency of the flotation, a correlation between the removal rate and the contact angle of the same solution at a flat surface is shown in Figure 6. The flotation experiments with the group of carbonate-containing surfactants showed an increased removal rate with an increasing contact angle, indicating the favorable effect of partial wetting for the stable attachment of the particles to the air bubbles.

Since both parameters depend on the carbonate content of the surfactant head groups, this can be considered an additional degree of freedom in the selection of surfactants for flotation processes. Furthermore, since the different surfactants influence further foam properties, such as bubble size, foam density, and foam rheology, which also influence the performance of the process, no stronger correlation with a single parameter can be expected in this complex system. This was demonstrated by the positive correlation of the enrichment of the particles with the diffusion coefficients of the surfactant monomers, depicted in Figure 8. The surfactants with the highest diffusion coefficients adsorbed faster at the surfaces of the bubbles that provided the greatest surface area, on which the particles could attach. At the same time, the higher diffusivity guaranteed a faster repair mechanism for ruptures in the foam lamellae, increasing the lifetime of the foam, during which the water drainage increased the enrichment of the particles.

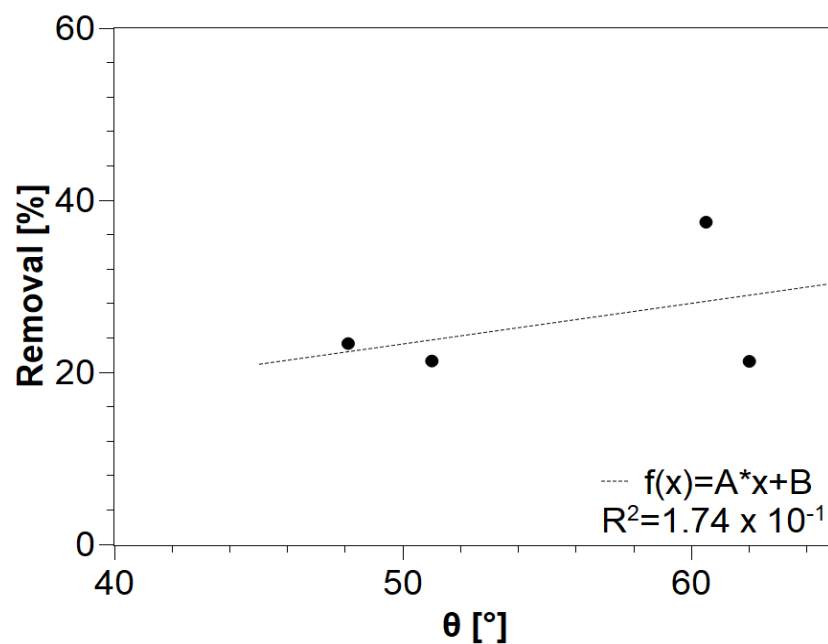


Figure 6. Correlation between removal rates and contact angles of surfactant solutions (1 g/L) on a flat PET surface.

The other parameter controlling the removal was the stability of the bubbles under study in terms of the half-life time of the foam. A positive correlation was obtained between these two parameters and is shown in Figure 7.

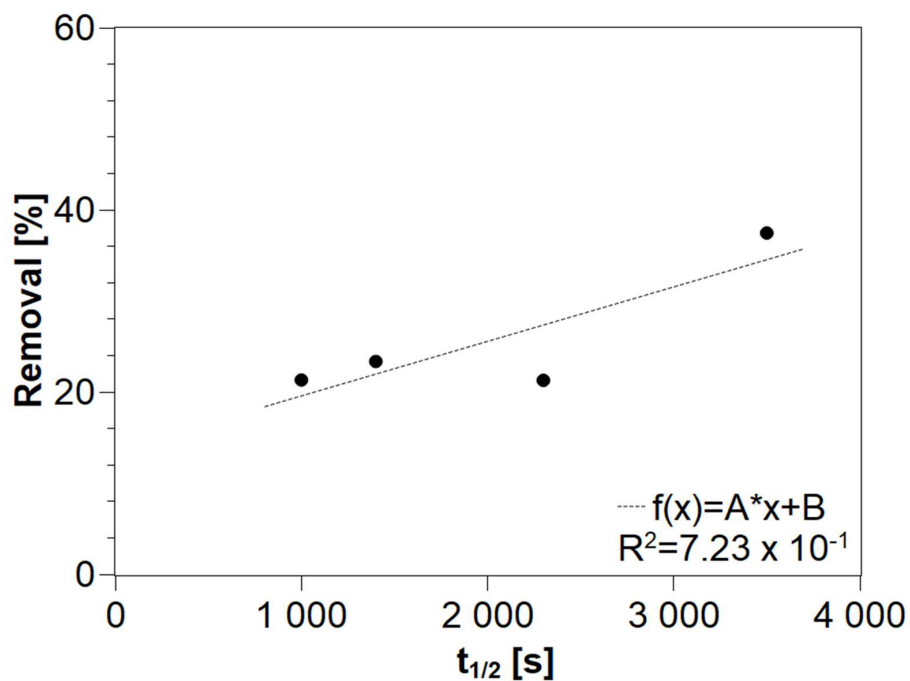


Figure 7. Correlation between removal rate and half-life time of surfactant foams.

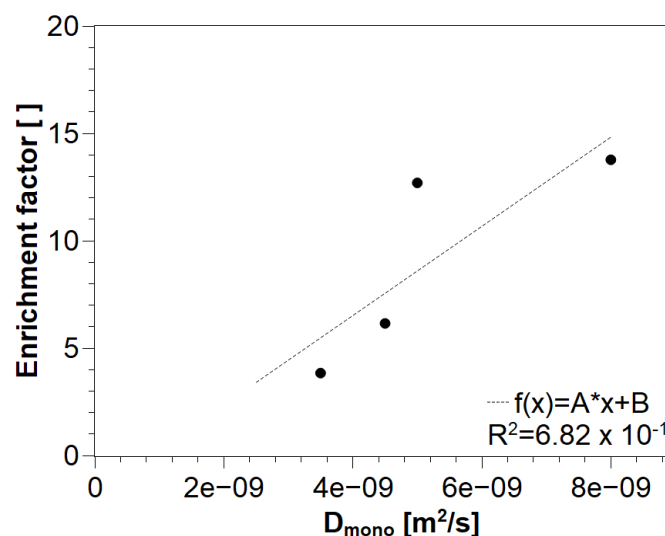


Figure 8. Correlation between diffusion coefficient of surfactants and enrichment of particles.

5. Conclusions

As a conclusion and answer to the initial questions, we can state that the obtained results demonstrate the suitability of the use of carbonate-modified nonionic surfactants in flotation processes for the removal of microplastic particles. Together with the improved biodegradability, the carbonate content and its impact on important surfactant properties allow a resolution of the countercurrent trends between the removal rate and enrichment factor for conventional nonionic surfactants. Consequently, this provides an option for finding much more efficient operating conditions by tuning surfactants to a particular level of diffusivity combined with a medium-range contact angle of their aqueous solutions on polymer surfaces. The diffusion coefficient of the surfactant monomer, the half-life time of the foam, and the contact angle of the surfactant solutions are important descriptors that control the performance of the flotation. Since these three parameters depend in different ways on the carbonate content of the surfactant headgroup, a compromise needs to be identified for every material. Due to the weaker impact of the contact angle on the removal, priority can be given to the diffusivity and the foam stability, which both increase with an increasing number of CO₂ units per head group.

The next steps in the development of a flotation process for microplastic (MP) removal would be a test with mixed MPs and the optimization of the surfactant concentration for increasing the removal rate to the required level. In a continuous process, this would require a dosing strategy that establishes the most efficient steady-state concentration of surfactant in the system.

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References

- Wang, J.; Nguyen, A.V.; Farrokhpour, S. A critical review of the growth, drainage and collapse of foams. *Adv. Colloid Interface Sci.* **2016**, *228*, 55–70. [\[CrossRef\]](#)
- Kanokkarn, P.; Shiina, T.; Santikunaporn, M.; Chavadej, S. Equilibrium and dynamic surface tension in relation to diffusivity and foaming properties: Effects of surfactant type and structure. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *524*, 135–142. [\[CrossRef\]](#)
- Kawale, D.; van Nimwegen, A.T.; Portela, L.M.; van Dijk, M.A.; Henkes, R.A.W.M. The relation between the dynamic surface tension and the foaming behaviour in a sparger setup. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *481*, 328–336. [\[CrossRef\]](#)
- Ampatzidis, C.D.; Varka, E.-M.A.; Karapantsios, T.D. Interfacial activity of amino acid-based glycerol ether surfactants and their performance in stabilizing O/W cosmetic emulsions. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *460*, 176–183. [\[CrossRef\]](#)
- Wang, K.; Lu, Y.C.; Xu, J.H.; Luo, G.S. Determination of Dynamic Interfacial Tension and Its Effect on Droplet Formation in the T-Shaped Microdispersion Process. *Langmuir* **2009**, *25*, 2153–2158. [\[CrossRef\]](#) [\[PubMed\]](#)
- Baret, J.C.; Kleinschmidt, F.; Harrak, A.E.; Griffiths, A.D. Kinetic aspects of emulsion stabilization by surfactants: A microfluidic analysis. *Langmuir* **2009**, *25*, 6088–6093. [\[CrossRef\]](#)
- Fainerman, V.B.; Mys, V.D.; Makievski, A.V.; Petkov, J.T.; Miller, R. Dynamic surface tension of micellar solutions in the millisecond and submillisecond time range. *J. Colloid Interface Sci.* **2006**, *302*, 40–46. [\[CrossRef\]](#)
- Miller, R.; Aksenenko, E.V.; Fainerman, V.B. Dynamic interfacial tension of surfactant solutions. *Adv. Colloid Interface Sci.* **2017**, *247*, 115–129. [\[CrossRef\]](#)
- Buzzacchi, M.; Schmiedel, P.; von Rybinski, W. Dynamic surface tension of surfactant systems and its relation to foam formation and liquid film drainage on solid surfaces. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *273*, 47–54. [\[CrossRef\]](#)
- Manousakis, M.; Avranas, A. Dynamic surface tension studies of mixtures of hydroxypropylmethylcellulose with the double chain cationic surfactants didodecyldimethylammonium bromide and ditetradecyldimethylammonium bromide. *J. Colloid Interface Sci.* **2013**, *402*, 237–245. [\[CrossRef\]](#)
- Chang, H.; Wang, Y.; Cui, Y.; Li, G.; Zhang, B.; Zhao, X.; Wei, W. Equilibrium and dynamic surface tension properties of Gemini quaternary ammonium salt surfactants with hydroxyl. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *500*, 230–238. [\[CrossRef\]](#)
- Young, T., III. An essay on the cohesion of fluids. *Philos. Trans. R. Soc. Lond.* **1805**, *95*, 65–87. [\[CrossRef\]](#)
- Shinoda, K.; Lindman, B. Organized surfactant systems: Microemulsions. *Langmuir* **1987**, *3*, 135–149. [\[CrossRef\]](#)
- Tamura, T.; Kaneko, Y.; Ohya, M. Dynamic Surface Tension and Foaming Properties of Aqueous Polyoxyethylene n-Dodecyl Ether Solutions. *J. Colloid Interface Sci.* **1995**, *173*, 493–499. [\[CrossRef\]](#)
- Yada, S.; Suzuki, T.; Hashimoto, S.; Yoshimura, T. Adsorption dynamics of homogeneous polyoxypropylene-polyoxyethylene alkyl ether nonionic surfactants at the air/water interface. *J. Mol. Liq.* **2018**, *255*, 208–214. [\[CrossRef\]](#)
- Shojaimehr, T.; Schwarze, M.; Lima, M.T.; Schomäcker, R. Correlation of performance data of silica particle flotations and foaming properties of cationic and nonionic surfactants for the development of selection criteria for flotation auxiliaries. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *649*, 129159. [\[CrossRef\]](#)
- Zhang, W.; Nasset, J.E.; Rao, R.; Finch, J.A. Characterizing frothers through critical coalescence concentration (CCC)95-hydrophile-lipophile balance (HLB) relationship. *Minerals* **2012**, *2*, 208–227. [\[CrossRef\]](#)
- Beran, E.E.; Hull, S.; Steininger, M. The Relationship Between the Chemical Structure of Poly(alkylene glycol)s and Their Aerobic Biodegradability in an Aqueous Environment. *J. Polym. Environ.* **2013**, *21*, 172–180. [\[CrossRef\]](#)
- Wonyen, D.; Kromah, V.; Gibson, B.; Nah, S.; Chelgani, S. A Review of Flotation Separation of Mg Carbonates (Dolomite and Magnesite). *Minerals* **2018**, *8*, 354. [\[CrossRef\]](#)
- Tupinamba Lima, M.; Kurt-Zerdeli, S.N.; Brüggemann, D.; Spiering, V.J.; Gradzielski, M.; Schomäcker, R. The dynamics of surface adsorption and foam formation of carbonate modified nonionic surfactants. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *588*, 124386. [\[CrossRef\]](#)
- Hu, M.; Chen, M.; Li, G.; Pang, Y.; Wang, D.; Wu, J.; Qiu, F.; Zhu, X.; Sun, J. Biodegradable hyperbranched polyglycerol with ester linkages for drug delivery. *Biomacromolecules* **2012**, *13*, 3552–3561. [\[CrossRef\]](#) [\[PubMed\]](#)
- Baker, I.J.A.; Matthews, B.; Soares, H.; Krodziewska, I.; Furlong, D.N.; Grieser, F.; Drummond, C.J. Sugar fatty acid ester surfactants: Structure and ultimate aerobic biodegradability. *J. Surfactants Deterg.* **2000**, *3*, 1–11. [\[CrossRef\]](#)
- Spiering, V.J.; Ciapetti, A.; Tupinamba Lima, M.; Hayward, D.W.; Noirez, L.; Appavuo, M.-S.; Schomäcker, R.; Gradzielski, M. Substituting EO by CO₂ in the Head Group of Nonionic Surfactants Changes their Phase Behavior Completely. *ChemSusChem* **2020**, *13*, 601. [\[CrossRef\]](#) [\[PubMed\]](#)
- Langanke, J.; Wolf, A.; Hofmann, J.; Böhm, K.; Subhani, M.A.; Müller, T.E.; Leitner, W.; Gürtler, C. Carbon dioxide (CO₂) as sustainable feedstock for polyurethane production. *Green Chem.* **2014**, *16*, 1865–1870. [\[CrossRef\]](#)
- Lima, M.T.; Spiering, V.J.; Kurt-Zerdeli, S.N.; Brüggemann, D.C.; Gradzielski, M.; Schomäcker, R. The hydrophilic-lipophilic balance of carboxylate and carbonate modified nonionic surfactants. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *569*, 156–163. [\[CrossRef\]](#)
- Trujillo-Cayado, L.A.; Ramírez, P.; Pérez-Mosqueda, L.M.; Alfaro, M.C.; Muñoz, J. Surface and foaming properties of polyoxyethylene glycerol ester surfactants. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *458*, 195–202. [\[CrossRef\]](#)
- Li, W.C.; Tse, H.F.; Fok, L. Plastic waste in the marine environment: A review of sources, occurrence and effects. *Sci. Total Environ.* **2016**, *566–567*, 333–349. [\[CrossRef\]](#)

28. Sun, J.; Dai, X.; Wang, Q.; van Loosdrecht, M.C.M.; Ni, B.J. Microplastics in wastewater treatment plants: Detection, occurrence and removal. *Water Res.* **2019**, *152*, 21–37. [[CrossRef](#)]
29. Bui, X.T.; Vo, T.D.H.; Nguyen, P.T.; Nguyen, V.T.; Dao, T.S.; Nguyen, P.D. Microplastics pollution in wastewater: Characteristics, occurrence and removal technologies. *Environ. Technol. Innov.* **2020**, *19*, 101013. [[CrossRef](#)]
30. Ranjani, M.; Veerasingam, S.; Venkatachalapathy, R.; Mugilarasan, M.; Bagaev, A.; Mukhanov, V.; Vethamony, P. Assessment of potential ecological risk of microplastics in the coastal sediments of India: A meta-analysis. *Mar. Pollut. Bull.* **2021**, *163*, 111969. [[CrossRef](#)]
31. Umar, A.; Caldwell, G.S.; Lee, J.G.M. Foam flotation can remove and eradicate ciliates contaminating algae culture systems. *Algal Res.* **2018**, *29*, 337–342. [[CrossRef](#)]
32. Silva, E.J.; Chaprão, M.J.; Silva, I.A.; Brasileiro, P.P.F.; Almeida, D.G.; de Luna, J.M.; Rufino, R.D.; Santos, V.A.; Sarubbo, L.A. Biosurfactant application as alternative collectors in dissolved air flotation system. *Chem. Eng. Trans.* **2018**, *64*, 547–552. [[CrossRef](#)]
33. Goswami, A.; Hassan, P.A.; Bhagwat, S.S. Static and dynamic surface tension behaviour of a triblock copolymer and a non ionic surfactant mixture. *Colloids Surf. A Physicochem. Eng. Asp.* **2015**, *484*, 190–196. [[CrossRef](#)]

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