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From dairy waste to value-added bio-based surfactants

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ABSTRACT

Cheese whey permeate, the main waste stream of dairy industry, was used as a starting material for the production of bio-based surfactants (SFAEs). Specifically, the first step in the sustainable chemoenzymatic synthesis of *n*-butyl 6-*O*-palmitoyl-D-glycosides (Fischer glycosylation followed by enzymatic esterification) was optimized by a chemometric study. The surfactancy of the prepared isomeric mixtures was deeply investigated in terms of static and dynamic interfacial tension and emulsifying capability over time.

Surfactants are a class of compounds characterized by an amphiphilic structure, which can find applications in almost every industrial sector due to their ability in stabilizing disperse systems [1]. In recent years, concerns about the effects of petroleum-based products over the environment have moved the research in finding green and sustainable substitutes to conventional tensides [2].

Sugar fatty acid esters (SFAEs) are non-ionic surfactants characterized by peculiar physico-chemical properties, *i.e.* surface and interfacial tension reduction ability, low-toxicity and biodegradability. These qualities make SFAEs of great interest for their use in pharmaceutical, cosmetic and food industries [3,4]. They are made by a sugar ring (that acts as a polar head), and of a hydrophobic fatty tail. Interestingly, both parts can be derived from renewable sources, such as biomass and wastes [5].

In dairy industry, large amount of cheese whey is obtained as by-product of cheese making processes. This agro-food waste contains valuable milk proteins which are recovered by ultrafiltration generating a secondary by-product, namely cheese whey permeate (CWP). It is composed mainly by lactose (*ca.* 50 g L^{-1}), lipids (4–5 g L^{-1}), vitamins and mineral salts, which are responsible for CWP high biological and chemical oxygen demand levels. This fact, along with its high production load, makes CWP an environmental and disposal problem [6]. The spreading over fields and the piping into lakes or rivers are the simplest ways for CWP disposal. However, these discharging modes cause serious pollution issues, *i.e.* they affect the physical and chemical structure of soil, decreasing the crop yield. Moreover, the high consumption of dissolved oxygen in water reduces the aquatic life, as well as creates risks of eutrophication [7]. The stringent legislation regarding waste disposal prohibits the dumping of CWP into waterways, encouraging academia and industries in finding potential alternatives for the valorization of this agro-food waste [8].

Nowadays, part of the generated CWP is directly employed in the food industry as sugar and salt substitute and for the preparation of sports beverages and prebiotics [9]. Furthermore, it can be used for the production of recombinant proteins and to support the growth of microbial cell factories [6]. Since CWP is mainly composed of lactose, it can be used as carbon substrate in several biotechnological processes to produce lactic, propionic and acetic acids [9], bioethanol [10] and biohydrogen [11].

A potential alternative for the upgrading of CWP is represented by the exploitation of lactose present in this waste as building block for the synthesis of bio-based tensides, according to the circular economy concept for which wastes can become the feedstock for the production of high value-added products [12].

The chemical synthesis of lactose-based esters requires acid or base catalysts, the use of activated acyl donors, hazardous solvents and high temperatures, resulting in high energy costs and undesired by-products formation. Moreover, protection/deprotection steps are needed to achieve regioselectivity [13]. These drawbacks can be solved by using enzymes as biocatalysts [14]. Unfortunately, even this strategy has some limitations: the enzymatic esterification of lactose with different fatty acids needs long reaction time and proceeds with moderate yields due to

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the low solubility of this sugar in common organic solvents [3,4,15,16].

However, since lactose is a disaccharide constituted by galactose (Gal) and glucose (Glc) linked together *via* a glycosidic bond, it can be easily hydrolysed into its monosaccharide components, *i.e.* Glc and Gal, which can be used as polar head of SFAEs. In our previous studies, a sustainable two-step chemoenzymatic protocol was used for the preparation of glucose and galactose-based surfactants [17,18]. Specifically, a solvent-free enzymatic esterification is preceded by sugar derivatization through Fischer glycosylation. The latter is required to overcome the very different solubilities of sugars and fatty acids in common organic solvents. Although several studies on the synthesis of glucose and galactose fatty acid esters have been carried out [19,20], to the best of our knowledge, the chemoenzymatic synthesis of SFAEs using cheese whey permeate as raw material has been poorly investigated [18,21,22]. Herein, we report *i)* the synthesis of sugar fatty acid esters deriving from cheese whey permeate; *ii)* the investigation, through a chemometric study, of the optimal Fischer glycosylation reaction conditions to reduce side-reactions, concomitantly increasing yield and selectivity toward pyranosides isomers; *iii)* the evaluation of physico-chemical properties of selected bio-based surfactants.

Since cheese whey permeate is a complex matrix, before using it as a raw material, its chemical composition was evaluated by NMR and elemental analysis. The latter highlighted the low nitrogen content of this waste, corroborating the almost complete removal of cheese whey protein (see **Table S1**). Moreover, ^{1}H NMR spectrum recorded in D_2O showed the presence of several metabolites, such as organic acids and vitamins (see **Fig. S1**) in accordance with the analysis of *de Divitiis* et al. [6]

D-lactose (**Lac**), present in CWP as the major component, was enzymatically hydrolysed with the food-grade commercially available β-galactosidase Saphera® 2600 L (Fig. 1a). According to the manufacturer datasheet [23], the reaction was performed at optimum enzyme/substrate ratio (2.4 %, *w*/w), at CWP spontaneous pH (~ pH 6.0) and mild temperature (50 °C). After 6 h, a 1:1 mixture of D-glucose and D-galactose (**Glc Gal**) was obtained, as showed by ^{1}H NMR analysis, carried out in D_2O (see **Fig. S3**).

Then, **Glc Gal** was submitted to Fischer glycosylation (Fig. 1b) using as a first approach the reaction conditions previously selected [17]. Specifically, **Glc Gal** was suspended in dry *n*-butanol (*n*-BuOH) (1.8 % *w/v*) in the presence of the macroreticular acid resin Amberlyst® 15 (Amb) at 120 °C for 6.5 h. *n*-Butyl D-glycosides (**Gly Mix**) were obtained in low yields due to caramelization side-reactions, probably favoured by the impurities (organic acids, vitamins and mineral salts) naturally present in CWP. Any attempt to preliminarily remove these impurities (*i.e.*, ion exchange column chromatography, filtration, ultrafiltration) was unsuccessful. Moreover, Fischer glycosylation led to the formation of a mixture of eight isomers which differ for the type of sugar (glucose or galactose), the ring size of glycosides (pyranosides or furanosides) and the configuration of the anomeric position (α and β), see Fig. 1b [24]. ^{1}H NMR analysis, carried out in D_2O, showed higher amount of furanosides derivatives, both for glucose and galactose. Even this prevalence of the five-membered ring derivatives can be considered a drawback since, in previous works, the influence of the ring size over physico-chemical properties of surfactants was investigated, demonstrating the better ability in reducing interfacial tension of pyranosides isomers [25]. Thus, to increase yields, experiments were performed by varying reaction temperature and time (see **Table S2**). By lowering the temperature down to 50 °C, few side-reactions were observed, but the yield remained scarce. Instead, at 80 °C for 24 h, a small increase in the reaction yield was gained. However, the problem of side-reactions was not solved.

In the attempt of overcoming all these issues, other two acid resins, based on functionalized silica, *i.e.* SiliaBond® Propylsulfonic Acid (SCX-2) and SiliaBond® Tosic Acid (SCX), were tested as heterogenous catalysts in the Fischer glycosylation. It can be noted that, usually, this reaction is industrially performed by using H_2SO_4 or *p*-toluenesulfonic acid as homogeneous catalyst. However, heterogenous catalysts can

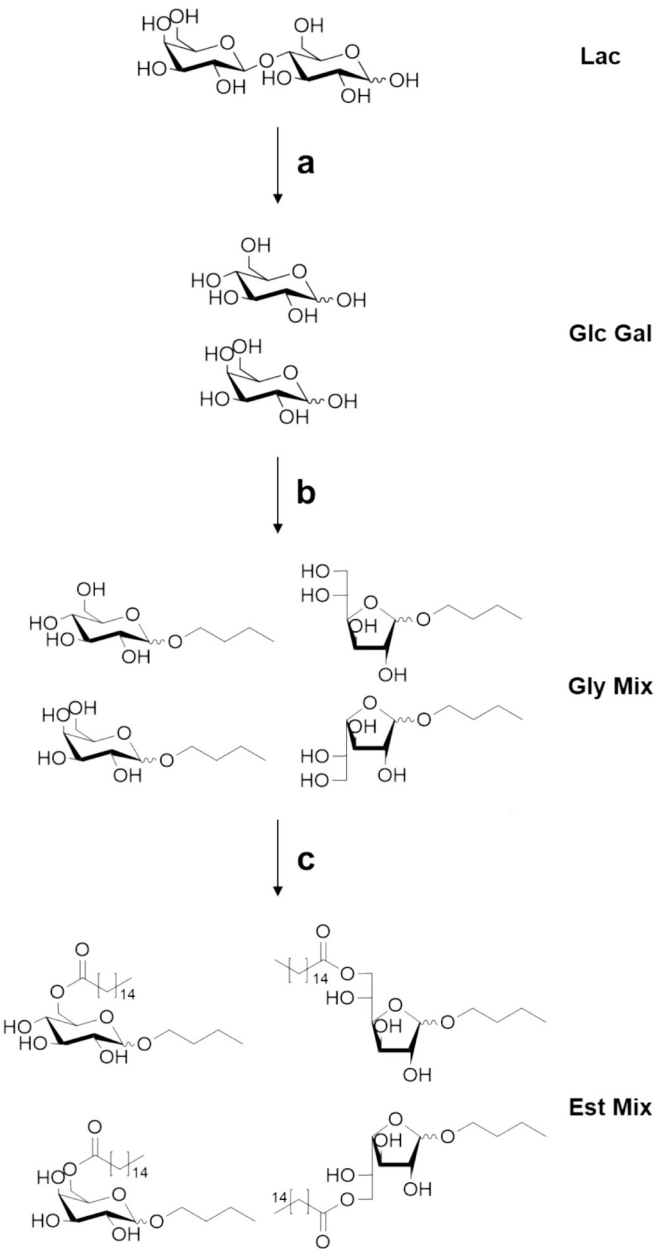

Fig. 1. Synthesis of alkyl glycoside fatty acid esters. Reagents and conditions: **a**) Saphera® 2600 L (2.4 % *w*/w), pH: 6, 50 °C, 6 h; **b**) *n*-BuOH, acid resins, reaction conditions of the chemometric study, see **Table S2**; **c**) palmitic acid (molar ratio 1:1), Novozym® 435 (10 % w/w), 80 °C, 8 h, 30 mmHg.

represent an environmentally friendly alternative able to solve several disadvantages related to homogeneous catalysis. In particular, acid resins can be easily recovered by filtration and recycled, moreover wastes are not generated, reducing the overall economic and environmental impact, in accordance with the first principle of Green Chemistry [26]. Despite this, yields were not substantially improved.

Thus, we thought that caramelization side-reaction could be partially induced by the poor solubility of **Glc Gal** in *n*-BuOH. In order to favour the initial solubilization of the sugar mixture, a small amount of water was added. According to *Monsan* et al. [27], *n*-BuOH is only slightly soluble in water and a biphasic system is obtained above 9 %*v*/v of H_2O. Herein, to remain under the saturation limit of *n*-butanol, the minimum amount of water required for the complete solubilization of **Glc Gal** was used (5 %*v*/v). Working at temperatures equal or even higher than 80 °C, H_2O is removed by evaporation, thus shifting the equilibrium

toward the products formation. Therefore, by carrying out the reaction in *n*-BuOH/H_2O system, a series of experiments were performed by varying the type of resin (Amb, SCX-2 and SCX, identified according to the sulfonic acid content of 4.70, 0.63 and 0.54 meq g^{-1}, respectively), the equivalents of acid catalytic sites (5, 10 or 20 meq), the starting concentration ($c_{Glc\ Gal}$ 1.8 % or 0.9 %*w/v*) and the relative moles ($mmol_{Glc\ Gal}$ from 0.5 to 10) of D-glucose and D-galactose mixture, time (6.5 and 24 h) and temperature (50, 80, 100 or 120 °C). Specifically, at the same concentration ($c_{Glc\ Gal}$ 1.8 %w/v), by doubling the equivalents of catalytic sites, **Gly Mix** were obtained in good yields (65–80 %) and pyranosides derivatives (Py) were formed in higher amount with all the three resins. Carrying out the reaction at 100 or 120 °C, yields and isomeric ratios remained unvaried. At 80 °C a slight increase in the formation of furanosides (Fu) was observed for Amb and SCX-2, probably due to the mechanism of Fischer glycosylation that in milder reaction conditions favours furanosides isomers [28]. On the contrary, SCX seems to be more selective for pyranosides, even at a lower temperature. Moreover, performing Fischer glycosylation at a lower concentration ($c_{Glc\ Gal}$ 0.9 %*w/v*) and higher equivalents of catalytic sites (20 meq), **Gly Mix** were obtained in high yields (78–93 %) and Py were favoured with all the three resins. However, caramelization reaction was mostly reduced only using SCX as catalyst.

Despite Fischer glycosylation is a well-known reaction, it was not straightforward since several parameters influence both yield and isomeric ratio. Therefore, a chemometric study was performed adopting the data reported in **Table S2.** Loading plots reported in **Fig. 2a** and **b** show the main correlations of some investigated variables (red arrows): firstly, there is a significant direct proportionality of both the initial glucose/galactose moles and the catalysts' S-content with the caramelization phenomenon. Indeed, FTIR analyses of the used catalysts revealed a higher adsorption of possible caramelization by-products together with reagents and reaction products onto the Amb resin with respect to the other two functionalized silica catalysts (see **Fig. S10**). In addition, the Fischer glycosylation yield seems to be directly correlated to the amount of the adopted catalytic sites. Besides, focusing on the green arrows depicted in Fig. 2a, the increase of resins' S-content appears to play a critical role in favouring the formation of furanoside derivatives which, in turn, are inversely related to the presence of pyranosides. Among all the synthesized **Gly Mix**, two compounds were selected according to their different specific features: actually, the score plot (Fig. 2c) clearly shows two main samples' families (highlighted in black and red colours) that resemble the Py/Fu isomeric composition. Among them, the 34_P27 and 78_P89 (also called **Amb Gly Mix** and **SCX Gly Mix** in the Supplementary material, respectively) were chosen since the former had a significant caramelization degree and a high Fu content, whereas the latter showed negligible side-reactions together with an optimal yield and great Py amount (see **Table S2,** and **Fig. S4–6**). Both of them, obtained starting from 1.8 %*w/v* of **Glc Gal** and a reaction time of 24 h, were then submitted to solvent-free enzymatic esterification with palmitic acid as acyl donor (Fig. 1c), according to a protocol reported elsewhere [17,18]. The immobilized lipase B from *Candida antarctica*, Novozym® 435, was selected as the biocatalyst since it exhibited better catalytic efficiency and operational stability with respect to other tested lipases such as those from *Thermomyces lanuginosus*, *Pseudomonas cepacia*, *Rhizomucor miehei*, *etc.* used both in free and immobilized forms. The reactions were performed at 80 °C, in a glass oven B-585 Kugelrohr under rotation to avoid the enzyme beads breaking due to magnetic stirring. Moreover, they were carried out under reduced pressure (30 mmHg) to favour water removal, thus shifting the equilibrium toward the formation of products. *n*-Butyl 6-*O*-palmitoyl-D-glycosides (**Amb Est Mix** and **SCX Est Mix**) were obtained in moderate yields (25 % and 40 %, respectively). The isomeric ratios resulting from this step (roughly calculated by ^{1}H NMR analysis carried out in DMSO-d_6 after proton exchange, see **Fig. S7–9**) were mostly dependent from those resulting from Fischer glycosylation with slight modification due to lipase selectivity.

The ability of **Amb Est Mix** and **SCX Est Mix** in reducing the (milli-Q) water/sunflower oil interfacial tension (IFT) was evaluated with the du Noüy ring method [29]. IFT measurements of the two samples (**Fig. S11**) were compared with the previously reported IFT data of their corresponding isolated couples of anomers, *i.e. n*-butyl 6-*O*-palmitoyl-D-glucopyranosides (**Est Glc Py**), D-glucofuranosides (**Est Glc Fu**), D-galactopyranosides (**Est Gal Py**), D-galactofuranosides (**Est Gal Fu**), and their experimentally obtained mixtures (**Est Glc Py + Fu** and **Est Gal Py + Fu**) [17,18,25]. All the reference tensides were tested at 3.0 and 4.5 mM concentrations and pyranosides derivatives were able to reduce the IFT from 26 mN m^{-1} (the water/sunflower oil IFT in the absence of tensides) to values lower than 4 mN m^{-1}. On the contrary, furanosides could not induce such IFT reduction due to their worse packing capacity [25]. Instead, more complex systems such as **Amb Est Mix** and **SCX Est Mix,** composed of mixtures of pyranosides and furanosides, require higher surfactants concentration (7.5 mM) to reach interfacial tension reduction comparable to that of pyranosides-based ones. Moreover, it was possible to appreciate the better IFT reduction ability of **SCX Est Mix**. This can be explained by looking at the different isomeric ratio, richer in pyranosides derivatives in **SCX Est Mix** with respect to those of **Amb Est Mix** (Py/Fu: 90/10 *vs* 22/78).

In addition to the static IFT, we also studied the dynamics of the oil/

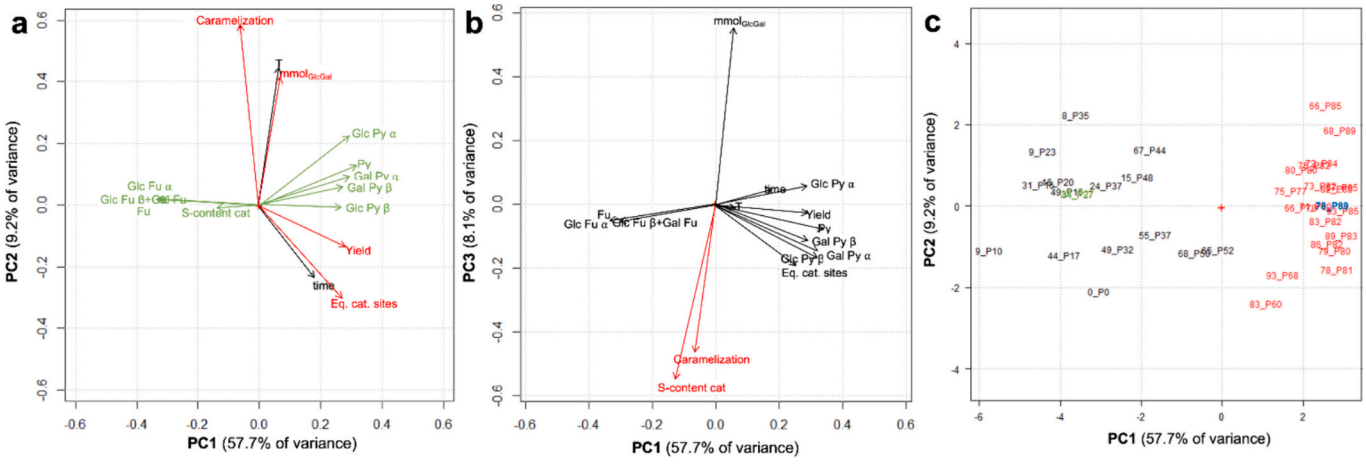

Fig. 2. Loading plots of **a)** PC2 *vs* PC1, **b)** PC3 *vs* PC1 for a total of explained variance of around 66 % for both cases by Principal Component (PC) analysis. **c)** Score plot of PC2 *vs* PC1 (samples labelled as yield_%Py). 34_P27 and 78_P89 are respectively highlighted in green and blue since they were both used for the further emulsification step. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

water interface stabilized by the surfactants by means of oscillating drop measurements (see the details in the Supplementary material). Such experiments give information on the ability of the surfactant molecules to diffuse at the interface, as well as on its rheological properties, as a function of the deformation rate. The elastic (E') and viscous (E") components of the viscoelastic modulus of **Amb Est Mix** and **SCX Est Mix** are reported in Fig. 3. When increasing the frequency of deformation, it is possible to detect a slight increase in E' (trending to a plateau) for both samples and a decrease in E", more marked for **Amb Est Mix**. Specifically, the resulting E' values suggest no major difference in terms of interfacial elasticity, instead, in the case of the E" component, a significant variation between **Amb Est Mix** and **SCX Est Mix** was found when increasing the deformation frequency. The ability to rearrange the interface after mechanical deformation is different between the two samples, even though interfacial rheology and emulsion stability are not directly related [30]. These trends are also found in the dynamic interfacial tests performed on isolated couples of anomers (**Est Glc** and **Est Gal**, **Py** and **Fu**) and their relative mixtures (**Py** + **Fu**), given as references (**Fig. S13**). In particular, **Est Glc Fu** seems the major responsible for the E" *vs* frequency trend.

Hence, the ability of **Amb Est Mix** and **SCX Est Mix** in stabilizing emulsions was evaluated through confocal microscopy images (**Fig. S14** and **S15**) at two different concentrations (3.0 and 4.5 mM). The droplets size distribution of both emulsions fresh and 72 h aged was evaluated and reported in **Figs. S14e,f** and **S15e,f**. At higher surfactant concentration, fresh emulsions (**Fig. S14b** and **S15b**) showed very small droplets size (around 1 μm), whereas at 3.0 mM (**Fig. S14a** and **S15a**) a broader droplets size distribution, up to 20 μm, was observed. It is worth noting that after 72 h of ageing, an increase in droplets diameter is appreciable for both concentrations especially in the case of **Amb Est Mix** (**Fig. S14c,d**) reasonably because of emulsion-breaking processes leading to droplets coalescence.

In conclusion, this paper outlines an innovative method for the cheese whey permeate valorization. Bio-based surface-active molecules were obtained through a low environmental impact synthetic process since it implies the use of a relevant waste as raw material, mild reaction conditions, few synthetic steps with cheap purification procedure. A chemometric approach was used to optimize the Fischer glycosylation step, mandatory for the surfactant synthesis. The starting amount of reagents, the equivalents of catalytic sites, the S-content and the type of the catalyst were identified as the main parameters influencing the yields and the isomeric ratio of the obtained glycosides. The pyranosidic content resulted to be crucial for the final surfactant features of the bio-based tenside mixtures. Specifically, **SCX Est Mix**, which is characterized by high amount of pyranosides-based compound (Py/Fu: 90/10), showed a higher ability in reducing the interfacial tension with respect to **Amb Est Mix** (Py/Fu: 22/78). The better surfactancy was corroborated by a narrower droplets size distribution and a more viscous interface, which induce longer stabilization of the W/O emulsions produced with **SCX Est Mix**.

CRediT authorship contribution statement

Giorgia Ballabio: Writing – original draft, Visualization, Validation, Investigation, Data curation. **Sara Sangiorgio:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Data curation, Conceptualization. **Eleonora Pargoletti:** Writing – review & editing, Visualization, Validation, Investigation. **Rita Gelli:** Visualization, Validation, Investigation, Data curation. **Massimo Bonini:** Writing – review & editing, Project administration, Conceptualization. **Marco Rabuffetti:** Validation. **Giuseppe Cappelletti:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Giovanna Speranza:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

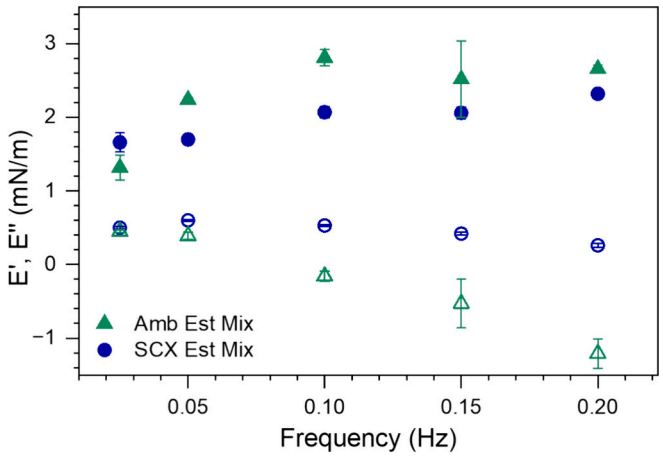

Fig. 3. E' (full markers) and E" (empty markers) of sample **Amb Est Mix** (triangles) and **SCX Est Mix** (circles) at concentration 3.0 mM in sunflower oil at different drop oscillation frequencies at the oil/water interface.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.colcom.2024.100807.

References

[1] K.S. Birdi, Surface and Colloid Chemistry: Principles and Applications, CRC Press, 2009.
[2] I.M. Banat, R.S. Makkar, S.S. Cameotra, Potential commercial applications of microbial surfactants, Appl. Microbiol. Biotechnol. 53 (2000) 495–508, https://doi.org/10.1007/s002530051648.
[3] M.K. Walsh, R.A. Bombyk, A. Wagh, A. Bingham, L.M. Berreau, Synthesis of lactose monolaurate as influenced by various lipases and solvents, J. Mol. Catal. B Enzym. 60 (2009) 171–177, https://doi.org/10.1016/j.molcatb.2009.05.003.
[4] D.R. Perinelli, S. Lucarini, L. Fagioli, R. Campana, D. Vllasaliu, A. Duranti, L. Casettari, Lactose oleate as new biocompatible surfactant for pharmaceutical applications, Eur. J. Pharm. Biopharm. 124 (2018) 55–62, https://doi.org/10.1016/j.ejpb.2017.12.008.
[5] I.J.A. Baker, B. Matthews, H. Suares, I. Krodkiewska, D.N. Furlong, F. Grieser, C. J. Drummond, Sugar fatty acid ester surfactants: structure and ultimate aerobic biodegradability, J. Surfactant Deterg. 3 (2000) 1–11, https://doi.org/10.1007/s11743-000-0107-2.
[6] M. de Divitiis, D. Ami, A. Pessina, A. Palmioli, B. Sciandrone, C. Airoldi, M. E. Regonesi, L. Brambilla, M. Lotti, A. Natalello, S. Brocca, M. Mangiagalli, Cheese-whey permeate improves the fitness of Escherichia coli cells during recombinant protein production, Biotechnol. Biofuels Bioprod. 16 (2023) 1–19, https://doi.org/10.1186/s13068-023-02281-8.

[7] F. Carvalho, A.R. Prazeres, J. Rivas, Cheese whey wastewater: characterization and treatment, Sci. Total Environ. 445–446 (2013) 385–396, https://doi.org/10.1016/j.scitotenv.2012.12.038.
[8] P.M.R. Guimarães, J.A. Teixeira, L. Domingues, Fermentation of lactose to bio-ethanol by yeasts as part of integrated solutions for the valorisation of cheese whey, Biotechnol. Adv. 28 (2010) 375–384, https://doi.org/10.1016/j.biotechadv.2010.02.002.
[9] L.T. O'Donoghue, E.G. Murphy, Nondairy food applications of whey and milk permeates: direct and indirect uses, Compr. Rev. Food Sci. Food Saf. 22 (2023) 2652–2677, https://doi.org/10.1111/1541-4337.13157.
[10] C.S. Murari, D.C.M.N. da Silva, G.L. Schuina, E.F. Mosinahti, V.L. Del Bianchi, Bioethanol production from dairy industrial coproducts, Bioenergy Res. 12 (2019) 112–122, https://doi.org/10.1007/s12155-018-9949-5.
[11] C. Fernández, B. Carracedo, E.J. Martínez, X. Gómez, A. Morán, Application of a packed bed reactor for the production of hydrogen from cheese whey permeate: effect of organic loading rate, J. Environ. Sci. Health A 49 (2014) 210–217, https://doi.org/10.1080/10934529.2013.838885.
[12] C.S.K. Lin, A.A. Koutinas, K. Stamatelatou, E.B. Mubofu, A.S. Matharu, N. Kopsahelis, L.A. Pfaltzgraff, J.H. Clark, S. Papanikolaou, T.H. Kwan, R. Luque, Current and future trends in food waste valorization for the production of chemicals, materials and fuels: a global perspective, Biofuels Bioprod. Biorefin. 8 (2014) 686–715, https://doi.org/10.1002/bbb.1506.
[13] M. Ferrer, M.A. Cruces, F.J. Plou, E. Pastor, G. Fuentes, M. Bernabé, J.L. Parra, A. Ballesteros, Chemical versus enzymatic catalysis for the regioselective synthesis of sucrose esters of fatty acids, Stud. Surf. Sci. Catal. 130 (2000) 509–514, https://doi.org/10.1016/S0167-2991(00)81008-3.
[14] M. Enayati, Y. Gong, J.M. Goddard, A. Abbaspourrad, Synthesis and characterization of lactose fatty acid ester biosurfactants using free and immobilized lipases in organic solvents, Food Chem. 266 (2018) 508–513, https://doi.org/10.1016/j.foodchem.2018.06.051.
[15] M. Verboni, S. Lucarini, A. Duranti, 6′ -O-lactose ester surfactants as an innovative opportunity in the pharmaceutical field: from synthetic methods to biological applications, Pharmaceuticals 14 (2021) 1306, https://doi.org/10.3390/ph14121306.
[16] X. Zhang, F. Song, M. Taxipalati, W. Wei, F. Feng, Comparative study of surface-active properties and antimicrobial activities of disaccharide monoesters, PLoS One 9 (2014) e114845, https://doi.org/10.1371/journal.pone.0114845.
[17] S. Sangiorgio, E. Pargoletti, M. Rabuffetti, M.S. Robescu, R. Semproli, D. Ubiali, G. Cappelletti, G. Speranza, Emulsifying properties of sugar-based surfactants prepared by chemoenzymatic synthesis, Coll. Interf. Sci. Commun. 48 (2022) 100630, https://doi.org/10.1016/j.colcom.2022.100630.
[18] R. Semproli, M.S. Robescu, S. Sangiorgio, E. Pargoletti, T. Bavaro, M. Rabuffetti, G. Cappelletti, G. Speranza, D. Ubiali, From lactose to alkyl Galactoside fatty acid esters as non-ionic biosurfactants: a two-step enzymatic approach to cheese whey valorization, Chempluschem 88 (2023) e202200331, https://doi.org/10.1002/cplu.202200331.
[19] F. Björkling, S.E. Godtfredsen, O. Kirk, A highly selective enzyme-catalysed esterification of simple glucosides, J. Chem. Soc. Chem. Commun. 14 (1989) 934–935, https://doi.org/10.1039/C39890000934.
[20] H. Akita, E. Kawahara, M. Kishida, K. Kato, Synthesis of naturally occurring β-d-glucopyranoside based on enzymatic β-glycosidation, J. Mol. Catal. B Enzym. 40 (2006) 8–15, https://doi.org/10.1016/j.molcatb.2006.01.031.
[21] M. Enayati, Y. Gong, A. Abbaspourrad, Synthesis of lactose lauryl ester in organic solvents using aluminosilicate zeolite as a catalyst, Food Chem. 279 (2019) 401–407, https://doi.org/10.1016/j.foodchem.2018.12.027.
[22] A. Decesaro, T.S. Machado, Â.C. Cappellaro, A. Rempel, A.C. Margarites, C. O. Reinehr, M.N. Eberlin, D. Zampieri, A. Thomé, L.M. Colla, Biosurfactants production using permeate from whey ultrafiltration and bioproduct recovery by membrane separation process, J. Surfactant Deterg. 23 (2020) 539–551, https://doi.org/10.1002/jsde.12399.
[23] Novozymes, Dairy Application Sheet, 2023.
[24] B. Estrine, S. Marinkovic, J. François, Synthesis of alkyl Polyglycosides from glucose and xylose for biobased surfactants: synthesis, properties, and applications, in: Biobased Surfactants: Synthesis, Properties, and Applications, Elsevier, 2019, pp. 365–385, https://doi.org/10.1016/B978-0-12-812705-6.00011-3.
[25] S. Sangiorgio, E. Pargoletti, G. Ballabio, M. Rabuffetti, G. Cappelletti, L. Raimondi, G. Speranza, Unveiling the role of the ring size in the sugar-based tensides surfactancy by interfacial studies and molecular dynamics, J. Mol. Liq. 408 (2024) 125350, https://doi.org/10.1016/j.molliq.2024.125350.
[26] A.A. Chaugule, A.R. Jadhav, H. Kim, Polyvinyl trisulfonate ethylamine based solid acid catalyst for the efficient glycosylation of sugars under solvent free conditions, RSC Adv. 5 (2015) 104715–104724, https://doi.org/10.1039/c5ra20300g.
[27] P.F. Monsan, F. Paul, V. Pelenc, E. Boures, Enzymatic production of α-butylglucoside and its fatty acid esters, in: Ann. N. Y. Acad. Sci., Blackwell Publishing Inc., 1996, pp. 633–641, https://doi.org/10.1111/j.1749-6632.1996.tb33268.x.
[28] D.F. Mowery, Chromatographic Adsorption. IV. Cation exchange resins as catalysts in glycoside formation, J. Am. Chem. Soc. 77 (1955) 1667–1669, https://doi.org/10.1021/ja01611a075.
[29] B.P.L. du Noüy, An interfacial tensiometer for universal use, J. Gen. Physiol. 7 (1925) 625–631, https://doi.org/10.1085/jgp.7.5.625.
[30] L. Zhang, H.Q. Sun, L. Zhang, Z.Q. Li, L. Luo, S. Zhao, Interfacial dilational rheology related to enhance oil recovery, Soft Matter 7 (2011) 7601–7611, https://doi.org/10.1039/c1sm05234a.