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Co-melting of solid sucrose and multivalent cation soaps for solvent-free synthesis of sucrose esters

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Abstract—Sucrose fatty acid esters, useful as mild surfactants, have been synthesised in good yields in a solvent-free medium. High contents of monoesters and low saponification rate have been observed. The co-melting of sucrose and a multivalent cation soap such as magnesium or zinc soaps, under basic conditions, allowed the formation of a homogeneous reaction mixture, where solid sucrose was fully dissolved. The kinetic monitoring profiles are similar to reactions in homogeneous solutions, with fast initial formation of monoesters. As a consequence, conversion of sucrose in sucrose esters occurred in good yields. The specificity of multivalent cation soaps compared to monovalent cation soaps, for example, potassium stearate, was pointed out.

Sucrose fatty acid esters with low degree of substitution (typically 1–4 fatty chains grafted on sucrose) are developed today as very mild and non toxic emulsifiers in food, cosmetics, pharmaceutics, agrochemicals or polymers.[1–4] Additionally, these surfactants are entirely coming from renewable materials. The synthesis is usually achieved by reaction of sucrose with fatty acid esters in DMSO or DMF, with a base as catalyst. The reaction, performed in a homogeneous solution, yields to a distribution of monoesters, diesters, triesters and more, directly related to the stoichiometry of sucrose and fatty ester.[5,6]

In order to develop a more environmentally friendly and a more economical large scale synthesis, solvent-free processes are discussed. The literature and patents deal with methods where solid sucrose, solid basic catalyst and the fatty acid ester are allowed to react at high temperature, typically 130–180 °C. The reaction mixture takes the form of a viscous paste. Alkali cations soaps or sucrose esters are often added as emulsifiers, in proportions from 1 to 15 wt %, in order to improve the dispersion of the solid and hydrophilic sucrose in the liquid fatty ester (Fig. 1).[7,8]

However, the occurrence of solid interfaces impairs the conversion of both sucrose and fatty acid ester. It leads to a large change in the reactivity, in the final distribution of sucrose esters and in the saponification rate. Indeed, sucrose esters produced during the reaction, being amphiphilic or lipophilic and molten at the reaction temperature, are much more reactive than the solid un-substituted sucrose. Yet the reaction tends to give a high amount of highly substituted sucrose esters. By this solvent-free process, obtaining a good conversion of sucrose and high yields in monosubstituted sucrose (monoesters) remains a difficult task. However they correspond to the most desirable products in terms of their emulsifying properties.

The topic of dealing with solid interfaces is a recurrent problem when one wants to switch from a solvent process to a solvent-free process. Recently, for example, it has been shown that a good reactivity in a solvent-free synthesis can be attributed to a favourable co-melting

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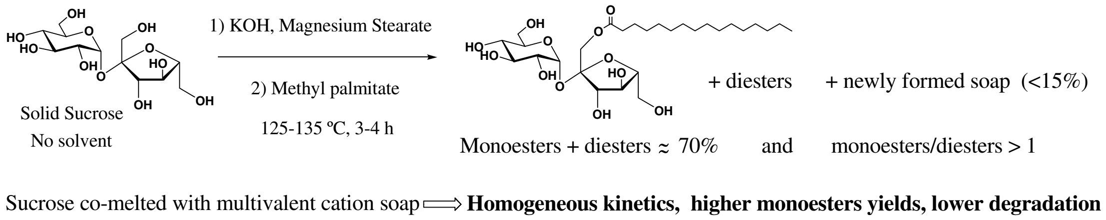

Figure 1. Solvent-free transesterification of sucrose.

of the two reactants, thanks to hydrogen bonding.[9] In the case of the transesterification of sucrose, solving the problem does not appear easy, first because sucrose cannot melt without decomposition (caramel) and secondly because the hydrophilicity of sucrose does not match the hydrophobicity of the fatty ester.

In this work, the aim was to find a way to make sucrose soluble in the fatty ester, by suppressing the solid interface, without adding any organic solvent. In order to keep a good environmental profile, adding a toxic additive or a supplementary product difficult to separate from the mixture was also ruled out. A first method was to perform the activation of sucrose with the base in an homogeneous aqueous solution (see e.g., Ref. 7c). In this case, the complete removal of water before proceeding to transesterification provided at best a vitreous, but still solid sucrate, which was not at all miscible with the fatty ester. In order to impair solidification of sucrate and to make it miscible with the fatty ester, it appeared possible to mix it with fatty acid soaps in high enough amounts. This method was described in some works, where 15–30 wt % of anhydrous alkali metal soaps were added.[10] Our results with this method compared well with those in Ref. 10 (Table 1, entries 5 and 6).[11] The global yields in sucrose esters were fairly good but the distribution between monoesters and polysubstituted sucrose esters did not compare with homogeneous reactions. The latter remained much higher than the former.

It appeared that the use of multivalent cation soaps such as magnesium stearate, zinc stearate and more could bring advantages over alkali cations soaps, owing to some of their specific properties. First, they display a much lower melting point than alkali cation soaps, from 110 to 180 °C instead of 250–300 °C.[12] Moreover, it was anticipated that the complexing ability of sugars and polyols towards multivalent cations[13–15] could lead transiently to the formation of a sucrate-cation-fatty carboxylate complex, potentially miscible with the fatty ester thanks to the complexed fatty chain. This phenomenon has already been shown to be effective for transport of monosaccharides through a liquid membrane, by using lipophilic phosphoric acids.[16] Otherwise, multivalent cation salts or soaps have been proposed as basic catalysts or to make sucrose recycling easier in solvent-free syntheses of sucrose esters. In these cases, a homogenisation phenomenon specifically due to these cations has not been reported.[17,18,10]

In this study, we explored various conditions for making the solvent-free transesterification of sucrose using either multivalent cation soaps or potassium stearate as additives. Reactivity of the mixtures was compared by taking into account three criteria: the texture and homogeneity of the reaction mixtures (viscous pastes), the kinetic profiles, and the final distribution of the products, especially, the monoesters/diester molar ratio, as a marker of the mean substitution degree. Analysis of the complex reaction mixtures, containing fatty acid,

Table 1. Transesterification of sucrose in the presence of mutivalent and monovalent cations soaps

Entry	Soap	wt soap × 100 / Total wt	Base equiv mol/sucrose	Conditions	Reaction time (h)	Monoesters	Diesters	Total mono + di	Mono/di	Saponification	Methyl palmitate	Kinetic profile
1	**MgSt**	**18**	**1**	(1)	**4**	**41**	**33**	**74**	**1.24**	**13**	**12**	Figure 2
2	MgSt	19	0.33	(1)	8	19	27	46	0.70	12	22	
3	MgSt	12	1	(1)	3	29	30	59	0.97	18	5	
4	ZnSt	18	1	(1)	4.5	46	43	89	1.07	9	0	
5	KSt	18	1	(1)	3.5	25	30	55	0.83	32	9	
6	KSt	25	1	(1)	3.25	27	31	58	0.87	21	5	Figure 3
7	**MgSt**	**0.7**	**0.33**	(2) (a)	**5.5**	**15**	**25**	**40**	**0.60**	**14**	**6**	Figure 4
8	KPa	0.7	0.33	(1)	7.5	15	31	46	0.48	15	4	
9	KPa	0.7	1	(2)	7	18	22	40	0.82	30	10	

St = stearate; Pa = palmitate with either Mg, Zn or K as cation. When possible, a different chain length for methyl fatty ester and added soaps has been chosen on purpose for easier quantification of the saponification rate during the reaction. This latter has been obtained either directly, or by deducting the soap added at t_0. Yields correspond to mol % versus methyl palmitate. The stoichiometry sucrose/methyl palmitate is 2.4. Experimental conditions: (1) In a 500 ml mixer with counter-rotating blades, sucrose (100 g), base, soap and 0–20 ml of water are mixed together at 75–100 °C for 1 h. The mixture is dried under vacuum for 30–60 min and then, melted methyl palmitate is added. The mixture is allowed to react under vacuum at 125–135 °C, for 3–8 h. (2) icing sugar and base are mixed with soap for 1 h at 120 °C. Next steps are the same as in conditions (1). (a) The base is K_2CO_3 instead of KOH.

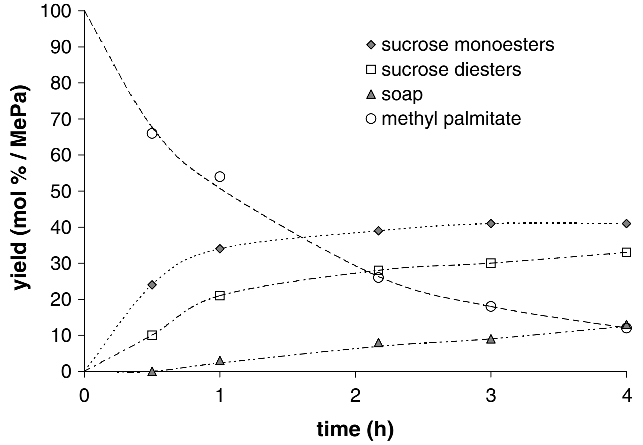

Figure 2. Solvent-free transesterification with 18 wt % of magnesium stearate (and 1 equiv base).

fatty acid methyl ester, sucrose monoesters, diesters and more, displaying various regiochemistry patterns, have been made by HPLC according to methods described previously.[19,20]

In the hypothesis of the formation of a sucrate-cation-fatty carboxylate complex, high proportions of base and soap have been used. When 1 equiv of potassium hydroxide versus sucrose and 1 equiv of magnesium or zinc soap versus methyl palmitate were used (≈18 wt %/total wt), the texture of the reaction mixture and the reactivity changed drastically compared to the reaction made according to other solvent-free procedures (potassium soap or sucrose esters as additives). Before adding methyl palmitate, a smooth paste is obtained. Observation with a microscope showed that no sucrose particles remained. This 'sucrate–Mg-soap' paste mixed easily with the melted methyl palmitate, and led to a homogeneous smooth paste, getting progressively thicker as the reaction progressed. The reaction kinetics switched from a heterogeneous profile, displaying sigmoid shape with long induction time (e.g., Figs. 3 or 4)[8a,21], to a typical homogeneous reaction profile, with early formation of high contents of monoesters (Fig. 2). The distribution of the final products changed also from mainly polysubstituted sucroesters (monoesters < diesters) (Table 1, entries 1 and 4) to mainly monosubstituted esters, at similar saponification rate[22] (Table 1, entries 7 and 8).

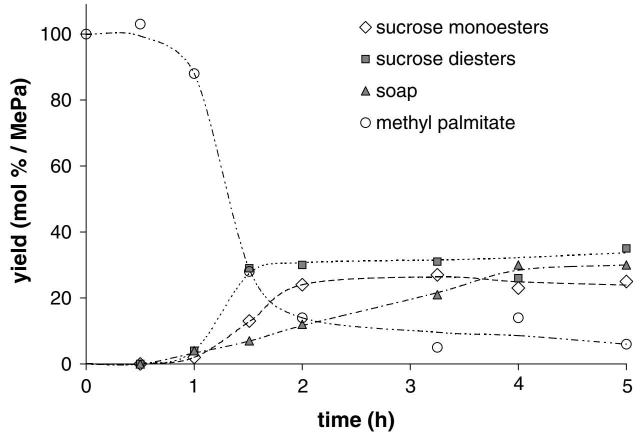

Figure 3. Solvent-free transesterification with 25 wt % of potassium stearate (and 1 equiv base).

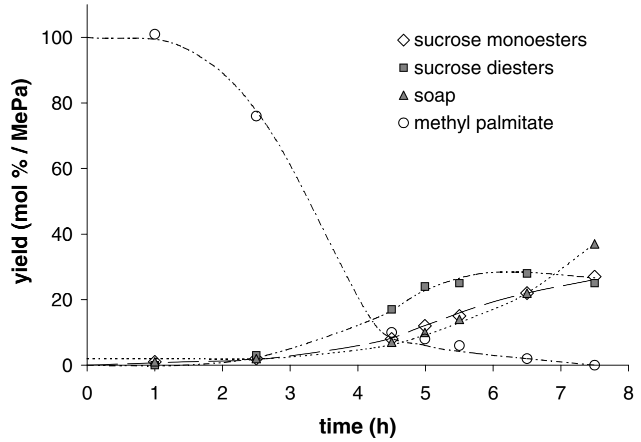

Figure 4. Solvent-free transesterification with 0.7 wt % of magnesium stearate (and 0.33 equiv base).

The specificity of multivalent cations in this process has been shown by using the same proportions of potassium stearate (18%) or higher (25%) (Table 1, entries 5 and 6 and Fig. 3). Before adding methyl palmitate, at 130 °C, a powder of 'sucrate–K-soap' is obtained, instead of a paste. This effect illustrates the effect of the soap melting point during this first step. When the melted methyl palmitate was added, it did not mix easily with the powder. Formation of lumps in a liquid, and later, a lumpy paste occurred. A monoesters/diesters ratio <1, a high rate of saponification, and a heterogeneous kinetic profile were observed.

Other conditions with magnesium stearate have been used. By decreasing the stoichiometry of the base from 1 to 0.33 equiv, an homogeneous paste, a slower reaction and a final monoesters/diesters ratio <1 were obtained (Table 1, entry 2). Decreasing the amount of magnesium stearate from 18% to 12% first led to the formation of a homogeneous sucrate paste. Further, after the addition of methyl palmitate, a bad homogenisation, a lower monoesters/diesters ratio and a higher saponification rate were observed (Table 1, entry 3). Thus, both the amount of multivalent cation soap and the amount of base are significant for obtaining homogeneous behaviour and high conversion in monoesters.

Quite interestingly, increasing the stoichiometry of the base (up to 1 equiv/sucrose) led to a faster reaction in all cases, but when using potassium soap, high saponification rate were obtained. When magnesium or zinc soap were used, saponification was avoided despite this high content (Table 1, entry 1 vs 2, entries 5,6 vs 8,9).

In conclusion, in this work, we showed that it was possible to solubilise sucrose in a fatty ester, removing the solid interface without using a solvent, by co-melting sucrose and a multivalent cation soap under basic conditions. The solubilisation phenomenon is evidenced by the absence of any solid particles remaining and by a reactivity similar to what can be obtained by solubilisation in a solvent. In a way, the process could be related either to a phase transfer phenomenon, or to a solubilisation in a molten salt (nearly a ionic liquid, since the melting temperature is not far from 100 °C). The multivalent cation can be chosen among the most harmless and biocompatible cations, typically magnesium,[23] in order to get an environmentally friendly process. Other multivalent cations could possibly give similar results. After a neutralisation step, metal hydroxides could be recovered and recycled in the desired multivalent cation soap by reaction with fatty acid. The resulting mixture of sucrose esters–fatty acid could be worked-up according to methods already described in some patents. For example, methods based on the fractional crystallisation or partition of fats, in water, ethyl acetate, alcohols or mixtures could allow the stepwise separation of the fatty acid fraction. Some methods are also based on the precipitation with the same multivalent cations.[24,25]

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12. Melting points: magnesium stearate: mp = 145 °C. Zinc stearate, mp = 130 °C. Potassium stearate: mp = 265 °C.
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20. Distribution of regioisomers was determined on selected final mixtures, according to the HPLC method described in: Molinier, V.; Wisniewski, K.; Bouchu, A.; Fitremann, J.; Queneau, Y. *J. Carbohydr. Chem.* **2003**, *22*, 657–669, The 6′,1′ and 6-substituted monoesters were the main regioisomers. The other regioisomers accounted for a very low percent of the mixture.
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24. See, for example, Matsumoto, S.; Hatakawa, Y.; Nakajima, A. EP Patent 0,448,996, 1991; James, K. GB Patent 1,500,341, 1978.
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