Filtration in Hydrophobic Media: 1. Evidence of Molecular Selection by Crossflow Filtration of Butter Oil

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ABSTRACT: The oils and fats industry needs well-identified fractions with well-defined physical properties for its final formulated products. In view of future applications, a triglyceride partition phenomenon of butter oil on a hydrophobic membrane is investigated by crossflow filtration. Triglycerides are separated into four groups according to their molecular weight and unsaturation index, leading to behavior that can be interpreted in terms of consistent stereochemical parameters.
JAOCS 72, 1139–1142 (1995).

KEY WORDS: Butter oil, crossflow filtration, filtration, hydrophobic media, triglyceride.

Because they are used in new formulations the complexity of natural fats has become an acute problem in connection with the necessary control of the physical properties of the final formulated products. The industry needs well-identified fractions from fats to have a large variety of textures and tastes at hand. Under multistep fractionation at various temperatures, liquid and solid components can be separated from a homogeneous phase. For example, cryofractionation processes are operated on a large scale to fractionate butterfat (1) as well as vegetable oils. The obtained high- and low-melting fat fractions are now available for the formulation industry; however, further development of such products is precluded by the high cost of these fractions.

The fact that no alternative to thermal treatment has been applied to fats may raise questions, and no significant progress has occurred in this field during the last two decades. For instance, separation techniques with membranes have not entered this area. Nowadays, the development of these techniques, applied to purification or fractionation of oils and fats, is an economic challenge of major importance.

From a fundamental point of view, several studies on the operation and interpretation of membrane separations in hydrophilic media exist and rely on particle/membrane interactions (2–4). Conversely, similar research with hydrophobic media produced poor results.

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Concerning the specific area of vegetable oils, several papers and patents deal with the problem of refining by membrane separation (5–8). Most of the authors have carried out separation experiments with oil/solvent solutions to extract some specific components such as phospholipids or sterols (9). The subsequent elimination of the solvent by evaporation is difficult and alternative membrane techniques have been suggested (10). A number of reverse osmosis and ultrafiltration membranes have been assayed to check their resistance toward refining solvents and their oil retention capacity (11,12).

However, no large-scale development of solvent separation after refining by a membrane technique has appeared from these studies. The problem is mainly due to legislation or regulations concerning solvent residues (especially hexane). These solvents must be evaporated by distillation, and, as a consequence, the membrane separation becomes useless.

To the best of our knowledge, there have been no observations made on any oil or melted fat partitioning through a membrane. Hence, no hydrophobic interaction phenomenon has been described, except in some particular cases where surface-active molecules in polar solvents are used (13).

In the present paper, the molecular partition phenomenon of a melted fat on a hydrophobic membrane has been investigated. Considering the complexity of the mechanisms involved, crossflow filtration appears to be an adequate technique for a preliminary approach to the partition phenomenon and its interpretation.

MATERIALS AND METHODS

Materials. Butter oil was obtained by centrifugation of commercial butter after melting at 60°C (Union Beurriere, Vesoul, France). A laboratory-made 8-cm diameter stainless-steel crossflow microfiltration unit was used, in line with a variable-speed peristaltic pump. The membrane used was a 6-cm diameter fritted stainless-steel disc, 2-mm thick with 0.5-μm diameter pores (Schumacher, Gonesse, France). Cleaning after each experiment was done according to the following procedure: after circulation of sodium hydroxide (0.05%, vol/vol) for 20 min at 80°C and rinsing with warm distilled

water, the membrane was put upside down and the procedure was repeated. The membrane was dried thereafter for 14 h at 105°C to eliminate all traces of water.

Methods. The procedure consisted of two consecutive crossflow filtrations at 50°C: (i) from an initial charge volume V_i, the filtration was stopped when the volume of filtrate reached 0.5 Vi; (ii) the filtrate obtained (F_1) was subjected to a second cycle, leading to filtrate F_2. A typical experiment lasted 8 h. The crude product F_0 and the filtrates F_1 and F_2 were checked by high-performance liquid chromatography (HPLC) for triglyceride (TG) composition according to Bornaz *et al.* (14). Each experiment was done in triplicate with a coefficient of variation of less than 5%.

RESULTS AND DISCUSSION

A "filtration performance index" (λ), expressed in %, is calculated according to the following equation:

$$\lambda(\%) = \frac{(F_{i,k} - F_{i,0}}{F_{i,0}} \quad [1]$$

where $F_{i,0}$: proportion of TG (i) in the crude product; $F_{i,k}$: proportion of TG (i) in the filtrate through cycle k. Therefore, if λ_i is positive, the relative permeability of the membrane to element (i) is strong. On the contrary, if λ_i is negative, the relative permeability is weaker.

Taking into account the structural and stereochemical complexity of the butter oil biochemical composition, the results are expressed by collecting the TG in four groups: (i) group S: saturated TG; (ii) group M: monounsaturated TG; (iii) group D: diunsaturated TG; and (iv) group T: triunsaturated TG.

Such an interpretation is justified by evaluation of the chromatograms obtained in a previous study (14). Under HPLC conditions, butterfat samples are separated into TG classes that differ by acyl carbon number (CN) and double-bond number (ND) simultaneously. According to El-Hamdy and Perkins (15), the criteria of separation are equivalent carbon number (ECN) and theoretical carbon number (TCN). In the present study, two equations were used to identify TG occurring in butterfat: ECN = CN − 2 × ND was employed to characterize each class, and TCN = CN − f_i ND allowed peak identification in each class. In a typical HPLC chromatogram, most of the peaks seem to have a uniform pattern in their retention times and intensities, so that association with certain TG classes might be well facilitated, especially in peaks 1–32, which can be separated visually as eight quartets (14). Each TG class is characterized by different ECN, as found by Frede and Thiele (16). In such an instance, each group of TG (S, M, D, T) corresponds mainly, in the same order, to the first, second, third, and fourth peaks of each quartet observed in these chromatograms. Such a subdivision is far from perfect because the calculation of the TG proportion is based on a random distribution of the fatty acids on the glycerol skeleton. According to the discussion above and in view of interpretation of the different behaviors, an average molecular weight (MW) can be calculated for each of the 32 peaks appearing in the chromatograms (Table 1). Therefore, the filtration performance index is linked to MW in each of the two consecutive filtrations (first and second cycle) (Figs. 1–4).

TABLE 1
Average Molecular Weight (MW) for Each Triglyceride Peak[a]

Peak number	Average MW	Peak number	Average MW	Peak number	Average MW
1	834	12	882	23	727
2	860	13	750	24	759
3	886	14	783	25	876
5	806	15	824	26	666
6	833	16	880	27	799
7	859	17	722	28	732
8	884	18	750	30	638
9	778	19	777	31	667
10	807	21	878	32	698
11	866	22	694		

[a]Peaks No. 4, 20, and 29 are missing because of unreliable detection.

Saturated TG (group S). In this group, MW varies from 600 to 850 daltons. After the first cycle, Figure 1 shows that an inversion of the filtration performance index is located around the average MW of 750 daltons. The relative permeability of the membrane is therefore higher for all TG with a MW of less than 750 daltons, *vice versa*. Moreover, the distribution of the MW after a second filtration cycle confirms the retention of heavy molecules as light molecules increase in the filtrate.

Triunsaturated TG (group T). The MW range of group T is narrow (from 874 to 886 daltons), but the specific retention

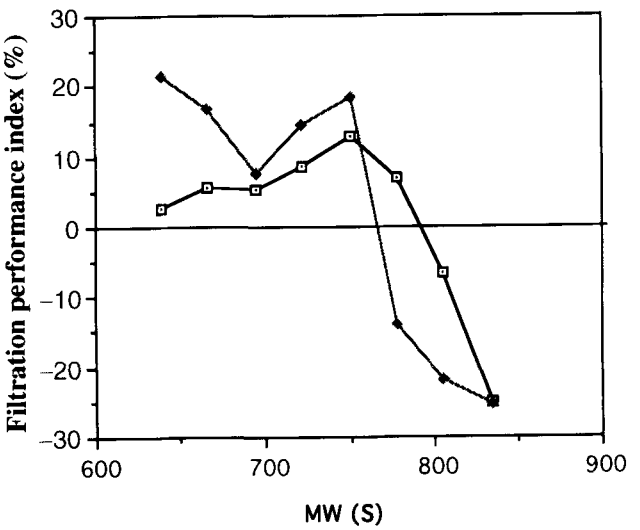

FIG. 1. Filtration performance index (λ) as a function of the average molecular weight (MW) of saturated triglycerides (group S): □, first cycle; ◆, second cycle.

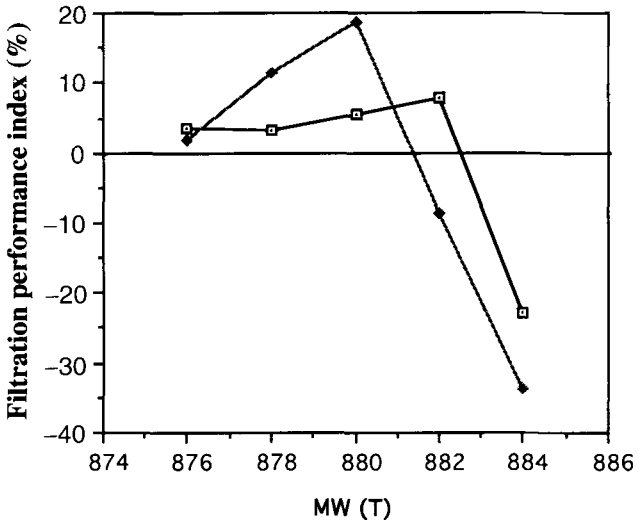

FIG. 2. Filtration performance index (λ) as a function of the average molecular weight (MW) of triunsaturated triglycerides (group T): □, first cycle; ◆, second cycle.

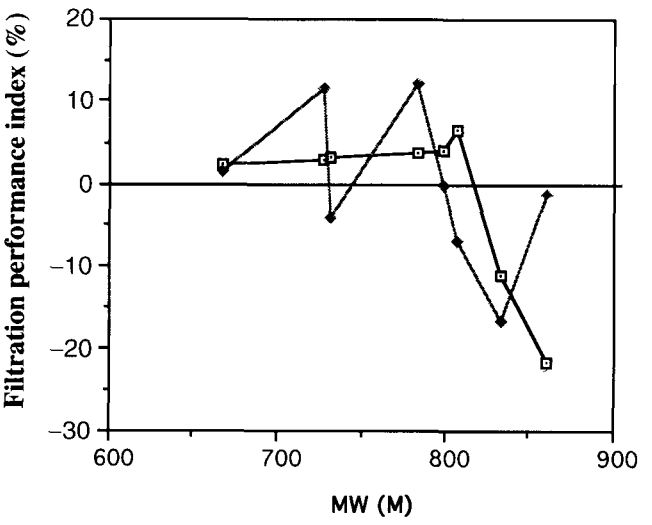

FIG. 3. Filtration performance index (λ) as a function of the average molecular weight (MW) of monounsaturated triglycerides (group M): □, first cycle; ◆, second cycle.

phenomenon is similar: The inversion point is located at 882 daltons for the first cycle. As observed in group S, the inversion point measured in the first cycle is slightly higher than in the second (Fig. 2). It is noticeable that this point is higher than for saturated TG. In fact, it is well known that double bond-containing chains are sterically more compact than saturated ones.

Nevertheless, the narrow MW range demonstrates that the phenomenon does not only depend on stereochemistry, and that the interpretation is not only linked to the "threshold cut-off," expressed in terms of MW, as is commonly stated for hydrophilic filtration.

Mono- and diunsaturated TG (groups M and D). Although they are shaped similarly, Figures 3 and 4 show less clear behavior. This could be linked to the sterical complexity induced by the double bonds in the TG molecule. For monounsaturated molecules, the inversion point is observed at *ca.* 800 daltons, and at 830 daltons for diunsaturated TG.

The notion of the inversion point, in terms of MW, is subject to the previous discussion. A simple comparison of these thresholds with the unsaturation index leads to consistent results, in keeping with well-known stereochemical data.

Considering this first set of experiments, a molecular sieving-type separation in a hydrophobic medium looks realistic, with an increasing inversion point parallel with the unsaturation index of the TG. Nevertheless, the criterion of this molecular selection appears to be different and certainly more complex than the one that is commonly used under hydrophilic conditions. All things considered, the size of the molecules is certainly far smaller than the size of the membrane pores. Thus, several parameters may be involved in the interpretation of this phenomenon: a discrepancy of the flow speeds, allowing some molecules to cross the membrane better than others, a preferential adsorption of some molecules

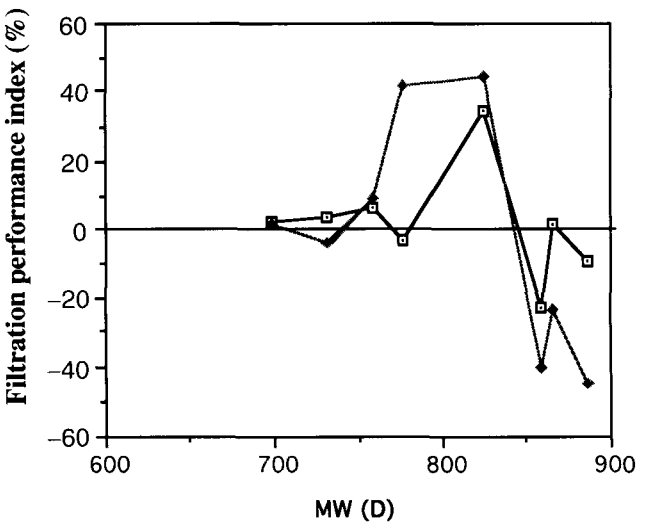

FIG. 4. Filtration performance index (λ) as a function of the average molecular weight (MW) of diunsaturated triglycerides (group D): □, first cycle; ◆, second cycle.

on the membrane and, even, an intersolubilization that leads to some molecular organization in the liquid.

The interpretation of the observed partition phenomenon needs to be confirmed by other experimental designs, for instance, tangential filtration. The study of particle–particle and particle–membrane interactions would be of great use. In view of this, the work is continuing in our laboratory.

REFERENCES

1. Déroanne, C., *Lait 39*:551 (1976).
2. Maubois, J.L., and G. Brulé, *Ibid. 62*:484 (1982).

3. Chang, S.Y., R.T. Toledo and H.S. Lillard, *J. Food Processing and Preservation 12*:253 (1989).
4. Van Den Berg, G.B., and C.A. Smolders, *Chemicaoggi 8*:23 (1990).
5. Gupta Sen, A.K., U.S. Patent 4,062,882 (1977).
6. Serafini, G., F. Camurati and E. Fedeli, *La Rivista Delle Sostanze Grasse 7*:65 (1988).
7. Koseoglu, S.S., *Oils & Fats International 7*:16 (1991).
8. Forsell, P., M. Kervinen, M. Alkio and K. Poutanen, *Fat Sci. Technol. 9*:355 (1992).
9. Ajana, H., and A. Hafidi, *Rev. Franc. des Corps Gras 39*:333 (1992).
10. Kuk, M.S., R.J. Hron and G. Abraham, *J. Am. Oil Chem. Soc. 66*:1374 (1989).
11. Koseoglu, S.S., J.T. Lawhon and E.W. Lusas, *Ibid. 57*:315 (1990).
12. Koseoglu, S.S., and D.E. Engelgau, *Ibid. 67*:239 (1990).
13. Faure, M., and J. Legault-Demar, *Bull. Soc. Chim. Biol. 32*:509 (1950).
14. Bornaz, S., G. Novak and M. Parmentier, *J. Am. Oil Chem. Soc. 69*:1131 (1992).
15. EL-Hamdy, A.H., and E.G. Perkins, *Ibid. 58*:867 (1981).
16. Frede, E., and H. Thiele, *Ibid. 64*:521 (1987).

[Received July 19, 1994; accepted February 16, 1995]