Crossflow Filtration of Oils on Metal Oxides. Influence of Chemical Composition of the Layer

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ABSTRACT: A new technique of fat fractionation was described in which butter oil and a formulated oil (olive, grapestone, coconut, and linseed) have been submitted to crossflow percolation at 45°C on different metal oxides layers (Al_2O_3, TiO_2, ZrO_2) of various thickness. The metal oxides layers were used in order to highlight the interaction between triglycerides (TG) and filtering materials. Experiments have been checked by high-performance liquid chromatography and by differential scanning calorimetry. Partition number was used to take the double bonds into account, and nonpolarity index was used to estimate the relative hydrophobicity of TG molecules. Results point out a two-step complex partition phenomenon: The filtering layer that is initially hydrophilic is coated by less hydrophobic TG acting as a second interface with hydrophobic characteristics. The three tested metal oxides did not provide comparable patterns. The specific property of aluminum oxide is related to a better polarizability of the Al–O bond.

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KEY WORDS: Hydrophobicity, interaction, metal oxides, nonpolarity index, triglycerides.

A lot of work has been done since the early 1990s in the field of oil and fat filtration. However, there has been no real industrial application for this process (1–3), even though some tangential filtration techniques have been tested, especially in refining (4,5) and fractionation (6,7). In fact, membrane separation processes in the oil and fat area may be shown in two ways: the first one concerns cryofractionation (8) at a crystal filtration step, the second one acts as a single homogeneous phase supported by molecular membrane interactions in hydrophobic media (9).

The present paper deals with the second approach and aims at understanding fat fractionation without a solvent using compressed metal oxide layers and at improving the knowledge on the relationship between oils (mainly considered as triglycerides, TG) and some materials that might be used as filtering agents. The understanding of the different interactions existing between the molecules of TG and the filtering agent is quite difficult but necessary so as to optimize the process and its applications. As is known, the composition of fats and oils determines their chemical and physical properties. The modification of this composition by a physical process requires the understanding of these interactions. In the food industry, tangential filtration remains the most widely used technique for yield reasons, but the complexity of the phenomenon occurring throughout the compressed metal oxide layers does not allow the interpretation of TG retention (10). This is the reason why the experiments have been done on a simple crossflow filtration device already used for the demonstration of TG partition in a previous work (7). The original compressed metal oxide layer has been replaced by layers of various thickness made from a series of metal oxide powders widely used in the making of fritted membranes.

Butter oil has been used in the first set of experiments because of its complexity; it contains the largest variety of TG characterized by various carbon chain lengths, unsaturation, and location on the glycerol skeleton. Such a composition exhibits a large panel of interface properties especially concerned with hydrophobicity. Nevertheless, owing to the complexity of this material, it has been necessary to use a formulated oil in order to study the individual molecular behavior, i.e., influence of unsaturation and carbon number of individual TG.

MATERIALS AND METHODS

Materials. Butter oil was supplied by Union Beurrière (Vesoul, France) and melted at 45°C prior to each experiment. The composition of milkfat was given in a previous work (11).

In order to obtain a large set of individual TG in equal proportions, which are easy to identify by high-performance liquid chromatography (HPLC) (see method below), a formulated oil was prepared by mixing olive, grapestone, and hydrogenated coconut and linseed oils, 25% (w/w) each. All were purchased from homogeneous commercial batches. The formulated oil gave 27 TG chromatographic peaks, each corresponding most of the time to one TG and in some few cases to two TG (Table 1). Solvents used for the analysis of TG by HPLC (acetone, acetonitrile, dichloromethane) were of HPLC grade (Chromanorm™, Prolabo, France).

Filtering materials. Hydrophilic powdered metal oxides (Al_2O_3, TiO_2, and ZrO_2) were used in various quantities (5, 20, 40, 80 g) corresponding to 1–20 mm of layer thickness. Each layer was compacted under the same constant pressure (12 kN · m^{-2}, 2 h) using a computerized Instron® universal testing machine (model 1122; Instron®, Buc, France). Gypsum-containing aluminum oxide (Al_2O_3 "G" type) was also used after plastering for 12 h at 100°C.

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TABLE 1
Identification of the Triglycerides of the Formulated Oil[a]

Peak	Rt (min)	Name	Surface (%)	PN	ECN	MW	NPI
1	6.42	CCC	0.66	30	30.00	554	60.94
2	7.62	LaCC	4.02	32	32.00	582	67.90
3	9.27	LaLaC	5.26	34	34.00	610	75.23
4	10.10	LnLnLn	9.77	36	34.74	872	165.70
5	11.33	LaLaLa	5.42	36	36.00	638	82.94
6	12.37	LLnLn	3.63	38	36.44	874	166.06
7	14.26	LaLaL, LaCO	3.29	38	37.28, 37.40	718	107.7
8	14.50	LaLaM	0.7	38	38.00	666	99.90
9	15.37	LLLn	0.63	40	38.14	876	166.44
10	15.83	OLnLn	3.35	40	38.61	876	166.44
11	16.60	PLnLn	0.99	40	39.16	850	155.83
12	18.22	LaLaO	1.92	40	39.45	720	108.00
13	19.00	LLL	19.32	42	39.84	878	166.82
14	19.70	LaMM	0.79	40	40.00	694	99.50
15	21.23	OLLn	0.33	42	40.31	878	166.82
16	21.38	PLLn, SLnLn	0.34	42	41.16	865	164.40
17	23.62	MMM	1.00	42	42.00	722	108.30
18	24.95	OLL	7.28	44	42.01	880	167.20
19	26.38	OOLn	4.84	44	42.48	880	167.20
20	26.95	PLL	0.49	44	42.56	854	156.57
21	30.88	PPLa	0.29	44	44.00	750	117.50
22	33.10	OOL	3.22	46	44.18	882	167.60
23	34.75	SLL	3.14	46	44.56	882	167.60
24	40.63	POL	0.13	46	44.73	856	156.94
25	43.62	OOO	13.35	48	46.35	884	168.00
26	46.78	OOP, SOL	5.26	48	46.90, 46.70	871	159.70
27	62.68	PSO	0.48	50	49.45	860	157.67

[a] Rt, retention time; PN, partition number (Eq. 1); ECN, equivalent carbon number (11); MW, molecular weight; NPI, nonpolarity index (Eq. 2); C, capric acid; La, lauric acid; Ln, linolenic acid; L, linoleic acid; O, oleic acid; M, myristic acid; P, palmitic acid; S, stearic acid.

Differential scanning calorimetry (DSC). The thermodynamic properties of butter oil [melting points and solid fat content (SFC) at 20°C] were determined with a PerkinElmer (Norwalk, CT) Pyris 1 differential scanning calorimeter according to Deroanne *et al*. (12).

TG determination. An HPLC analyzer system from Waters® (Saint Quentin-en-Yvelines, France) was used. The apparatus included two pumps (Waters model 510 HPLC), an autosampler (Waters model 717 Plus) thermostated at 32°C, and an integral thermostated column compartment maintained at 32°C. Data were computed by using Millenium™ 2101 software (Waters). The chromatographic columns were two Nova-Pak C18, 4 µm, 150 × 3.9 mm, stainless-steel, and connected in series. The column effluent passed through an evaporative light-scattering detector (Sedex 55; SEDERE, Alfortville, France) set at 38°C; the inlet gas pressure (from air compressor) was 2.5 bar (13).

Identification of TG was done by calculation of the partition number (PN) (11,14):

$$\text{PN} = \text{CN} - 2\ \text{DN} \qquad [1]$$

where CN is the carbon number and DN the number of double bonds.

Coupling HPLC with gas–liquid chromatography (GLC) was used to identify the different chromatographic TG peaks according to the random fatty acids distribution method (14).

The nonpolarity index (NPI). Hydrophobicity was characterized by NPI as defined by Van der Waal (15) who used this parameter for ester polarity calculation in lipid chemistry:

$$\text{NPI} = \frac{\text{CN} \times \text{molecular weight}}{\text{carboxyl (COO}^{-}\text{ number)} \times 100} \qquad [2]$$

The higher the index, the lower the affinity for a metallic (hydrophilic) surface is. However, the insaturation degree is not taken into consideration in calculating this index.

Crossflow filtration. The formulated oil and butteroil were percolated on metal oxides layers to study the partition of the TG on a filtering material exhibiting hydrophilic behavior. The parameters under consideration were time, chemical composition, thickness of the filtering layer, and driving pressure. Experiments were carried out at 45°C under a driving pressure varying from 0 to 10 bar on an Amicon model 402 ultrafiltration device, with a capacity of 400 mL and designed for 70-mm diameter membranes (44 cm^2 effective). The TG were checked for composition by HPLC and SFC was calculated by DSC analysis. The composition of the filtrate was compared to the initial composition by calculating for each peak a partition coefficient (PC) defined as follows:

$$\text{PC}_i\ (\%) = \left(1 - \frac{F_i}{I_i}\right) \cdot 100 \qquad [3]$$

where F_i = percentage of the TG_i in the filtrate and I_i = percentage of the TG_i in the original composition of butter oil.

The PC (%) is an indicator of the evolution of the composition of the filtrate after a fractionation, as a function of the initial composition. In fact, when the partition coefficient [PC_i (%)] is negative, it indicates that the specific TG_i crosses over the compressed metal oxide layer and that the amount of TG_i in the filtrate is higher than that in the initial composition. It should be stressed that even though the F and I in the PC_i calculation are percentages of the total HPLC response, the absolute mass discrepancy between filtrate and retentate composition should be reported to the mass fraction x_i of the TG given for the formulated oil in Table 1.

RESULTS AND DISCUSSION

Influence of the metal oxide. (i) Percolation of butteroil on aluminum oxide under free discharge. Butter oil (350 mL) was allowed to filter freely across aluminum oxide layers (2.5 and 20 mm thick) at a flow rate of 3 mL/min.

The partition of TG occurred at the beginning of the percolation: low PN (peaks 1–11, corresponding to PN 26–36) were retained by the layer, while high PN crossed the material (peak 12 and over) (Fig. 1A). It should be emphasized that all TG are well known as nonpolar molecules, but they are considered more or less hydrophobic according to their structure and degree of unsaturation. One of the main characteristics of aluminum oxide is that polar TG were strongly adsorbed onto the layer, while nonpolar TG were almost free to percolate and were found mainly in the filtrate (16). This was probably due to the formation of hydrogen bonds, in addition to possible interactions with electron-rich molecule sites. In addition to the variation of TG composition during the first 15 min, another phenomenon was visible to the naked eye: The filtrate froze faster than initial butter oil did, thus confirming the crossing of molecules of high melting point. It should be remembered that, in a previous work carried out on a stainlesss-steel membrane (7), the inversion of retention was observed close to PN 40.

Increasing the layer thickness from 2.5 to 20 mm induced higher PC, but did not affect the overall behavior of the TG. TG were retained up to peak 13 and significantly crossed the layer from peak 18 (PN 40) (Fig. 1B).

All metal oxides were difficult to pack and the layers remained slightly heterogeneous. The effect of mechanical cohesion of the layer was checked by using a gypsum-containing aluminum oxide (Al_2O_3 G, Fig. 1C). The use of such a material allowed us to obtain a compact homogeneous surface generating very slow percolation. The very first droplets appeared after 35 min and the flow rate did not exceed 0.1 mL/min. The TG composition of the first drops indicated that TG with low PN (peaks 1–11) and peaks 16, 17, 24, 37, and 39 were retained by the layer.

The SFC of the filtrate obtained from aluminum oxide percolation, regardless of the thickness, increased significantly in the beginning of the filtration (Fig. 2). This could be explained by the crossing of TG with high PN and the corresponding retention of TG with low PN onto the layer. The immediate decrease of SFC following the initial increase in the filtrate could be due to the saturation of hydrophobic sites of aluminum oxide and its progressive coating by a thin oil layer, which built a novel interface completely different in terms of hydrophobic properties.

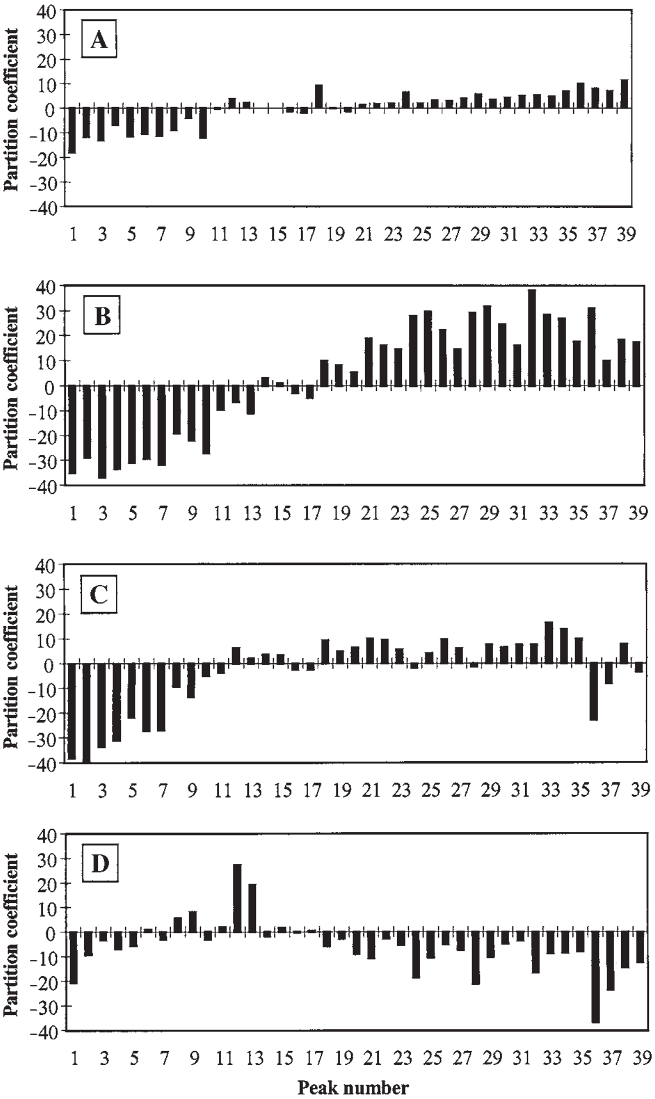

FIG. 1. Status of the partition coefficient between filtrate/initial butter oil after 1 min of crossflow filtration on metal oxide layers; (A) Al_2O_3, 2.5 mm thick; (B) Al_2O_3, 20 mm thick; (C) Al_2O_3 "G" (gypsum-containing Al_2O_3), 20 mm thick ; (D) TiO_2, 20 mm thick.

(ii) Percolation under pressure of butter oil on titanium oxide (TiO_2). The layer was 20 mm thick. Under the driving pressure of 0.8 bar, the filtrate ran out at 6 mL/min. The TG partition was somewhat confusing, with the following tendency: TG corresponding to low and very large PN did not cross the layer, although medium terms did (Fig. 1D). Even though the results are not shown, the behavior of the TG partition of TiO_2 at the first moment of fractionation is the same as that on aluminum oxide. However, after saturation of the hydrophilic sites, that is, after 10 min, the polarization equilibrium of TiO_2 was considered virtually immediate, contrary to the Al_2O_3 interface.

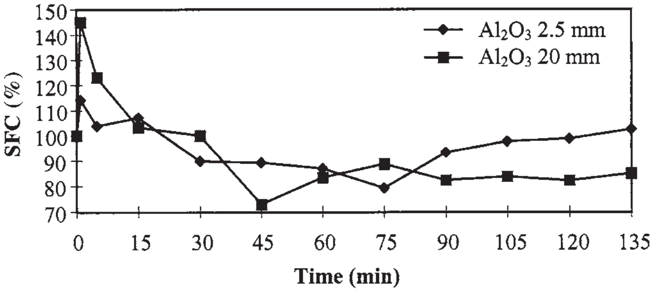

FIG. 2. Evolution of butter oil filtrate solid fat content (SFC) obtained after percolation on Al_2O_3 (2.5 and 20 mm thick). Basis 100 for initial butter oil.

(iii) Percolation of butter oil on zirconium oxide (ZrO_2) under free discharge. The layer was 40 mm thick. Although no pressure was applied on the layer, the filtrate dropped immediately at 3 mL/min. In the early minutes of the filtration, no variation of composition was observed. Some TG were retained after 15 min, but no reproducibility was made possible.

Influence of the driving pressure. (i) Percolation of butter oil on aluminum oxide under low driving pressure. The percolation was carried out as described above on a 40-mm-thick layer under a low driving pressure (0.1 bar). Under these conditions, the flow rate was 5.6 mL/min. The overall pattern of TG was similar to the previous one, but the amplitude of the phenomenon was higher at the beginning of the process. After 15 min, the partition decreased and all the TG crossed the layer at the end of the percolation, that is, after 100 min (Fig. 3A,B). These results are confirmed by an increase of up to 45% in filtrate SFC at the beginning of the percolation, as has been already observed without pressure (Fig. 2).

Influence of oil composition and process duration. The composition of the formulated oil was established in order to have a large variety of TG easily identifiable by HPLC. On a 40-mm-thick aluminum oxide layer, under free discharge, the flow rate was 8.3 mL/min. At the start of the process, two different behaviors were observed: first, retention of all peaks under number 9 (PN 40); second, crossing of peaks above number 9, except for peaks 12, 14, 17, 21 (Fig. 4A). After 15 min, almost all TG crossed the layer, except peaks 4 (LnLnLn), 7 (LaLaL), 13 (LLL), and 25 (OOO), which are mainly triunsaturated homogeneous TG (Fig. 4B) [where Ln is linolenic acid; La, lauric acid; L, linoleic acid; and O, oleic acid].

NPI allows interpretation in terms of hydrophobicity (Table 1): the aluminum oxide layer is able to hold TG with NPI <110, while higher terms cross the layer freely. Because the higher the NPI is, the more hydrophobic the molecule is, the aluminum oxide is able to share the TG according to their hydrophobicity. This statement can be strengthened by the conformation of the molecules at the interface. In the solid state, TG look like tuning forks. According to Brush *et al.* (17) and Dorset *et al.* (18), molecular bonds rotate freely in solution and when a TG is lo-

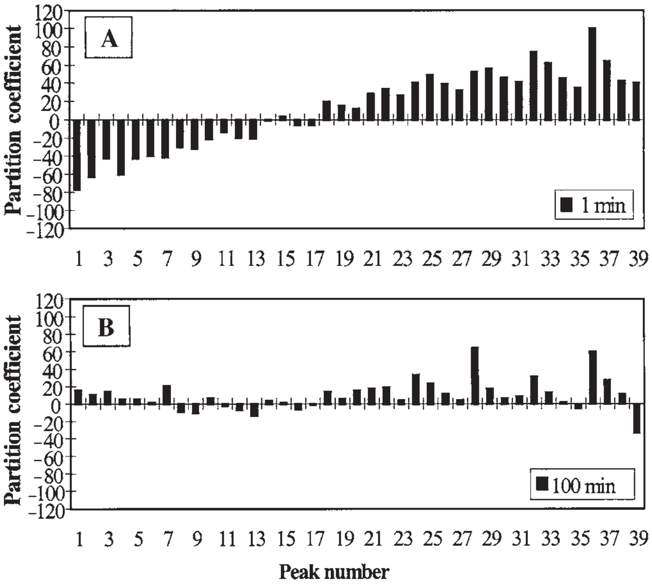

FIG. 3. Status of the partition coefficient between filtrate/initial butter oil on crossflow filtration under low driving pressure (0.1 bar) on Al_2O_3; (A) after 1 min; (B) after 60 min.

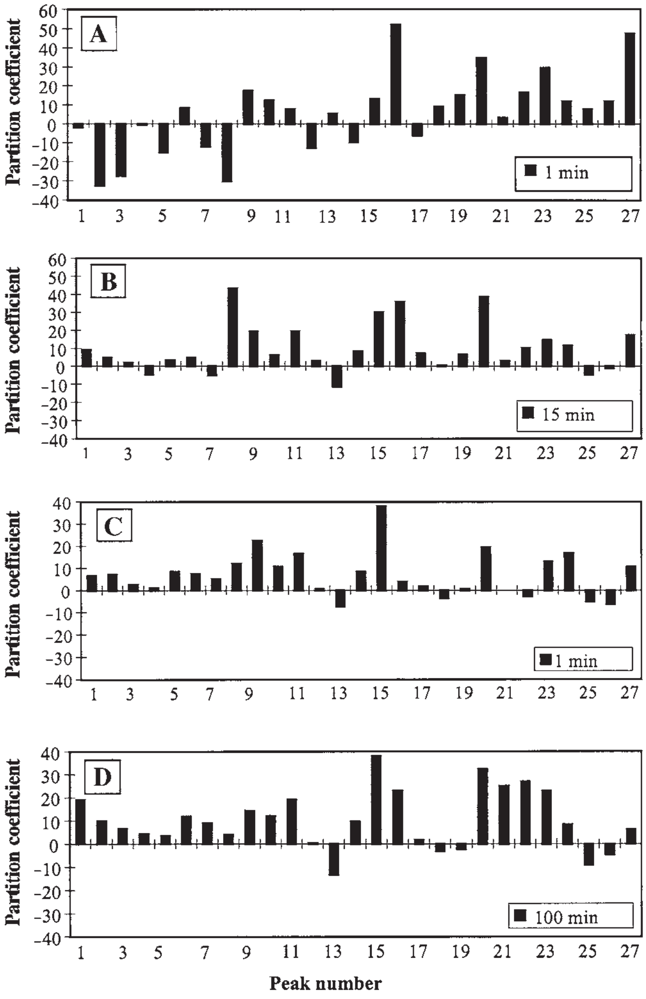

FIG. 4. Status of the partition coefficient between filtrate/formulated oil under crossflow filtration on Al_2O_3 [(A) after 1 min; (B) after 15 min] and on TiO_2 [(C) after 1 min; (D) after 100 min].

cated at a polar/nonpolar interface, the three fatty acid chains are oriented in the same direction toward the nonpolar phase, while the glycerol moiety faces the polar phase. Such a configuration allows maximal interaction on the hydrophobic side, between the fatty acid chains and the bulk of the oil, and on the hydrophilic side, between the three oxygen atoms of the ester bonds and the aluminum oxide. Therefore, the surface of the filtering layer is modified, it becomes hydrophobic, and the interactions with the TG are inverted. This could be an interpretation for the inverted behavior that is observed after a few minutes of filtration. The layer has become less polar because of the coating by the TG, which are now facing the nonpolar phase, so that the bulk only "sees" the nonpolar chains.

Thus, aluminum oxide should be considered under two states: the virgin initial state, and the other one, which appears after the coating by less hydrophobic TG. These TG are therefore adsorbed onto the material through hydrogen bonds and through the presence of permanent dipoles existing in the molecules. From this stage, more hydrophobic TG interact with this new layer and induce other types of interactions.

Similar interpretation may be given for the results obtained on titanium oxide using the formulated oil (Fig. 4C,D). Two behaviors can be depicted during the percolation: most TG cross the layer, except for some of them. One minute after the beginning of the process, peaks 13, 18, 19, 25, and 26 (LLL, OLL, OOLn, OOO, and OOP, respectively, where P is palmitic acid), are retained by the material. After 100 min, the TG that are held by the layer are the same (LLL, OLL, OOO, OOP), except for peak 19 (OOLn), which is replaced by peak 22 (OOL). These all are major TG and characterized by high NPI. Homogeneous triunsaturated TG LLL (peak 18) and OOO (peak 25) are strongly affected by interaction with the metal oxide. Obviously, the partition is not concerned with the molecular weight, but with the structure and especially with the degree of unsaturation.

All these experiments carried out under crossflow percolation on metal oxides point out a complex partition phenomenon, comprehensible altogether if two steps are taken under consideration. In the very first minutes of the percolation, the filtering layer acts as an hydrophilic surface, and generates a particular conformation of the less hydrophobic TG. This "trident" conformation coats the material and presents a full nonpolar interaction surface with the bulk of the oil. Therefore, throughout a second step of the percolation, which takes place after few minutes, the interactions with almost all the TG are inverted.

All filtering materials do not behave in the same manner. Aluminum oxide seems to be the most efficient agent according to its chromatographic properties and its ability to hold polar and unsaturated molecules. However, the electronic structures of the different oxides used are very close and there is no immediate explanation for such different behaviors, if not their ability to engage hydrogen bonding. Hydrogen bonds play an important role at the start of the percolation, that is to say, during the polarization step of the layer. Unlike other metal–oxygen bonding, the specific property of aluminum oxide is related to the better polarizability of the Al–O bond.

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