Determination of Solid Fat Content (SFC) of Binary Fat Blends and Use of These Data to Predict SFC of Selected Ternary Fat Blends Containing Low-Erucic Rapeseed Oil

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ABSTRACT: Several oils and fats often used for the industrial preparation of European shortenings were blended in binary systems. The equilibrium (after 48 h at 15°C) solid fat contents (SFC; determined by pulsed NMR spectroscopy) were measured and plotted against blend composition. SFC of the blends resulted from the SFC of each fat for the considered temperature as well as the type of interaction existing between those fats (namely, ideal behavior, monotectic interaction, eutectic interaction, and so on). The type of relationship fitted was dependent on the kind of interaction: Linear relationships were found for total compatibility between fats, and polynomial-type (order 2) relationships were found for fats exhibiting incompatibility. Some corresponding ternary oils and fats blends were also prepared and analyzed. Selected relationships (regression equations of the fitted curves) obtained for binary blends were combined in order to calculate the SFC of the corresponding ternary blends. Experimental values were generally close to predicted ones. The representation of SFC as a function of composition is interesting as it allows one to determine rapidly and easily the type of molecular interaction between two fats and also to determine equations that can be combined to calculate easily the SFC of corresponding ternary blends crystallized in the same way with a good accuracy. The texture (hardness) of several binary and ternary blends was also measured. The combination of the results obtained for SFC with the results obtained for the hardness of binary blends allows the prediction of the hardness of a corresponding ternary blend under the same conditions.

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KEY WORDS: Binary fat blends, shortening, solid fat content, ternary fat blends, texture.

Lipid shortenings are mixtures of oils and fats hydrogenated to various degrees, and they sometimes contain emulsifiers and other additives. The mechanical properties of edible fats are influenced by a series of factors, including the solid fat content (SFC), the polymorphism of the solid state, and the microstructure of the network of crystalline particles (1). SFC strongly influences the mechanical behavior of fats, although relying on SFC alone to predict hardness is unreliable (2,3). However in product development work involving oils and fats, the SFC profile of the oils and fats or their blends by pulsed NMR (pNMR) spectroscopy remains of considerable interest. Those profiles are used as a guideline to settle whether fat blends are suitable for specific applications. In margarine or shortening formulations, the SFC should be defined at a number of temperatures, typically from 15 to 40°C, to cover the range of use (4).

SFC of an oil and fat mixture results from the SFC for the considered temperature of each fat present in the blend and from the type of interaction existing between those oils and fats. Indeed, when oils and fats of different compositions are mixed, several behaviors can be observed: solid solution behavior (compatibility between fats), monotectic behavior, or eutectic behavior (5). Eutectic crystallization effects occur for (extreme) incompatibility between fats, leading to a m.p. of the solids present in the blend lower than the ones of the individual components. Eutectic systems shift to monotectic systems when the difference in the m.p. of the two components is 20°C or more (5).

The main objectives of this work were to study some physical characteristics, especially SFC, by pNMR of single fats and of several binary blends in order to determine the kind of molecular interactions involved, and also to predict physical properties of corresponding ternary blends using those results. As the hardness of a fat (shortening) is an important property that strongly influences the perceived texture of a food product, this physical macroscopic property was also estimated for selected blends.

Oils and fats involved in this study are commonly used in industrial European shortenings: anhydrous milk fat (AMF), palm oil (PO) and its fractions, partially hydrogenated palm oil (HPO), soybean oil (SO), low-erucic rapeseed oil (LERO), and partially hydrogenated low-erucic rapeseed oil (HLERO). HLERO and HPO, although containing *trans* FA (TFA), are still used in the formulation of some kinds of European shortenings (namely, cake shortenings). The HLERO/HPO/LERO mixture was first studied as a model because this system is commonly used in Europe as bakery or puff pastry shortening. The study was then extended to other fat systems containing natural nonhydrogenated oils and fats (i.e., LERO, AMF, PO and its fractions) hence with a lower TFA content.

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EXPERIMENTAL PROCEDURES

Materials. Commercial samples of LERO, HLERO, palm oil (PO), and HPO were supplied by Cargill, N.V. (Izegem, Belgium). AMF was kindly provided by Corman S.A. (Goé, Belgium). SO was obtained from Puratos (Groot-Bijgaarden, Belgium).

Sample preparation. Binary mixtures (w/w) of fats were prepared in 10% increments from 0 to 100%. Intermediate compositions also were prepared when necessary.

For the ternary mixtures, fats were blended in various ratios to cover the whole range of the ternary diagrams. All the mixtures were prepared according to the method of Danthine and Deroanne (4,6,7). Appropriate weight compositions (250 g) of the melted fats were mixed at 80°C (to erase crystal memory) in a clean, dry, and agitated glass vessel; samples of 50 g were put into a small plastic vessel and kept in liquid form at 50°C with gentle stirring for 15 min. Then they were statically crystallized in a freezer at −20°C for half an hour, in order to simulate on a laboratory scale an industrial scraped-surface heat exchanger. Samples were subsequently stored in a 15.0 ± 0.5°C controlled room for 48 h.

SFC determination. A pulsed NMR spectrometer (Minispec-mq20; Bruker, Karlsruhe, Germany) was used to measure the SFC after tempering the samples at 15.0 ± 0.5°C, as just described. Automatic calibration was made daily by using three standards (supplied by Bruker) containing, respectively, 0.0, 31.3, and 74.0% of solid.

Two separate procedures were used. (i) In determining SFC profiles, the NMR tubes were carefully filled in the 15.0 ± 0.5°C temperature-controlled room by means of a sampling device consisting of a glass tube with a tight fitting plunger. SFC was measured every 5°C from 15.0 to 55.0°C (4). (ii) In carrying out textural analysis, the NMR tubes were filled at 15 ± 0.5°C with tempered fat mixtures [as in (i)] and subsequently stored at 20°C for 1 h. The SFC was then determined isothermally at 20°C in order to compare the SFC values with data obtained by the textural analyses (7).

At least four replicates were performed for both procedures giving CV close to 5%.

Texture measurements. Texture measurements of the blends were carried out after tempering the samples at 15 ± 0.5°C. Samples were then held at 20 ± 0.1°C for 1 h before measuring them in a temperature-controlled room (20 ± 0.1°C) using an SMS TA.XT2i/5 texturometer (Stable Micro Systems, Surrey, United Kingdom).

Constant speed penetration. The texturometer with a cone probe (P/45C) was used in the penetration tests according to the method of Danthine and Deroanne (7). The probe penetrated the product at a constant speed of 0.5 mm/s to a distance of 5 mm. The maximum and final penetration forces were recorded. At least four penetration tests were run on each sample; two samples of each blend were analyzed. CV were all lower than 10%.

Construction of iso-line diagrams. Binary diagrams of iso-solid lines (compositions at which the SFC of a mixture is equivalent at a particular temperature) were constructed from the pNMR data (8). Ternary diagrams of iso-temperature lines (compositions of a mixture at which the requested temperature for a particular SFC is equivalent) were constructed from the pNMR data.

RESULTS AND DISCUSSION

SFC profiles. (i) Binary systems. One way to judge compatibility between two or more fats rapidly is to draw SFC iso-solid lines (8). Iso-solid lines are compositions at which the SFC of a mixture is equivalent at a particular temperature. In this study, SFC data at different temperatures vs. blend compositions were plotted. Corresponding SFC iso-solid lines in terms of temperature vs. blend composition were constructed from the same pNMR data in order to validate the new representation.

The cases of HPO/HLERO and HPO/PO binary blends are illustrated in Figures 1 and 2. Those binary mixtures can be qualified as ideal. There is a linear evolution of SFC vs. composition whatever the temperature, corresponding to the weighted average of the SFC of the original oils. The same is true in the iso-solid representation, where the interpolation of the data is also linear.

When two fats are mixed together, the SFC of the blend may be lower than the weighted average of the component fats. Sometimes the SFC can be lower than that of either fat. In those cases of incompatibility between fats, both SFC at different temperature vs. blend composition diagrams and iso-solids line diagrams are not linear between the two pure fats.

Figures 3A and 3B illustrate the behavior of the HLERO/LERO binary blends. This binary mixture can be qualified as nonideal. Indeed, the SFC vs. temperature and iso-lines are not linear. SFC of the present blend is lower than the one expected from linear regression, i.e., the weighted average one. There is a curvature of the SFC data (Fig. 4). The difference between the actual SFC lines and linearity may be attributed to a dissolution of some solid fat from one ingredient by liquid fat from the other ingredient. The further the actual observed SFC is below the weighted average of the SFC of the ingredients (linear interpolation), the greater the extent of dissolution of solid from one ingredient in liquid from the other.

The binary interaction of the HLERO/LERO blend is monotectic. This is consistent with previous results obtained by DSC for this mixture (4,6). Mixtures of HPO/LERO, PO/LERO, LERO/AMF, LERO/palm oil stearin, LERO/palm oil olein, SO/HPO, SO/PO, and SO/HLERO (data not shown) also demonstrated monotectic interactions.

This type of behavior is characteristic of eutectic systems that shift to monotectic systems when the difference in the m.p. of the two components increases (e.g., 20°C and above), and the high-melting component dissolves a substantial amount of the low-melting component (5).

The blends made of AMF and PO (Fig. 5), of HLERO and AMF (not shown), and of HLERO and PO (not shown) are three examples of eutectic interactions. The minimum in the SFC for the AMF/PO mixture is obtained for the 50% composition.

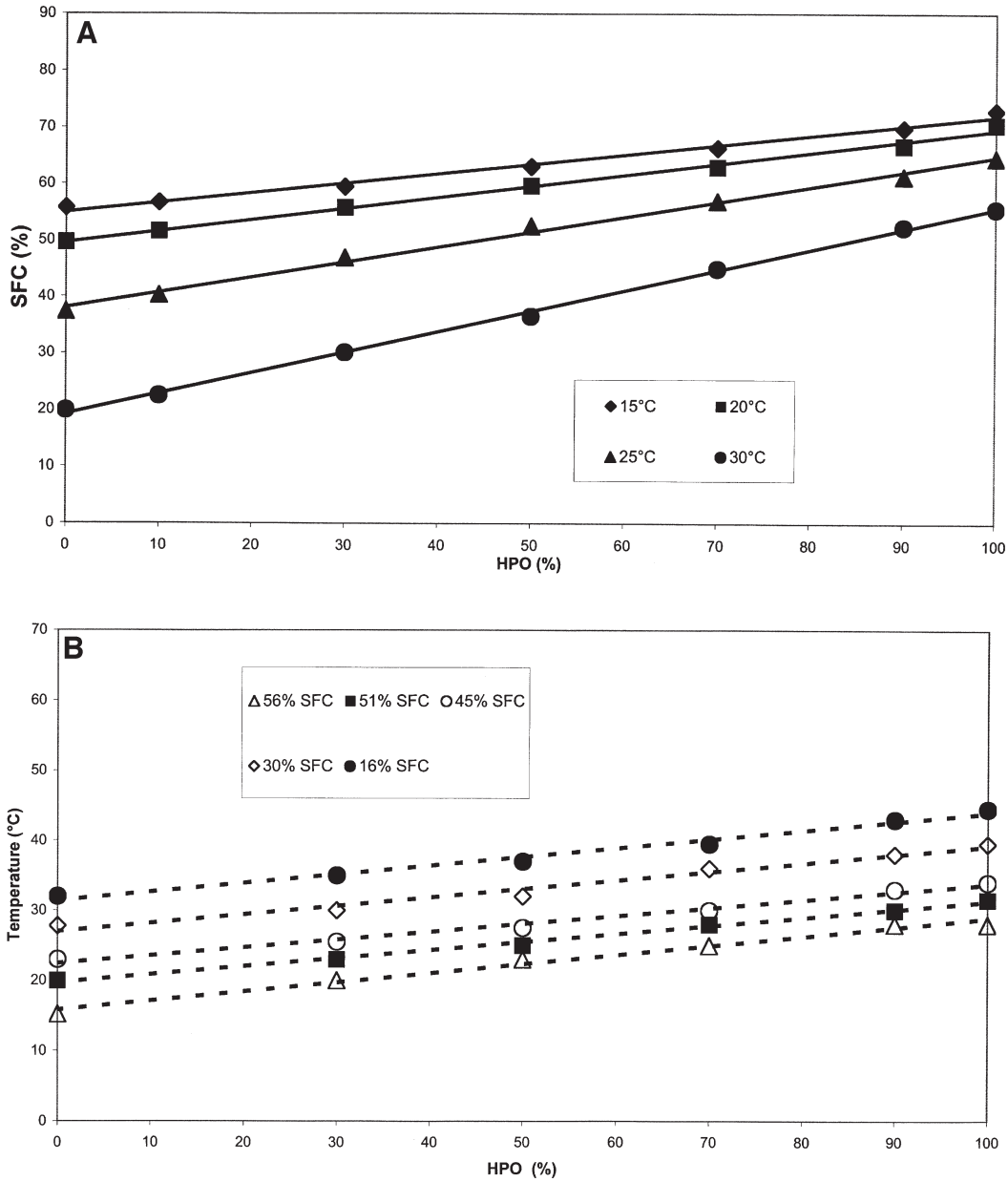

FIG. 1. (A) Solid fat content (SFC) vs. blend compositions for the mixture of partially hydrogenated low-erucic rapeseed oil and partially hydrogenated palm oil (HLERO/HPO); (B) iso-solid diagram for the HLERO/HPO mixture.

The curvatures of the graphs obtained by plotting SFC data vs. blend compositions of incompatible oils and fats allow fitting of second-order polynomial-type relations. The regression equations of the fitted relations are of the following type:

$$SFC_{X/Y}\, t = a[x]^2 + b[x] + c \qquad [1]$$

where t represents the temperature (°C); $[x]$ is the concentration of the fat coded X in the system; a, b, and c are dependent on the fats X and Y, on the temperature, on the thermal history and also on the type of interaction existing between the fats; $a + b + c$ corresponds to the SFC of the fat coded X at the temperature t, and c corresponds to the SFC of the fat coded Y at the temperature t. The ratio of a/b is characteristic of the interaction between the fats: A high value of the ratio is observed for a strong incompatibility between the fats (strong curvature). The a value for an ideal behavior is zero.

The curvature observed ranges from weak to strong depending on the fats, on the thermal history, and also on the temperature. For example, in the case of the HPO/LERO system, the curvature is greater at 25°C than at 15°C (see Table 1 for actual values). It may be that at low temperatures insufficient liquid fat is available for substantial dissolution of solid fat, hence the SFC data lie close to the weighted average line.This kind of representation (SFC data vs. blends compositions) is a useful tool to estimate rapidly and qualitatively the compatibility of

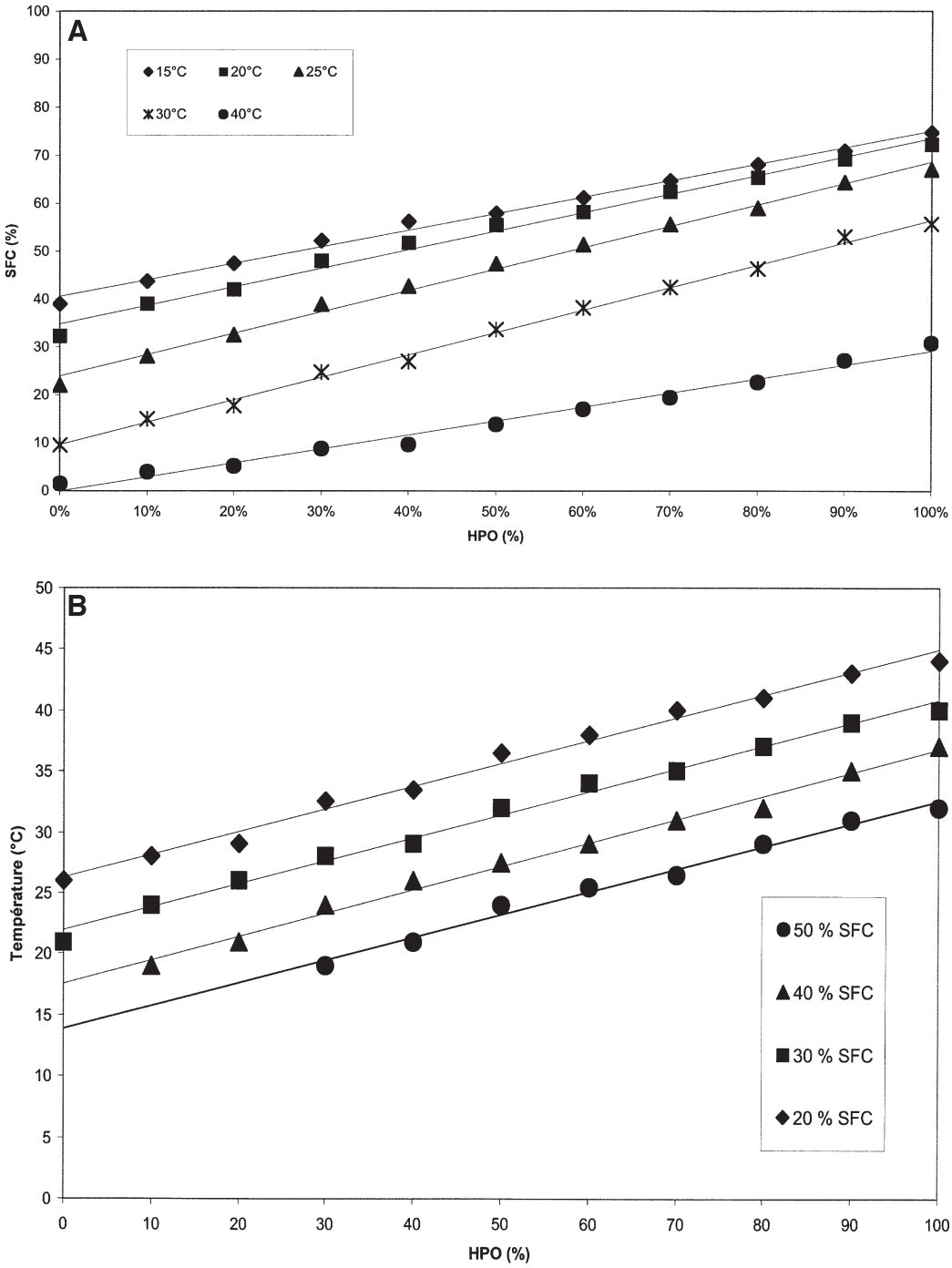

FIG. 2. (A) SFC vs. blend compositions for the HPO/PO mixture; (B) iso-solid diagram for the HPO/PO mixture. PO, palm oil; for other abbreviations see Figure 1.

binary fats without any further transformation of measured data.

(ii) Ternary systems. The aim of this work regarding SFC of ternary oils and fats blends was to predict SFC of a ternary blend from data obtained for binary blends. SFC data were plotted vs. blend compositions of several binary blends. Regression equations of the fitted curves were determined.

As just explained, linear relationships were observed for ideal blends, and second-order polynomial-type relationships were observed in the case of fats exhibiting incompatibility. Those equations were combined in a way to allow a "prediction" of the SFC for the corresponding ternary blends at a particular temperature.

For three perfectly compatible fats, such as for binary blends, SFC of the mixture corresponds to the weighted average of the SFC of the three original oils. Blends involving "incompatible"

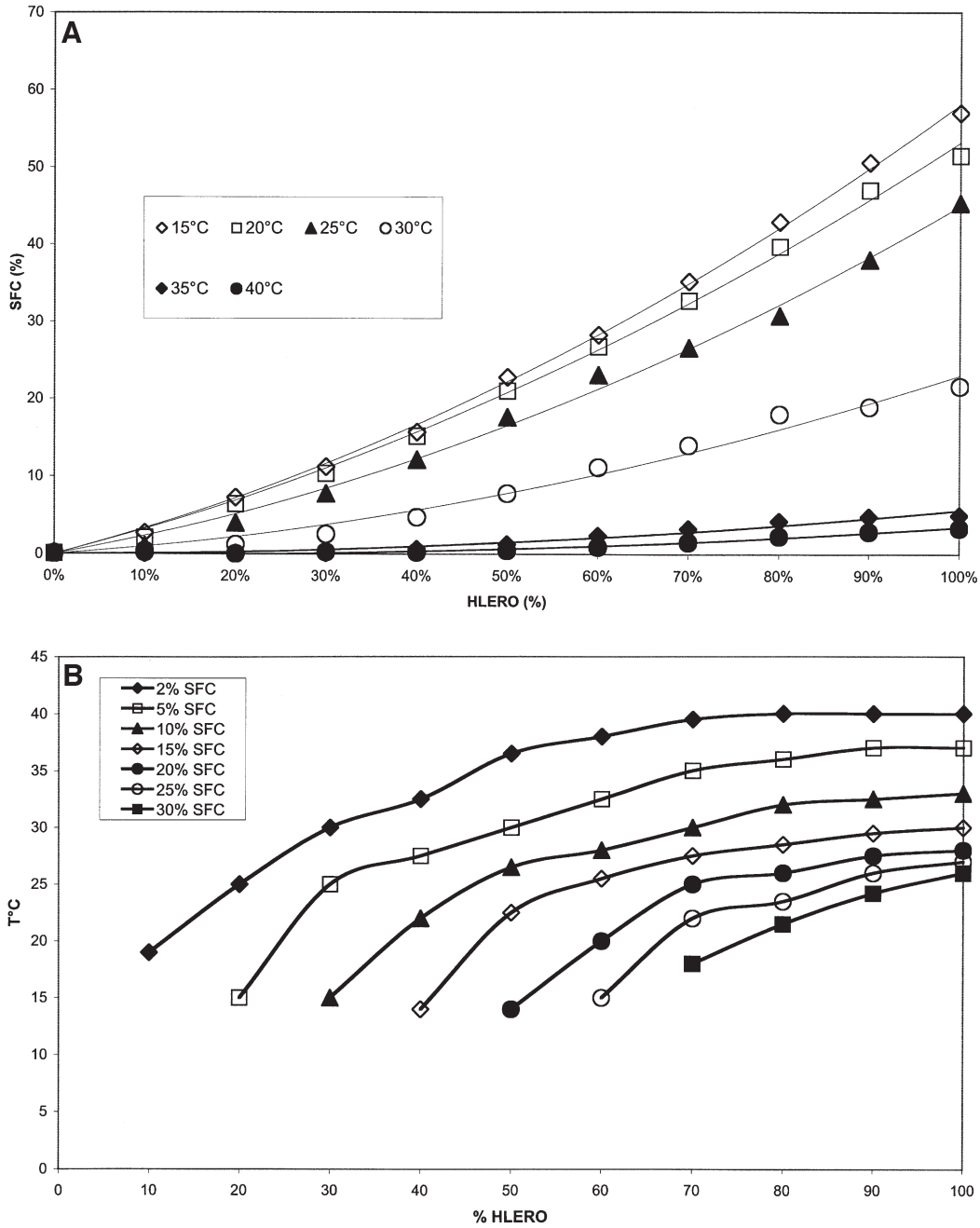

FIG. 3. (A) SFC vs. blend compositions for the HLERO/LERO mixture; (B) iso-solid diagram for the HLERO/LERO mixture. LERO, low-erucic rapeseed oil; for other abbreviations see Figure 1.

material do not follow this ideal behavior, which is the case for most of the ternary fat blends.

A method is proposed here to calculate easily the SFC of a ternary mixture using data obtained for binary blends, as exemplified herein, with the case of HPO/HLERO/LERO blends. This model system involves, on the one hand, a pair of fats that are compatible when mixed together, i.e., HPO/HLERO, and on the other hand two pairs of incompatible fats with monotectic interaction, i.e., HPO/LERO and HLERO/LERO. Based on the hypothesis that the component responsible for the nonideal behavior of the HPO/LERO/HLERO system should be LERO (HPO when mixed with HLERO has an ideal behavior (see first part of the Results and Discussion section on binary systems), equations obtained for binary blends involving the LERO component were used and combined.

If we assume that (i) the SFC of the HPO/HLERO blends corresponds to the weighted average of both components, and

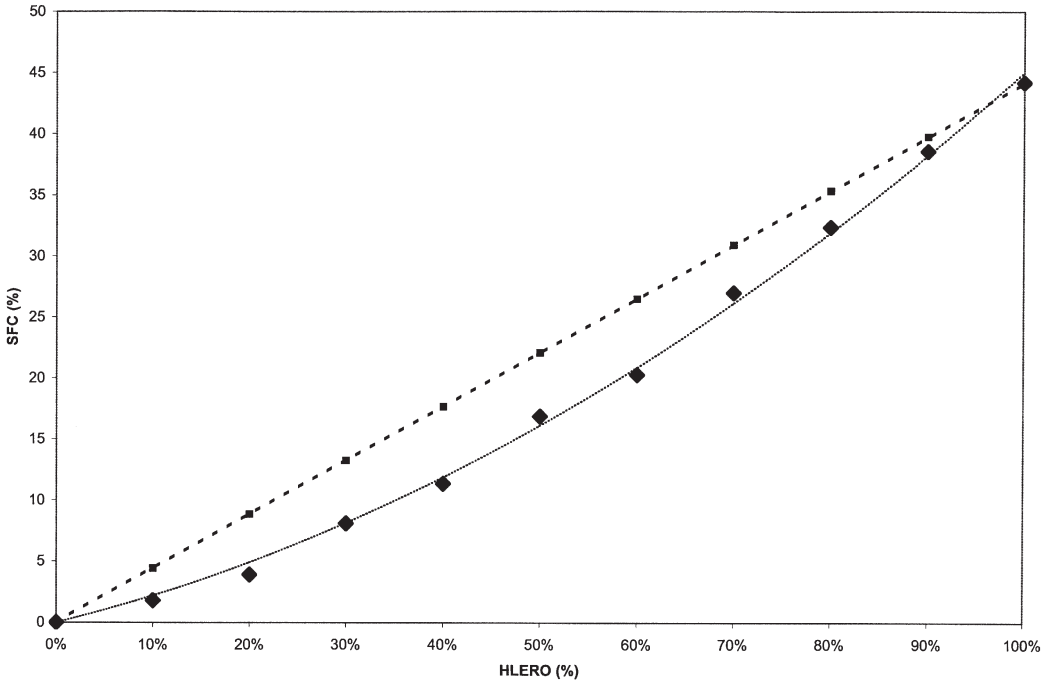

FIG. 4. Comparison of the weighted average SFC values (straight line) and the experimental SFC data for the HLERO/LERO mixture. For abbreviations see Figures 1 and 3.

(ii) the effect of LERO on the SFC of the binary HPO/LERO blend is represented by Equation 2,

$$SFC_t\ (HPO/LERO) = x\ [HPO]^2 + y\ [HPO] \quad [2]$$

then the effect of LERO on the SFC of the binary HLERO/LERO blend is represented by Equation 3,

$$SFC_{t\ (HLERO/LERO)} = w\ [HLERO]^2 + z\ [HLERO] \quad [3]$$

Equation 4, used for the determination of the SFC of the ternary blend (TB), results from the addition of Equations 2 and 3.

$$SFC_t\ (TB) = x\ [HPO]^2 + y\ [HPO] + w\ [HLERO]^2 + z\ [HLERO] \quad [4]$$

where $x + y$ = SFC of HPO and $w + z$ = SFC of HLERO. Actual values of the coefficients *x, y, w*, and *z* at 15°C are shown in Table 1 (six replicates).

Calculated data, obtained when using the proposed method, were compared with experimental data obtained following after the same crystallization and tempering procedure as for binary blends from which equations are derived. A comparison was also performed with theoretical weighted average values obtained from linear interpolation as in the case of ideal interactions. Table 2 illustrates both comparisons for a temperature of 15°C (six replicates).

Experimental values are generally very close to the SFC calculated according to the proposed method. However, for some restricted cases, the "ideal" weighted average SFC is more accurate than the values obtained according to the proposed method. In these cases, the calculations give results that are lower than the observed SFC values, and LERO is always present in the blends at a maximum concentration of 25%. This can be explained because the model is based on the fact that LERO, the liquid oil, is responsible for the monotectic behavior of the HLERO/LERO and HPO/LERO blends. A double calculation could be applied: (i) the proposed method for ternary compositions involving at least 25% of liquid oil and (ii) the weighted average one for estimating SFC of compositions close to the binary HPO/HLERO line.

Figure 6 illustrates the lines of iso-temperature for a SFC of 20% according to the three methodologies: calculated for an ideal blend (Fig. 6A), calculated according to the model proposed in this study (Fig. 6B), and experimental data (Fig. 6C).

Two full melting profiles of two compositions of the HPO/HLERO/LERO system are presented in Figure 7. In

TABLE 1
Actual Values of coefficients *x, y, w,* and *z* at 15°C and *x, y, m,* and *n* at 25°C in Equations 4 and 5

Coefficient	Temperature (°C)	Value
x	15	9.12 ± 0.70
y	15	63.6 ± 0.50
w	15	32.6 ± 1.50
z	15	24.5 ± 2.00
m	25	19.73 ± 1.64
n	25	2.11 ± 0.32
x	25	12.73 ± 1.32
y	25	55.07 ± 2.03

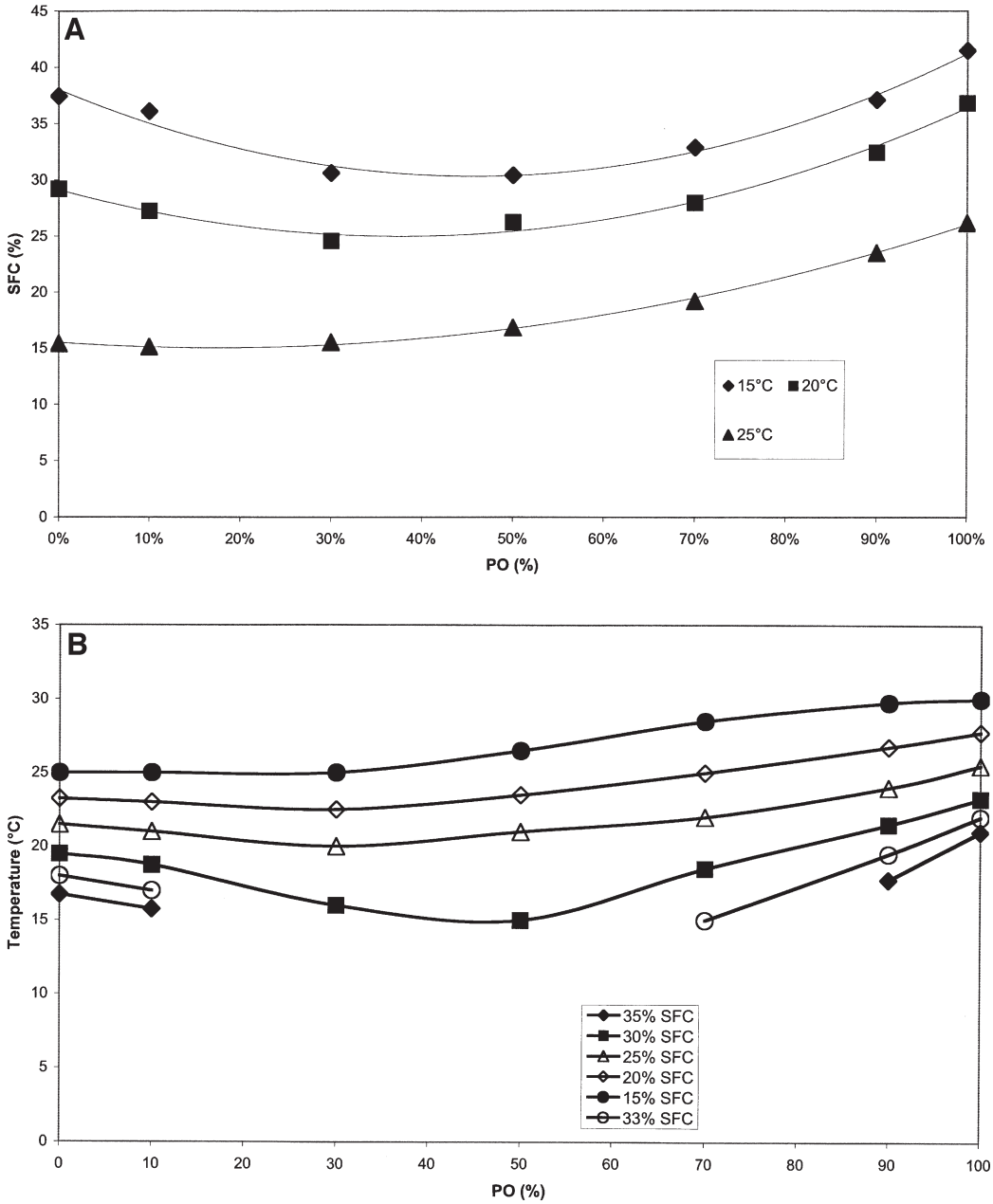

FIG. 5. SFC vs. blend compositions for the PO/AMF mixture; (B) iso-solid diagram for the PO/AMF mixture. AMF, anhydrous milk fat; for other abbreviations see Figures 1 and 2.

those figures, SFC is plotted against temperature for the three methodologies. Figure 7A depicts a blend of 50% HLERO, 5% HPO, and 45% LERO. The profile drawn according to the proposed model closely resembles the experimental profile. Figure 7B concerns a specific blend made of equal parts of HLERO, HPO, and LERO. In this case, a greater difference is observed at low temperature (high SFC).

The proposed method was then applied to another HPO/PO/LERO system. Like the first model, this system involves a pair of compatible fats, HPO/PO, and two pairs of incompatible fats with monotectic interaction, PO/LERO and HPO/LERO:

$$SFC_t\,(TB) = x\,[HPO]^2 + y\,[HPO] + m\,[PO]^2 + n\,[PO] \qquad [5]$$

The actual values of coefficients x, y, m, and n at 25°C are shown Table 1 (six replicates).

Comparison of calculated data obtained when using the proposed method was performed as just explained for the HPO/LERO/HLERO system. Table 3 illustrates both comparisons for a temperature of 25°C. The proposed method leads to the accurate prediction of results.

Relationship between texture and SFC. (i) Binary systems. The logarithms of hardness (expressed as maximum penetra-

TABLE 2
SFC Values (%) Obtained for Several Blends of HPO/HLERO/LERO at 15°C

Composition HLERO/HPO/LERO (%/%/%)	SFC (%) of an "ideal blend"[a]	SFC (%) calculated according to the proposed method[b]	SFC (%) Experimental data[c]	Differences between ideal SFC and experimental mean values	Differences between SFC calculated according to the proposed method and experimental mean values
54:5:41	34.4 ± 0.12	25.9 ± 0.53	26.1 ± 0.20	−8.3	0.2
50:5:45	32.2 ± 0.16	23.6 ± 0.51	24.7 ± 0.56	−7.5	1.1
58:1:41	33.8 ± 0.24	25.8 ± 0.54	25.2 ± 0.15	−8.6	−0.6
60:0:40	34.2 ± 0.21	26.4 ± 0.54	26.1 ± 0.21	−8.1	−0.3
0:40:60	29.2 ± 0.42	26.9 ± 0.07	26.6 ± 0.30	−2.6	−0.3
53.5:5:41.5	34.1 ± 0.12	25.6 ± 0.52	26.1 ± 0.22	−8.0	0.5
33.3:33.3:33.3	43.3 ± 0.42	34.0 ± 0.41	37.5 ± 0.11	−5.8	3.5
25:50:25	50.8 ± 0.46	42.2 ± 0.34	48.0 ± 0.45	−2.8	5.8
50:25:25	46.8 ± 0.23	36.9 ± 0.51	41.5 ± 0.58	−5.3	4.6
25:25:50	32.5 ± 0.22	24.6 ± 0.34	27.0 ± 0.50	−5.5	2.4
20:20:60	26.0 ± 0.21	19.3 ± 0.28	21.9 ± 0.52	−4.1	2.6
20:60:20	55.2 ± 0.32	47.6 ± 0.28	53.6 ± 0.13	−1.6	6.0
60:20:20	48.8 ± 0.26	39.5 ± 0.54	44.8 ± 0.20	−4.0	5.3

[a]Theoretical values obtained from linear interpolation as in the case of ideal interactions.
[b]SFC calculated according to the proposed method.
[c]Experimental data after the same crystallization and tempering procedure. HLERO, partially hydrogenated low-erucic rapeseed oil; HPO, partially hydrogenated palm oil; LERO, low-erucic rapeseed oil; SFC, solid fat content.

TABLE 3
SFC values (%) Obtained for Several Blends of HPO/PO/LERO at 25°C

Composition HPO/PO/LERO (%/%/%)	SFC (%) of an "ideal blend"[a]	SFC (%) calculated according to the proposed method[b]	SFC (%) Experimental data[c]	Differences between ideal SFC and experimental mean values	Differences between SFC calculated according to our method and experimental mean values
40:20:40	31.0 ± 0.21	25.3 ± 0.52	26.1 ± 0.78	−5.0	0.8
20:40:40	22.4 ± 0.13	15.5 ± 0.33	16.9 ± 0.45	−5.4	1.4
10:30:60	13.5 ± 0.12	8.0 ± 0.17	7.7 ± 0.24	−5.8	−0.3
30:10:60	22.1 ± 0.16	18.1 ± 0.42	15.0 ± 0.94	−7.2	−3.1

[a]Theoretical values obtained from linear interpolation as in the case of ideal interactions.
[b]SFC calculated according to the proposed method.
[c]Experimental data after the same crystallization and tempering procedure. PO, palm oil; for other abbreviations see Table 2.

tion force) of selected blends have been plotted against the logarithm of SFC, since our group has previously shown (7) that a linear relationship could be determined between those parameters. The slopes of these relationships are characteristic of the type of binary blends and are related to the microstructure of the samples (7).

(ii) Ternary systems. Because the linear relationships between hardness and SFC for HPO diluted in LERO and HLERO diluted in LERO had the same slope in binary blends, it was expected that the relationship between hardness and SFC of the ternary mixture should also be the same. The perfect overlapping of the three relationships is illustrated in Figure 8.

The representation of SFC as a function of composition is interesting, as it allows one to determine rapidly and easily the type of molecular interaction between two fats and also to determine equations that can be combined to easily calculate SFC of corresponding ternary blends crystallized in the same way. The subsequent combination of those results with the results obtained for the hardness of binary blends allows the prediction of the hardness of a corresponding ternary blend under the same conditions.

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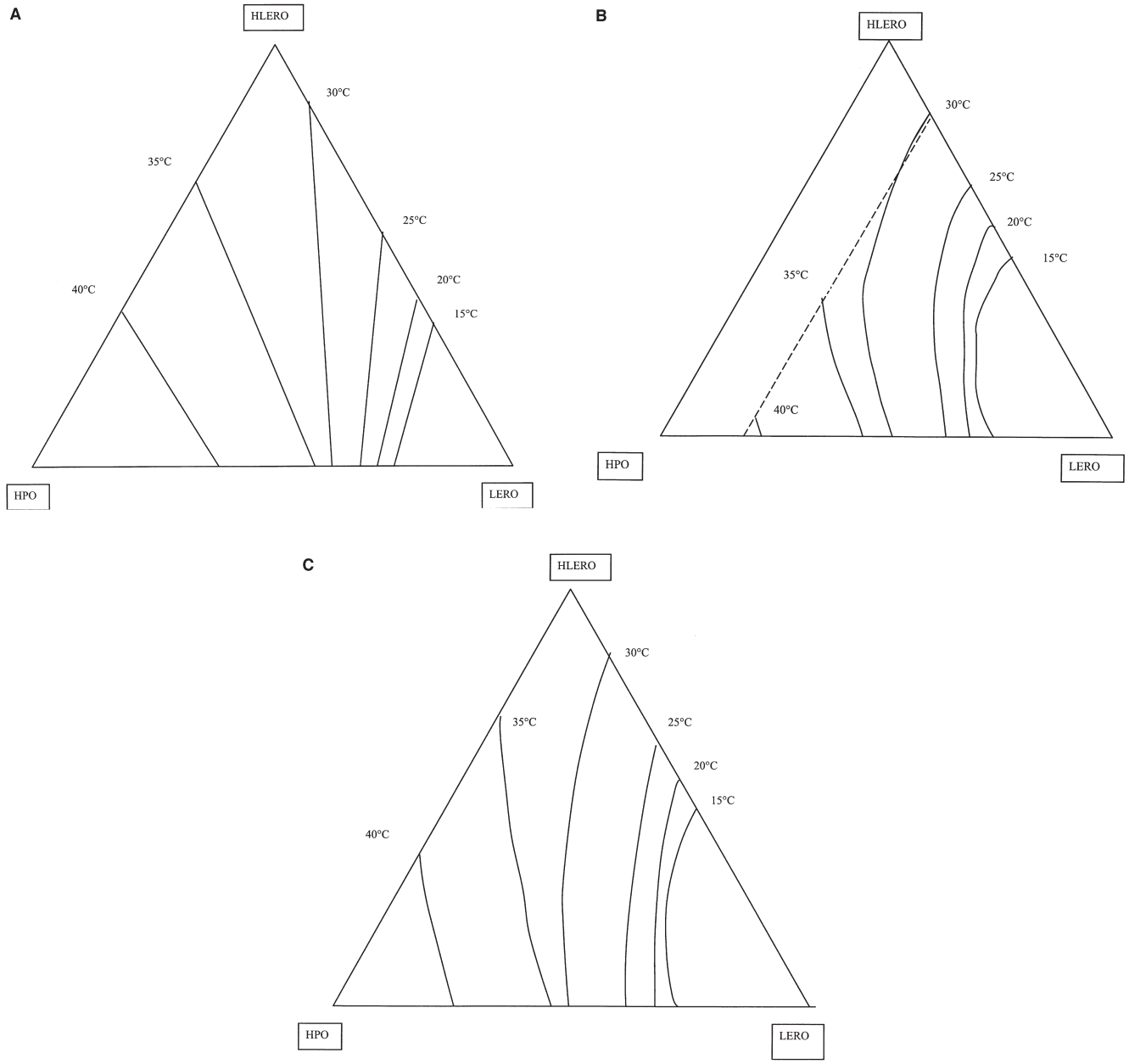

FIG. 6. Ternary diagrams illustrating iso-temperature lines at which the SFC of the HPO/HLERO/LERO mixture is 20%. (A) Ideal system; (B) data calculated according to the proposed method; (C) experimental data. For abbreviations see Figures 1 and 3.

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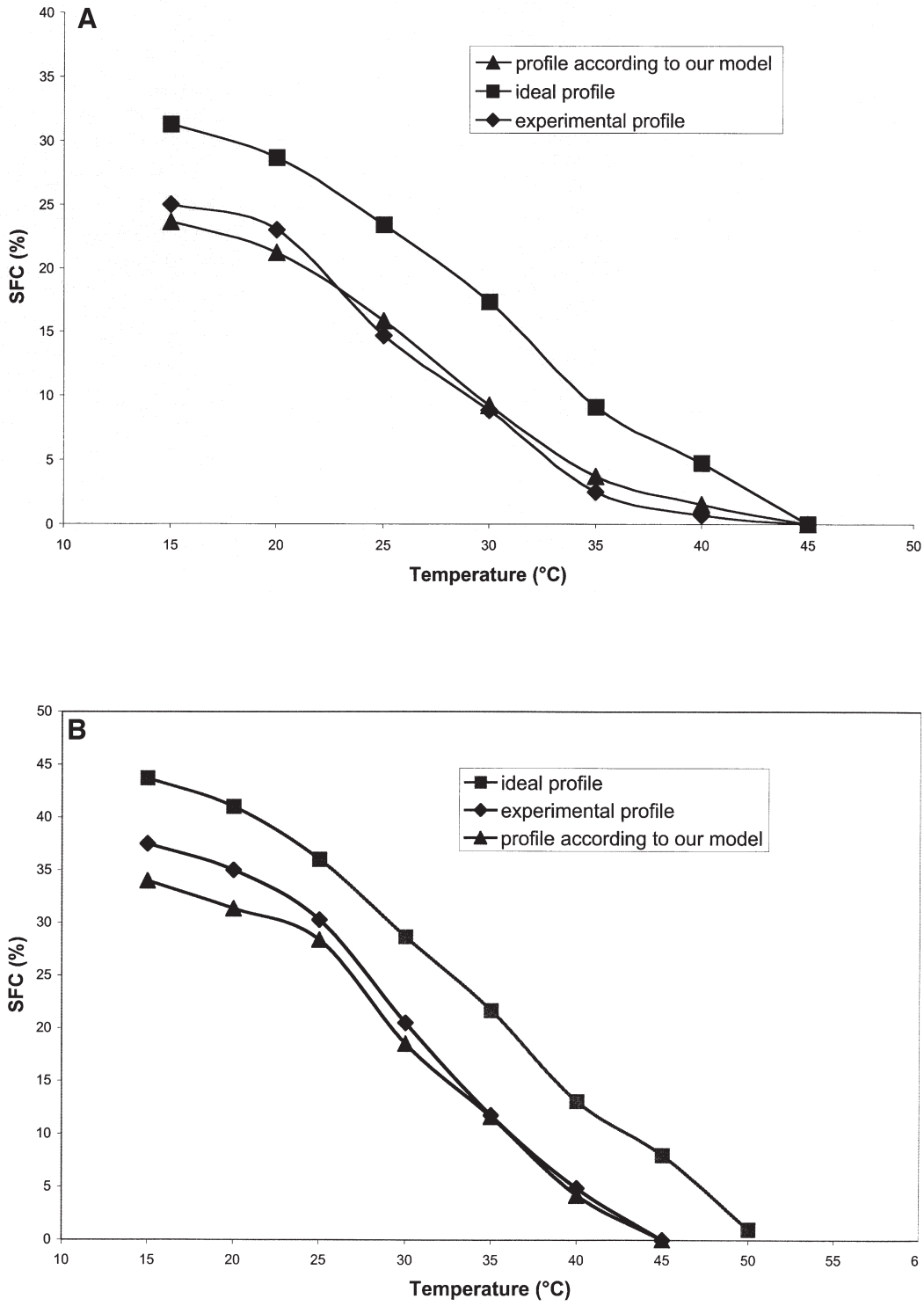

FIG. 7. SFC melting profiles according to the three methodologies: experimental, calculated for an ideal blend, and calculated according to the method proposed in this study. (A) For a specific blend made of 50% HLERO, 5% HPO, and 45% LERO; (B) for a specific blend made of equal parts of HLERO, HPO, and LERO. For abbreviations see Figures 1 and 3.

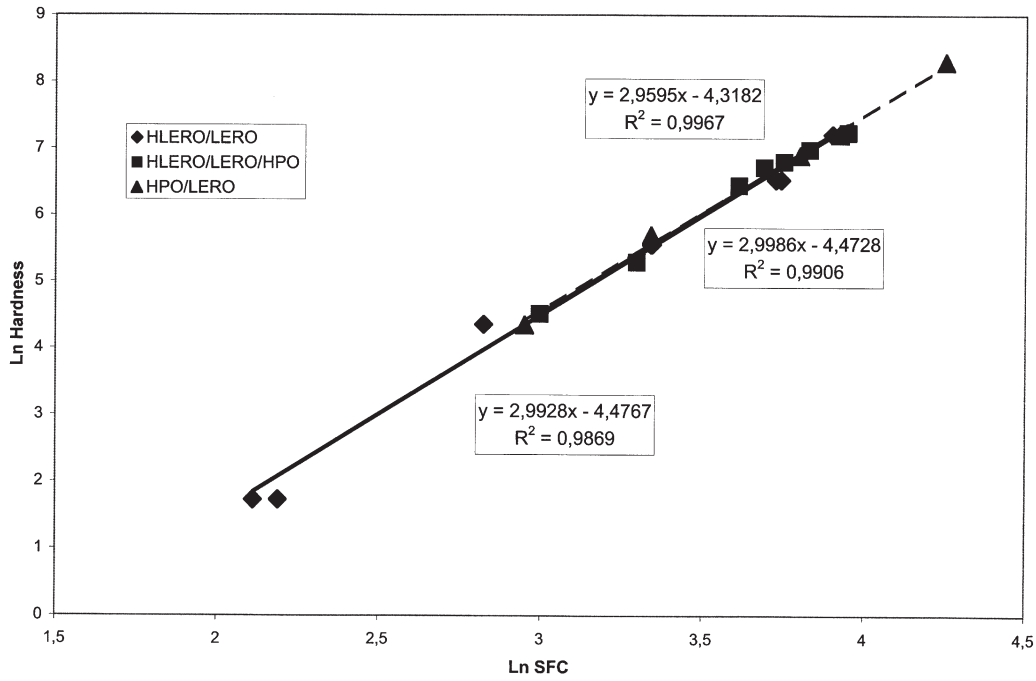

FIG. 8. SFC–texture linear relationships for the HLERO/LERO blend, for the HPO/LERO blend, and for the HPO/HLERO/LERO blend. For abbreviations see Figures 1 and 3.

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