Solubility of Hydrogenated Peanut Oil in Peanut Oil

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THE gravitational separation of peanut butter into an oil phase and a meal phase is an important problem in the manufacture and marketing of this product (3). The principal process (9) used for overcoming this difficulty involves the uniform incorporation of small amounts of hard peanut fat (hydrogenated peanut oil) (5, 7). Only enough hard fat need be dissolved in the product to insure the presence of sufficient crystals at room temperature to entrap the natural oil.

From dilatometric data on peanut butters it was concluded (8) by Singleton and Freeman that the effectiveness of the added hard fat was dependent upon the amount dissolved and its distribution throughout the oil in the product. No evidence of polymorphic transformations was noted. The only data available on the solubility of hydrogenated peanut oil in peanut oil are those of Hofgaard (4), which do not cover the range of concentrations pertinent to the present problem. Solubility measurements have therefore been made for a commercial hard peanut fat in a refined and bleached peanut oil with the purpose of providing basic information applicable to processes for the prevention of oil separation in peanut butter.

Materials. The hard peanut fat used was a commercial, almost completely hydrogenated peanut oil (5), having a Wijs iodine value of 5. The peanut oil was a refined and bleached oil, having the following characteristics: iodine value (Wijs), 93.2; thiocyanogen value, 72.5; total saturated fatty acid content, 17.3%; oleic acid, 57.4%; and linoleic acid, 25.3%.

Determination of solubilities. The solubilities were determined by the static method (6). For each composition weighed amounts of the hard fat and peanut oil were sealed in a glass tube. A glass bead was included to insure efficient stirring as the sample tubes were turned end-over-end in a constant temperature bath. Two temperatures were observed, one at which the last crystals of the hard fat just disappeared in the peanut oil, and the other at which a few crystals remained undissolved after prolonged agitation. The solubility temperature was taken as the mean of these two temperatures corrected for both thermometer calibration and emergent stem.

Results and Discussion

The solubility data, summarized in Table I, are in excellent agreement with those of Hofgaard (4), which however cover only concentrations of 10% of hard fat and above. The hard fat is completely melted at 67.8°C., and a temperature of about 57°C. is required to dissolve 9% of it in the peanut oil. Below this concentration the solubility temperature drops off rapidly with decreasing hard fat content. The solubility temperatures were unchanged by melting the mixtures and allowing them to cool gradually to room temperature. If cooled rapidly by immersion in an ice bath however, they exhibited lower solubility temperatures, which could not be accurately determined because an unstable crystal modification is involved.

TABLE I

Solubility of Hydrogenated Peanut Oil in Refined Peanut Oil and Nature of Tempered Mixtures

Hard fat[a]	Solubility temperature	Physical nature of mixture at room temperature after shock-chilling of melt and tempering at 33.6°C.
%	°C.	
0.63	42.8	Translucent liquid
1.20	45.6	Translucent liquid
2.03	49.5	Viscous, translucent fluid
5.28	52.9	Translucent, either non-fluid or, with agitation, fluid
9.09	55.5	Opaque solid
17.76	58.4	Opaque solid
25.69	60.8	Opaque solid
50.71	64.5	Opaque solid
75.37	66.2	Opaque solid
100.00	67.8	Opaque solid

[a] An almost completely hydrogenated peanut oil used widely in the manufacture of peanut butter (5).

It is well known that solid fats may exist in several crystal modifications (2a) depending on the temperature and chilling rate. On the basis of previous observations on lard and shortenings (1b) it is not surprising that rapid cooling of the molten mixtures of hard peanut fat and peanut oil resulted in the separation of a low-melting, finely divided solid. While this condition is apparently desirable in certain respects such as palatability (1d) and greater liquid-retentive ability (1a), it nevertheless has the drawback of a low melting or solubility temperature, about 37°C. when the hard fat concentration is 5%, and lower at lower concentrations. This condition could be responsible for some separation of oil, at least temporarily, until the transformation to the higher-melting modification would take place. This behavior is illustrated by the data presented in Table II for mixtures containing 5.28% hard fat which were shock-chilled from a molten condition to 0°C. prior to immersion in a constant temperature bath at each temperature given. Shock-chilling to —40°C. gave the same results.

TABLE II

Phase Behavior on Tempering Mixture Containing 5.28% Hard Peanut Fat After Shock-Chilling from Molten Condition

Tempering temperature	Behavior
°C.	
50.6	Melts to clear liquid
48.0	Melts to clear liquid
44.6	Melts to clear liquid subsequently becoming turbid[a]
37.5	Melts to clear liquid subsequently becoming turbid[a]
36.0	Transforms to higher-melting form without visible melting
34.2	Transforms to higher-melting form without visible melting

[a] Turbidity caused by formation of crystals of the higher-melting form.

Transformation of low-melting shock-chilled mixture to high-melting modification. Based on the information contained in Table II, a temperature (33.6° C.) was chosen, which would permit the transformation of the finely divided, low-melting form to the high-melting form without any visible signs of melting even in the 2.03% mixture. Tempering the shock-

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chilled 2.03 or 5.28% mixtures at 33.6°C. for 30 minutes was sufficient to permit extensive transformation of the crystals to the high-melting form, as evidenced by the lack of any perceptible melting at 44.6°C. in the 5.28% mixture, whereas prior to this treatment the shock-chilled sample melted completely at this temperature. After tempering complete melting did not occur until a temperature of 52-53°C. was reached. The shock-chilled 2.03% mixture tempered in the same manner was capable of withstanding 38°C. without any oil separation.

As shown in Table I, the tempered mixtures range from translucent liquids to opaque rigid plastic substances, depending upon the hard fat content and the temperature. This is in harmony with the general behavior of such materials (2b). The 5.28% mixture however may resemble either a rigid, translucent, plastic fat, or a partially melted plastic fat. Agitation during or after tempering produces the latter condition, which however is unstable, requiring an undetermined period of time to reset. If the material is not worked, the former condition results. Evidently there is a range of concentrations in the neighborhood of 5% where this thixotropic behavior (1c) is possible. Those mixtures containing less than 2% hard fat were always semiplastic or viscous liquids, depending on the hard fat content, and never set up as rigid plastic fats. In none of the tempered mixtures above 2% was separation of clear oil observed at room temperature (25-30°C.) even when the mixture was centrifuged for 20 minutes at 400 times gravity.

This information indicates that it should be possible to stabilize such a mixture by tempering in this manner, possibly due to the predominance of the higher-melting modification in the tempered product. The product would be expected to retain the crystal fineness (2c) essential for improved palatability and yet would withstand ordinary storage without separation of the oil.

Slowly cooled mixtures. All the mixtures given in Table I when melted and gradually cooled show grainy characteristics in the solidified hard fat. This was especially apparent in those hard fat concentrations of 10% or less where the granules of fat crystals tended to settle, especially with centrifugation, to give a clear supernatant oil. At concentrations above 10% the quantity of hard fat separating is large enough to mask any liquid oil, even under centrifugation. Agitation during the cooling period caused no perceptible difference in this behavior.

Conclusions

Data obtained on the solubility of hydrogenated peanut oil in refined peanut oil and the behavior of the mixtures on cooling indicate that freedom from oil separation on storage is largely determined by the nature as well as the amount of solid crystals present in the oil. The results suggest that the best procedure for prevention of oil separation would involve shock-chilling the molten mixture to produce the finely divided metastable crystalline modification followed by tempering at such a temperature as to permit transformation of the crystals into the more desirable higher-melting form without changing the finely divided state necessary for improved palatability.

The data imply that under controlled conditions any amount of the high-melting modification of the hard fat incorporated in peanut oil above the solubility temperature in excess of 2% should produce a mixture free from oil separation under average storage conditions. The choice of the actual concentration of the hard fat, above the minimum amount, would depend upon the degree of plasticity desired. Ambient temperature to which the mixture is likely to be subjected will influence to a considerable extent the selection of the hard fat content. The information obtained is of fundamental importance in connection with the problem of oil separation in peanut butter.

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The Eicosenoic Acid of Cameline Seed Oil

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FROM a previous investigation (1) it was concluded that the seed oil of *Camelina sativa,* Crantz, contains little if any erucic acid. This result contradicts statements found in a number of textbooks on oils which have been traced back to de Negri and Fabris (2) and older literature. It is also exceptional with regard to the observation pointed out by Hilditch (3) that all *Cruciferae* seed fats previously investigated, with the exception of *Hesperis matronalis,* contain 40-50% erucic acid.

Instead cameline seed oil was found to contain a considerable proportion of an eicosenoic acid in addition to linolenic, linoleic, oleic, saturated, and a monounsaturated hydroxy acid, the monounsaturated acids totalling 42.8%, the polyunsaturated acids 48.3% with more than twice as much linolenic as linoleic acid, and the saturated acids 8.9%. In addition to eicosenoic acid there was evidence of the presence of some higher monounsaturated acids not giving however the characteristic derivatives of erucic acid. The presence of eicosenoic acid became apparent when the dioxy acid (acid value 160.1), formed upon oxidation of cameline fatty acids, was compared to that obtained upon similar treatment from rape seed oil and was verified by the isolation upon elaidination of an acid melting at 43.5°C. hav-