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REFERENCES

1. Dornseifer, T. P., and J. J. Powers, Food Technol. *17*, 118 (1963).
2. Dornseifer, T. P., and J. J. Powers, Food Technol. *19*, 195 (1965).
3. Endus, J. F., V. R. Bhalerao and F. A. Kummerow, JAOCS *39*, 159 (1962).
4. Kumazawa, H., from abstract in JAOCS *40*, 472 (J. Oil Chem. Soc. Japan *10*, 531) (1963).
5. Kummerow, F. A., "Proceedings of the Flavor Chemistry Symposium." Campbell Soup Company, Camden, N.J. (1961).
6. Sahasrabudhe, M. R., and V. R. Bhalerao, JAOCS *40*, 711 (1963).
7. Tor, B., et al., from abstract in JAOCS *40*, 472. (J. Oil Chem. Soc. Japan *10*(9), 536) (1963).
8. Wishner, L. A., and M. Kenney, "Carbonyl Compounds Formed During Deep Frying," presented at Symposium on Thermal Oxidation and Polymerization, Fifty-fifth Annual Spring Meeting, American Oil Chemists Society, 1964.

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A Comparison of Nuclear Magnetic Resonance and Dilatometry for Estimating Solids Content of Fats and Shortenings

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Abstract

The percent solids values of fats and shortenings using nuclear magnetic resonance (NMR) and solid fat index (SFI) have been compared. The samples used were: blends of hard fat and safflower oil, safflower oil hydrogenated to varying degrees, and different types of shortenings.

This investigation demonstrated the empirical nature of the SFI technique and shows the nature of the deviations from the solids content determined by the NMR method. The magnitude of the deviation of SFI from the NMR solids content increased with the level of the solids. The SFI values and the NMR solids content were similar at the lower levels (SFI values of 10) but at the upper limit for the SFI method (SFI values of 50) the solids content by the NMR method can be 80% or more, a difference of 30 units.

Although the determination of solids content by NMR is reliable, the relationship between SFI values and NMR values for different types of samples is so variable that the calculation of the SFI value from percent solids by NMR, or percent solids from SFI values from prediction equations is not very reliable.

Since NMR measures the solids content more accurately than SFI and is applicable over the entire range of solids, 0 to 100%, it will be very useful in fat and oil research and control.

Introduction

THE OFFICIAL AOCS METHOD for SFI (1) or one of many modifications is used extensively to evaluate shortenings and blends of fats for their relative consistency and plastic properties. In its original form the solids content of a sample at a given temperature was estimated from the difference between the specific volume at a point on the curve at that temperature (for example B, in Figure 1) and the corresponding point on the extrapolated liquid curve, at the same temperature (for example A), divided by the difference between the specific volume at A on the extended liquid curve and C on the extended solids curve.

Because of the time required to establish both the liquid and solid portions of the curve, and the fact that the solids curve is relatively constant, it was decided by those concerned with these measurements to establish only the liquid curve and use the difference between the specific volume of the liquid curve and the specific volume at a point on the dilatometer curve as an index of the solid fat present at that temperature. The solid fat index (SFI) is a purely empirical value which has been very useful in research and for control of processes and quality of the finished product, although it is limited to evaluation at levels below 50 units.

The development of a broad line nuclear magnetic resonance (NMR) instrument offered a new approach to the determination of the solids in fats, blends and shortenings. It appeared to offer a means of measuring the solid fat content with greater accuracy and over the entire range from 0–100% solids. This technique was applied to a stabilized and unstabilized margarine oil by Chapman (3) and to soybean oil hydrogenated to varying degrees by Ferren (4). Both suggested using the technique for measuring the solids content of fats and shortenings but did not extend their investigations into this area.

A previous investigation by the authors (2) dealt with NMR measurements on fats containing less than 50% solids and comparison with SFI values for margarine oils which were below 30. This study showed that while the values were not equal, a prediction

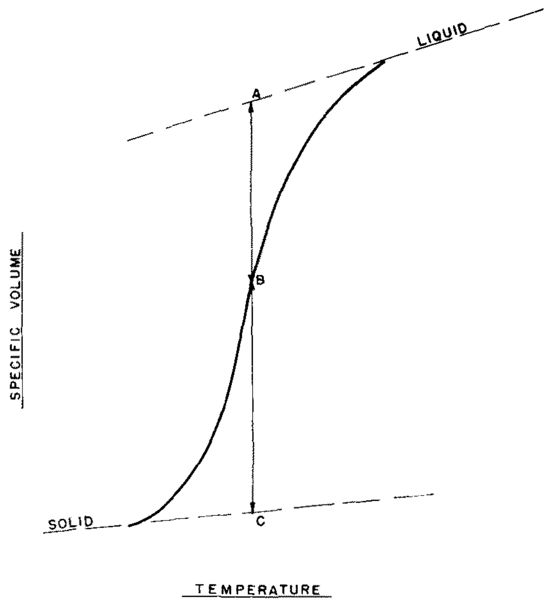

FIG. 1. Example of a dilatometer curve.

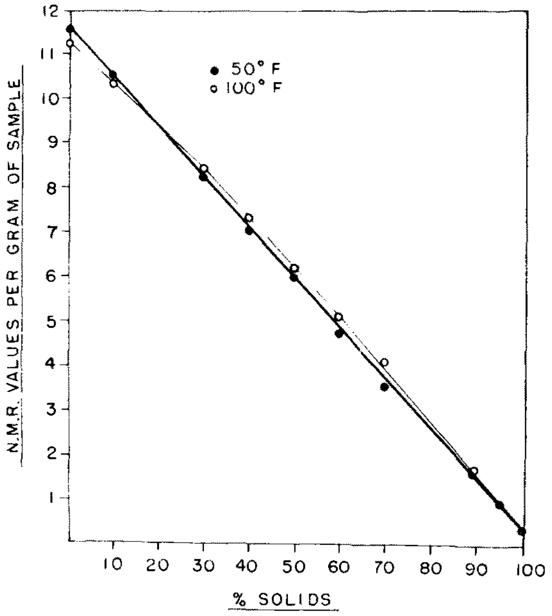

FIG. 2. Calibration curve for solids in fat and shortenings.

equation could be established for the relationship between SFI value and per cent solids by NMR. The deviation of the SFI from the per cent solids found by NMR has stimulated further inquiries into the relationship beyond those previously studied and into the region where SFI cannot be employed.

Experimental

The investigation being reported was undertaken to obtain more extensive information on the solids content of fats and shortenings by NMR over a wider range than could be covered by SFI, as well as, additional information on the relationship of solids content by NMR and SFI values in the region where SFI values can be obtained.

The SFI values were determined by the Official AOCS Method (1) and the NMR measurements were made following the procedure previously described (2).

The NMR spectrometer was calibrated using known blends of a hard fat (hydrogenated soybean oil with an iodine value of 3.5) with safflower oil. The calibration graph was prepared by plotting the signal obtained by NMR (millivolts per gram of sample due to the liquid portion) against the percent solids in the sample. Results are shown graphically in Figure 2 for data obtained at 50F and 100F, the temperature extremes employed in the SFI method.

The slightly higher instrument readings above 20% solids for 100F is probably due to a slight solubility of the hard fat in the oil at 100F. This difference would of course increase as the temperature is raised. In this investigation a calibration curve based on instrument reading on samples at 50F was used for determining the solids content of a sample from the NMR measurements because it represents a better relationship between solids and instrument measurement free from any solubility factors.

The first series of tests involved measurements on known blends of hard fat (I.V. 3.5) with safflower oil. The solids content by NMR and the SFI values were determined for each blend at 50, 70, 80, 92 and 100F. The per cent solids in the blend is marked on each curve (Fig. 3) showing the values for a given blend over the temperature range of 50F to 100F. These data indicate:

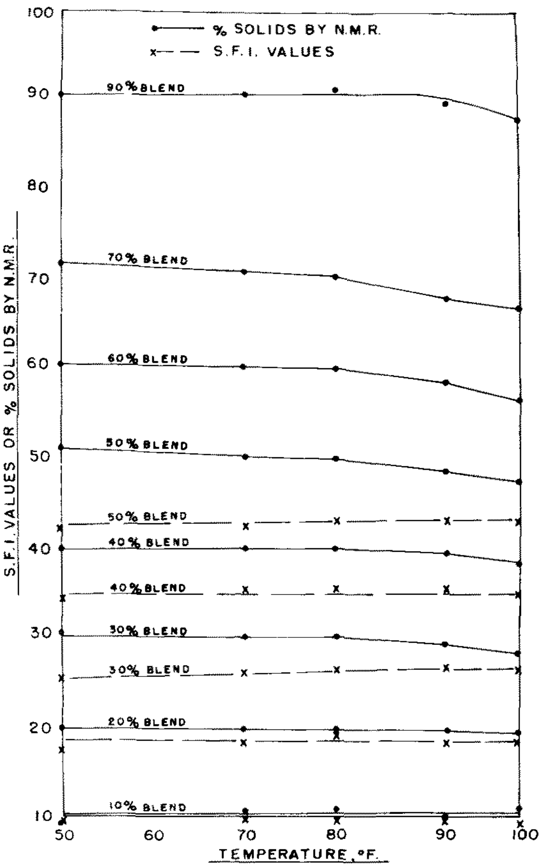

FIG. 3. Comparison of SFI values and percent solids by NMR at 50, 70, 80, 92 and 100F on blends of known composition.

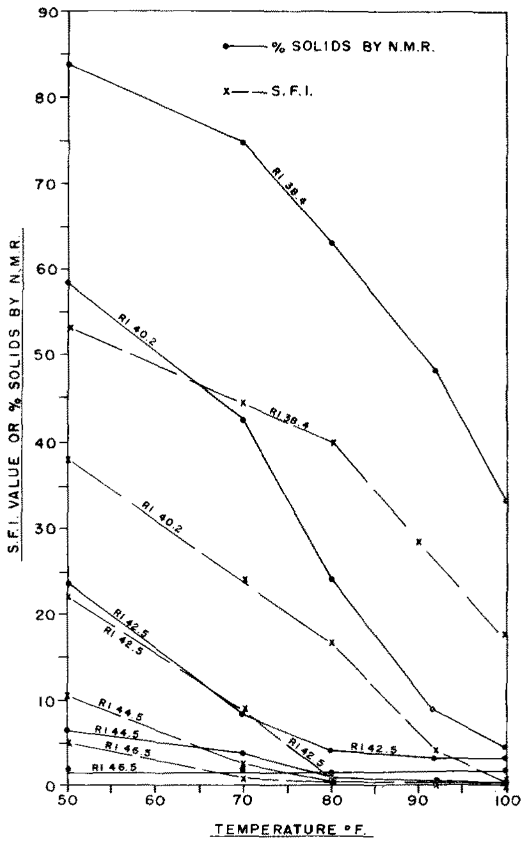

FIG. 4. Comparison of SFI values and percent solids by NMR at 50, 70, 80, 92 and 100F on hydrogenated safflower oil.

1. That the per cent solids by the NMR method were in good agreement with the known solids content, (per cent hard fat blended with the safflower oil) at all levels.
2. That the SFI values were the same as the per cent solids in the blend at the 10% level but were lower at the higher levels. The difference between the SFI value and the per cent hard fat present became greater as the hard fat content in the blend increased up to 50, the upper limit for the SFI method. A deviation of this type in the SFI values is not surprising but it does show that the SFI fails to indicate the actual magnitude of solids in glyceride blends as the solids increase.

In the next series of tests, a comparison was made of per cent solids content by NMR and SFI values on safflower oil hardened to various degrees, (hydrogenated to refractive indices of 46.5, 44.5, 42.5, 40.2 and 38.4 at 60C on the Butyro scale), at 50, 70, 80, 92 and 100F. The data are shown graphically in Figure 4. These tests show more strikingly the approximate nature of the SFI values which differ from the solids content by varying degrees depending upon the sample and the amount of solids present. While the SFI values are recognized as only an index of the solids content, we did not expect them to be as variable and as poor an index with increasing solids content as the data indicated. Some workers have looked upon the SFI as being comparable to the solids content and have pressed for extending the test to products with SFI values above 50. Why this is not practical is easily understood when such samples may actually contain 85% solids. It is surprising the SFI method has functioned as well as it has at these higher levels.

In the third series of tests, shortenings of various types were analyzed for solids content by NMR and SFI at 50, 70, 80, 92 and 100F. The data are given in Table I. The relationship between per cent solids by NMR and SFI is shown graphically in Figure 5 for 5 shortenings and 4 of the hydrogenated safflower oil samples.

In the graphical presentation one can observe the general relationship between NMR and SFI and at the same time the marked difference in the characteristic of the sample. It will be observed that in some cases the one value may change two-fold while the other changes only one-fold. This situation makes reliable predictions in specific cases impossible without previous knowledge of the system.

TABLE I

Shortening type	Method	SFI values and per cent solids by NMR at 50F	70F	80F	92F	100F
Vegetable	NMR	37.0	24.7	17.6	12.4	11.4
	SFI	27.2	20.1	19.3	15.2	7.0
Vegetable	NMR	34.8	16.1	12.5	11.1	5.1
	SFI	25.5	19.4	20.8	14.1	10.7
Vegetable	NMR	45.3	30.5	14.2	5.9	3.5
	SFI	36.8	21.0	14.1	3.2	0.3
Animal	NMR	34.5	25.8	18.9	14.6	11.3
	SFI	28.3	21.0	19.5	16.3	12.1
Animal	NMR	43.1	27.6	19.1	14.2	12.2
	SFI	31.4	19.2	17.5	11.9	6.0
Animal	NMR	35.5	17.9	14.3	9.9	5.8
	SFI	27.5	18.5	16.9	16.1	9.0
Animal	NMR	55.8	35.6	22.1	15.1	11.3
	SFI	37.6	28.0	22.5	16.0	14.3
Animal	NMR	31.9	21.0	13.8		
	SFI	28.8	23.1	16.3	9.3	5.0
Veg.-animal	NMR	29.6	27.9	25.6	21.4	17.6
	SFI	24.4	19.2	16.7	11.6	5.1
Animal-veg.	NMR	35.1	20.0	14.0	12.6	8.8
	SFI	24.5	16.9	12.9	12.3	8.5
Animal-veg.	NMR	35.5	21.6	15.1	11.6	9.7
	SFI	25.7	19.6	18.5	14.3	10.6
Animal	NMR	32.7	23.2	15.9	9.7	5.7
	SFI	28.6	23.5	16.5	12.3	9.7
Animal	NMR	22.2	16.3	15.2	10.7	7.2
	SFI	21.2	16.7	13.3	9.7	5.3
Animal	NMR	25.2	21.4	15.9	11.1	8.5
	SFI	20.9	14.7	12.6	9.2	5.0
Vegetable	NMR	51.1	40.9	24.0	15.0	7.8
	SFI	40.3	27.0	21.5	8.7	1.0
Hydrogenated safflower oil refractive index						
38.4	NMR	83.5	74.5	63.0	48.2	33.0
	SFI	53.0	44.7	40.2	28.2	17.8
40.2	NMR	58.5	42.5	24.0	8.7	4.7
	SFI	39.1	23.9	16.7	4.1	0.7
42.5	NMR	23.5	8.2	4.2	3.2	3.0
	SFI	22.2	8.4	1.6	0.0	0.0
44.5	NMR	6.5	3.8	1.3	0.0	1.0
	SFI	10.8	2.7	0.4	0.2	0.1

Discussion

The prediction equations calculated from the data in Table I are given in Table II. However, the dependence of SFI values on specific volume (which may vary with the blend of fats or triglycerides being measured) makes estimation of SFI values from per cent solids determined by NMR or the opposite only rough approximations although the precision of both methods is satisfactory (2). Estimates of the limits within which such values might lie are as follows. SFI values calculated from per cent solids determined by NMR may be expected to be within approximately ±4 at values of 10, and the uncertainty increases to approximately ±10 at the upper limit (50 SFI value). Calculation of the per cent solids determined by NMR from SFI values may be expected to be within ±6% solids at the 10% level and the uncertainty increased to ±10% at the 50% solids level (SFI value of approximately 34) and more at higher levels.

The uncertainty of the calculated values, either per cent solids from SFI values or SFI values from per cent solids, make such calculations of little value in predicting accurately one value from the other. In view of this situation and the fact that SFI is a less reliable index of the solids content, it appears that the per cent solids by the NMR method will be

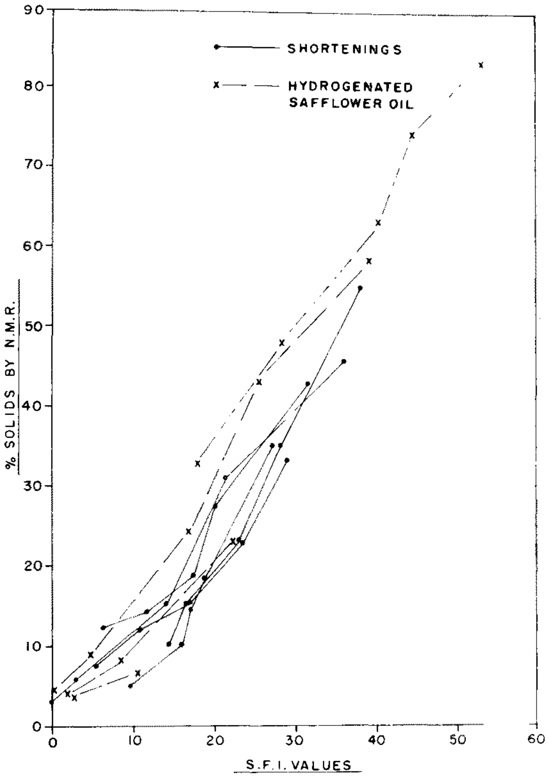

FIG. 5. Relationship of percent solids by NMR to SFI values from shortenings and hydrogenated safflower oil.

TABLE II

Prediction Equations for SFI Values and Per Cent Solids by NMR

Prediction equation
For all values
SFI value = 3.8550 + 0.6216 (% solids by NMR)
Per cent solids by NMR = 2.6542 + 1.4001 (SFI value)
For values less than 10
SFI value = 1.2454 + 0.6198 (% solids by NMR)
Per cent solids by NMR = 4.2963 + 0.5145 (SFI value)
For values 10 and higher
SFI value = 7.826 + 0.5206 (% solids by NMR)
Per cent solids by NMR = −10.1137 + 1.6990 (SFI value)

more valuable than SFI in the study of the solids content of fats and shortenings..

In addition to the advantages of NMR measurements given here, it is possible to condition separate samples at selected temperatures at the same time and then measure all at the end of the conditioning period instead of conditioning and reading at successively higher temperatures as in the SFI method. This appreciably reduces the elapsed time for a test. It also appears that it will be possible to extend the measurements to lower temperatures to gain information on products like winterized oils. The application of this technique to investigations of hydrogenation, interesterfication, processing, final formulations and similar phases of fat and oil research may be expected to extend the basic knowledge in this area.

REFERENCES

1. Official and Tentative Methods of the AOCS Solid Fat Index Method Cd 10-57.
2. Taylor, J. R., W. D. Pohle and R. L. Gregory, JAOCS *41*, 177–180 (1964).
3. Chapman, D., R. E. Richards and R. W. Yorke, JAOCS *37*, 243 (1960).
4. Ferren, W. P., and R. E. Morse, Food Tech. *17*, 1066–1068 (1963).

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Salts of Alkyl Esters of α-Sulfopalmitic and α-Sulfostearic Acids[1]

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Abstract

Lithium, ammonium, sodium, potassium, magnesium, and calcium salts of methyl, ethyl, propyl, isopropyl, butyl, isobutyl and secondary butyl esters of α-sulfopalmitic and α-sulfostearic acids were prepared for a study of structure-property relations. The esters are easily biodegradable, have good foaming, detergent and lime soap dispersing properties and resist acid and alkaline hydrolysis. The α-sulfopalmitates are more soluble.

Differences in the cation and the alcohol influence melting point, aqueous solubility, solubility in organic solvents, surface and interfacial tension, critical micelle concentration and emulsifying properties.

Introduction

ESTERS OF α-SULFO ACIDS are of current interest as biodegradable detergents, lime soap dispersing agents and wetting agents (1,3,8–10,12,13). Variations in the structure $RCH(SO_3M)CO_2R'$ or $[RCH(CO_2R')SO_3]_2M$ are easily possible by choice of the particular fatty acid, aliphatic alcohol, or salt. The present investigation is a systematic survey of 84 esters to better relate structure and properties.

Commercial α-sulfopalmitic acid and α-sulfostearic acid (Armosul-16 and Armosul-18, Armour Industrial Chemical Company) estimated to contain about 3–8% of impurities in the form of unsulfonated fatty acid and the homologous 16 or 18 C α-sulfo acid, were esterified with methyl, ethyl, propyl, isoproypl, butyl, isobutyl, and secondary butyl alcohols and neutralized to form lithium, ammonium, sodium, potassium, magnesium, and calcium salts. The properties measured included melting point, Krafft point, solubility in water and organic solvents, surface and interfacial tension, critical micelle concentration (cmc), calcium stability, metal ion stability, detergent, foaming, wetting, lime soap dispersing, and emulsifying properties, rate of hydrolysis, and relative ease of biodegradation.

Experimental

Preparation of the Esters

α-Sulfopalmitic acid, 0.6 mole (200 g), was dissolved in 250 ml of the selected alcohol and esterified by heating 6 hr at the reflux temperature. The reaction mixture was divided into 6 equal parts and the salts were formed by neutralization or double decomposition with calculated amounts of lithium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, magnesium chloride or calcium chloride. The precipitated salts were dried, dissolved in absolute ethanol, decolorized, and recrystallized from aqueous ethanol at −20C. The same procedure was used for esters of α-sulfostearic acid. The esters were obtained in a pure state as white powders with an overall average for metal analysis within 0.1% of the theoretical value. The average purity of the ammonium salt, estimated from neutralization equivalent, was 98%.

Properties

Melting points were determined with the Fisher-Johns apparatus, surface and interfacial tension was measured with the du Noüy tensiometer, critical micelle concentration by the pinacyanole chloride method, and biodegradability by the river water test (13). Krafft point, detergency, foam height, wetting time, calcium stability, stability to metal ions, and lime soap dispersing power were measured as in previous publications (12). Emulsifying properties were measured by the method of Griffin and Behrens (6).

Rate of hydrolysis under acid catalysis, a first order reaction, was measured by heating 0.01 mole of the sodium salt of the ester in 100 ml N/3 H_2SO_4 at 100C, withdrawing 10 ml aliquots for titration at selected time intervals. Rate of hydrolysis under al-

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[1] Presented at the AOCS Meeting in Houston, 1965.

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