Use of Pulsed Nuclear Magnetic Resonance to Predict Emulsion Stability[1]

J. TRUMBETAS, J.A. FIORITI, and R.J. SIMS,
General Foods Corporation, Technical Center, White Plains, New York 10625

ABSTRACT

Pulsed nuclear magnetic resonance (NMR) was used to measure extent of oil solidification during cooling of oil-in-water emulsions. "Percent interaction," derived from these measurements, was found to correlate well with actual resistance of the emulsion to creaming and phase separation during storage. Average oil droplet size gave a fair correlation with stability, but the correlation of required Hydrophile-Lipophile Balance (HLB) with stability was poor. Pulsed NMR cooling curve measurements on emulsions offer an improved method for prediction of emulsion stability.

INTRODUCTION

Probably the most important consideration in the formulation of food emulsions is their stability to creaming and phase separation. Selection of emulsifiers to maximize stability has been largely a trial-and-error procedure in the past (1). Attempts to improve on this situation resulted in the Hydrophile-Lipophile Balance (HLB) system which has been applied extensively to emulsions containing nonionic surfactants such as the Tweens and Spans (2). Use of this method requires a knowledge of both the optimum HLB for each oil and the HLB of the individual surfactants. Since in most cases the commercially available edible emulsifiers are mixtures, HLB cannot easily be determined from chemical structure.

In a previous paper, we described a pulsed nuclear magnetic resonance (NMR) method for measuring the extent of oil solidification during the cooling of an oil-in-water emulsion (3). Unstable emulsions showed little supercooling, whereas those which were relatively stable to creaming and phase separation were also resistant to oil solidification. The "percent interaction," derived from such measurements, or degree of supercooling, was found to relate directly to emulsion stability.

Recently we also described an improved pulsed NMR technique for determination of emulsion stability (4). Emulsion samples were aged at room temperature in constant bore tubes, which were lowered by a drive mechanism at constant speed through the magnet. The pulsed NMR signal response is recorded, giving a profile of oil distribution throughout the tube. Since each sample can be tested repeatedly at intervals during the aging process, this approach indicates quantitatively the rate at which the phases are separating.

It has been said that the lack of a clear-cut index of emulsion stability, and excessive reliance on subjective evaluation, have hindered the development of a useful theory for prediction of emulsion stability (5). The extent of phase separation is fairly easy to measure visually, but with creaming there is no well defined phase boundary. Particle size distribution of the dispersed phase, as a function of storage time, is one valid measure of emulsion stability (6). Also a hygrometer technique has been used to measure changes in density as separation occurs (7). A device has been patented for determining phase separation of emulsions by transmitted light to give a direct observation of the relative proportions of separated layers (8). Turbidimetric or nephelometric methods have also been used for this purpose (9). Incorporation of radioactive materials into the disperse phase was also suggested as a method for determining rate of separation and homogeneity (10).

Pulsed NMR measurements provide a new, rapid, and precise measurement of emulsion stability. Also it appears that by chilling the emulsion and measuring the resistance of the dispersed oil to solidification, values for "percent interaction" can be obtained which correlate well with observed emulsion stability.

EXPERIMENTAL PROCEDURES

Materials

Hydrogenated soybean oil was obtained from Archer-Daniels Midland Co., Decatur, IL. Coconut oil (92° m.p.) was from Capital City Products Co., Columbus, OH. Cocoa butter was produced by General Foods Corporation at Dover, DE. See Table I for fatty acid compositional analyses of these three oils.

Equipment and Methods

The Praxis Pulsed NMR (PR-103) Spectrometer, Praxis

TABLE I

Fatty Acid Composition (Relative %)

Carbon no.	92° Coconut oil	Cocoa butter	Hydrogenated soybean oil
8:0	8.6		
10:0	7.5		
12:0	31.8		0.1
14:0	23.9	tr	0.2
16:0	12.0	25.7	11.7
16:1		0.2	0.2
17:0			0.1
18:0	13.7	34.6	11.6
18:1	2.1	35.7	66.3
18:2	0.1	3.5	9.4
20:0	0.1		0.3
Total	99.8	99.7	99.9

---

[1] Presented at the AOCS Meeting in Chicago, September 1976.

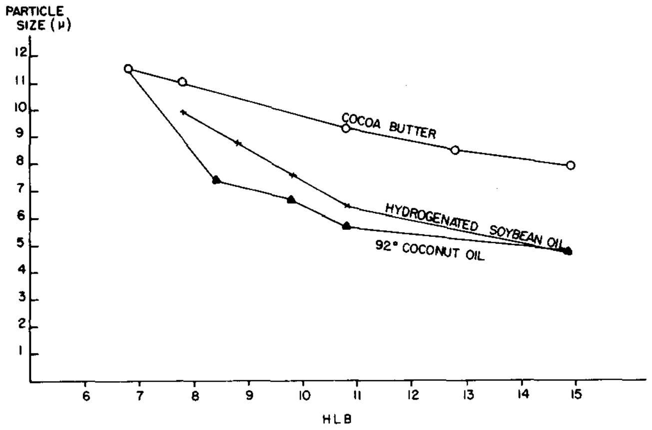

FIG. 1. Relationship between Hydrophile-Lipophile Balance (HLB) and average oil droplet size in emulsions.

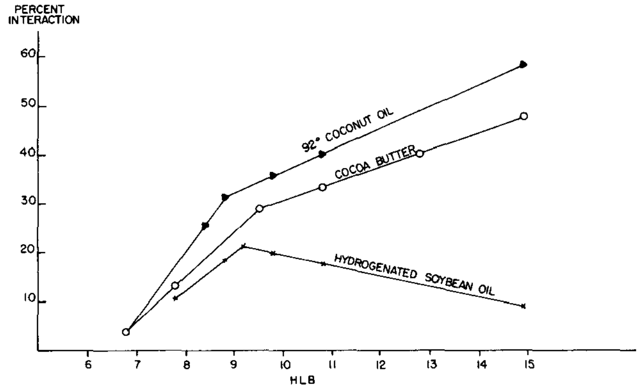

FIG. 2. Relationship between Hydrophile-Lipophile Balance (HLB) and percent interaction.

Corporation, San Antonio, TX, was used. Details of the instrument settings, the auxiliary equipment, and a schematic diagram of the assembly required to obtain cooling curves are all given in a previous paper (3). The method used to measure supercooling and the calculation of "percent interaction" are also described in this earlier paper. Details of the pulsed NMR emulsion stability method were reported recently (4).

The emulsions contained 24% fat, 1% Tween-Span combinations, and 75% water. Tween 60 (polyoxyethylene 20 sorbitan monostearate) and Span 60 (sorbitan monstearate) were products of ICI United States Inc., Wilmington, DE. Tween was dispersed in distilled water at 60 C, and Span was dispersed in the melted fat. The phases were mixed (100 g total weight) in a Waring Blendor for 5 min at high speed. Mixing speed, time of mixing, and initial temperature before mixing were kept constant to insure that all samples received approximately the same amount of work.

Average particle size determinations were made on the freshly prepared emulsions using a Coulter Counter, Model TAII, Coulter Electronics, Inc., Haileah, FL. All measurements were obtained with a 30 micron aperture cell (11). The required HLB values for the three fats: 9 hydrogenated soybean oil; 9 for 92° coconut oil; and 9-10 for cocoa butter, were supplied to us by ICI America, Inc. Fatty acid composition data (Table I) were obtained by gas liquid chromatography (GLC) of methyl esters using a Perkin Elmer 900 gas chromatograph equipped with a dual flame ionization detector. The column (10 ft x 1/8 in. OD 12% stabilized DEGS on 70/80 mesh Anakrom ABS) was run isothermally at 190 C.

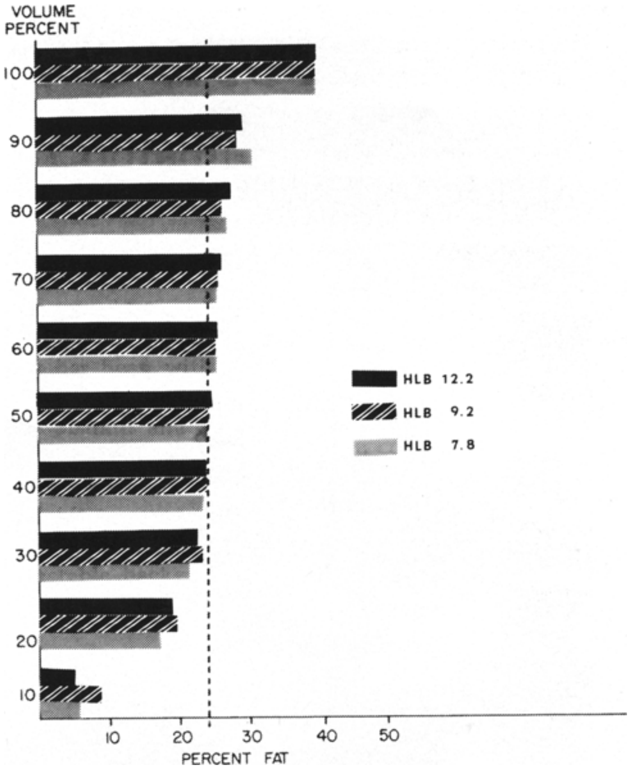

FIG. 3. Distribution of soybean oil in emulsions after 22-hr storage.

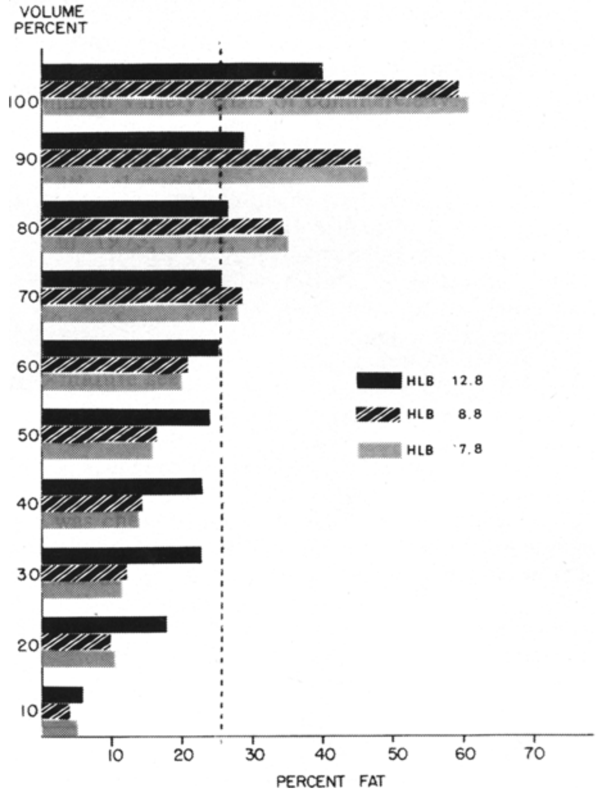

FIG. 4. Distribution of 92° coconut oil in emulsions after 22-hr storage.

RESULTS AND DISCUSSION

Three series of emulsions were prepared using hydrogenated soybean oil, 92° coconut oil, and cocoa butter, each with five different Tween:Span ratios. The

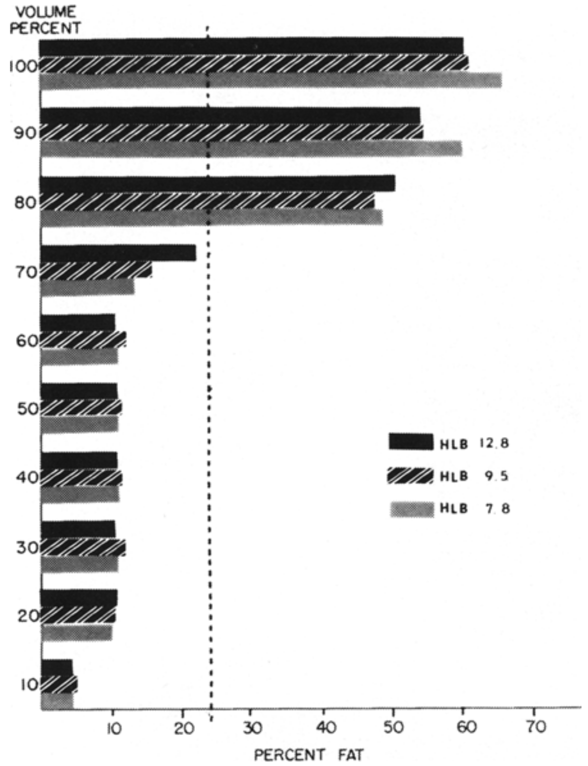

FIG. 5. Distribution of cocoa butter in emulsions after 22-hr storage.

objective was to obtain samples over a range of HLB values both below and above the required HLB for each of the oils. Average oil droplet size was then determined for each freshly prepared emulsion using the Coulter Counter. The data show a trend toward smaller particle sizes with increasing emulsifier HLB over the entire range tested (Fig 1). This inverse relationship was observed with all three oils. It has been suggested that, other things being equal, the emulsion having the smaller particle size will exhibit the slower creaming rate and have the greater stability (12).

Cooling curves were also run on each fresh emulsion to measure extent of fat solidification (degree of supercooling) (3). "Percent interactions" were calculated for each of the samples, and these numbers were plotted against HLB of each emulsifier combination (Fig. 2). With coconut oil and cocoa butter there were no optimum interactions, i.e., the interaction increased as the HLB of the emulsifier was raised over the range tested. However, a change in slope of the curve was observed with both of these oils quite near the required HLB values (8.8 for coconut oil and 9.5 for cocoa butter). With soybean oil there was a maximum interaction which coincided with the required HLB for this oil (9.2).

Storage tests were run on all of the samples at room temperature. At intervals, the pulsed NMR equipment was used to measure extent of creaming and/or phase separation (4). Fat distribution profiles in the storage tubes were obtained after 30 min, 2½ hr, 5 hr, and 22 hr. In the interests of brevity, only the data after 22 hr are presented here. Three emulsion samples for each oil have been selected, one at a low HLB, one at the required HLB, and a third at a high HLB (Figs. 3, 4, and 5). Selection of the data did not affect the conclusions which follow since all the results showed the same general trend.

The bar graphs are drawn to divide the emulsions into ten equal volume segments with 100 representing the top 10% in the stability tube and 10 the bottom 10%. The lengths of the bars represent the percentages of fat in each volume segment. The dotted vertical lines represent the fat distribution in the emulsions as originally prepared. As creaming occurs, the upper segments become rich in fat, whereas the lower segments become progressively more lean.

An inspection of Figures 3, 4, and 5 shows that in all cases the most creaming occurred at the lowest HLB. Collectively the bars representing HLB 7.8 showed the largest deviation from the vertical dotted line with each oil. All of the emulsions showed some degree of creaming after 22-hr storage, but none showed any sign of coalescence and phase separation.

Hydrogenated soybean oil (Fig.3) gave the best overall stability and also had slightly less creaming at the required HLB of 9.2 than at either the low or higher HLBs. Maximum interaction was also observed at HLB 9.2 (Fig 2). With 92° coconut oil, it is obvious that the best stability was obtained at the highest HLB, 12.8. The maximum interaction was also observed at HLB 12.8 with this oil. The differences in stability with the cocoa butter samples are somewhat more subtle. But if the plus and minus deviations from the vertical dotted line are totaled, for each emulsion, then the sample at HLB 12.8 is observed to have the best stability.

The findings are summarized in Table II. "Percent interaction" showed a maximum for all three oils at the HLB which also gave the best emulsion stability. Average particle size was the smallest at HLB 12.8 for all three oils, but soybean gave the best stability at HLB 9.2. Only soybean gave the best stability at its required HLB. Thus only "percent interaction" showed a complete correlation with resistance to creaming. Average particle size correlated fairly well with stability. The required HLB gave the poorest correlation.

Based on this work, it appears that "percent interaction," derived from pulsed NMR cooling curve measurements can be used to predict emulsion stability. Pulsed NMR represents an improvement over the HLB system both as a means to predict, and to actually measure stability of emulsions to creaming and phase separation.

REFERENCES

1. Krog, N., and J.B. Lauridsen, in "Food Emulsions," Edited by

TABLE II

Correlation Table

Emulsion stability at 22 hr	Required HLB[a]	Percent interaction	Average particle size
Hydrogenated soybean oil	Yes	Yes	No
Coconut oil	No	Yes	Yes
Coconut Butter	No	Yes	Yes

[a] HLB = Hydrophile-Lipophile Balance.

S. Friberg, Marcel Dekker, Inc., New York, p.69.
2. Griffin, W.C., J. Soc. Cos. Chem. 1:311 (1949).
3. Trumbetas, J., J.A. Fioriti, and R.J. Sims, JAOCS 53:722 (1976).
4. Trumbetas, J., J.A. Fioriti, and R.J. Sims, Ibid. 54:433.
5. Vold, R.H., and R.C. Groot, J. Sco. Cos. Chem. 14:233 (1963).
6. Levius, H.P., and F.G. Drommond, J. Pharm. Pharmacol. 5:743 (1953).
7. Sanders, H.L., H.R. Suter, and E.R. Gaverich, Soap Chem. Spec. 30(5):99 (1954).
8. Griffin, W.C., and R.W. Behrens, Anal. Chem. 24:1076 (1952), U.S. Pat. 2,673,484 (1954).
9. Bolton, M.E., and A.W. Marshall, Soap Sanit. Chem. 25(9):129 (1949).
10. Appino, J.B., J.E. Christian, and G.S. Banker, J. Pharm. Sci. 51:254 (1962).
11. Rowe, E.L., J. Pharm. Sci. 54(2)260 (1965).
12. Schwartz, A.M., and J.T. Perry, in "Surface Active Agents," Interscience Publishers, Inc., New York, 1949, p. 340.

[Received August 1, 1977]