

Oil and Water Determination in Emulsions by Pulsed Low-Resolution NMR

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ABSTRACT

A pulsed, low-resolution nuclear magnetic resonance (NMR) technique has been used for the oil and water determination in O/W emulsions. The method is based on the analysis of the longitudinal magnetization decay curve, that, due to the different relaxation times of oil and water, consists of 2 recognizable components. Correlation of NMR results with fat content is described. A good correlation between the NMR response and fat content by weight has been found. The rapidity and accuracy of the measurements are comparable to those of other techniques.

INTRODUCTION

The determination of oil and water content in emulsions is of great importance in food and cosmetic processing. It is therefore extremely important to develop new techniques which are rapid, accurate and which require a minimal sample pretreatment.

Nuclear magnetic resonance (NMR) spectroscopy has been successfully used to measure the oil and water content in emulsions as well as to determine their solid fat content, their stability and their dynamic state. Wide-line, high-resolution and pulsed low-resolution are the main NMR techniques used in this field.

For oil and water determination in aqueous emulsions and in commercial margarines, 2 wide-line NMR methods have been developed by Shanbhag et al. (1). They used the radiofrequency (RF) saturation method for the oil determination in laboratory-produced aqueous emulsions and suggested a different wide-line NMR method, based on the addition of $Mg(ClO_4)_2$ to the sample, for commercial margarines, obtaining a good reproducibility and an accuracy of $\pm 0.5\%$. Mansfield and Horn (2) compared the NMR method for moisture determination in margarines to different gravimetric methods and showed that the NMR technique is both rapid (~ 15 min/determination) and accurate ($\pm 0.27\%$).

In contrast, high-resolution NMR, due to the cost of the instrument, seems to be unsuitable for oil and water determination in these samples. For this reason, it has been used mainly in the study of the state of water in W/O emulsions (3) and in hydrophilic and lipophilic balance (HLB) determinations (4).

Finally, pulsed low resolution NMR has been used for determination of solid fat index (5-7) in margarines and for determination of emulsion stability (8-10). Although the pulsed low-resolution NMR technique has been successfully used for oil and water determination in oilseeds and olives (11,12), up to now, the only application to oil and water determination in emulsions was based on the free induction decay signal (FID) (9). Because of the general improvement of pulsed techniques and the advantages they offer, we believe that the use of this technique for oil and water determination in emulsions is quite suitable.

In this paper, we report the determination of oil and water content by pulsed low-resolution NMR in O/W emulsions. The method is based on the analysis of the longitudinal magnetization decay curve of the samples. It does

not require sample pretreatment or a trained operator and it can be completely automated.

EXPERIMENTAL

Materials

Mineral oil FU by Carlo Erba, Milan, Italy, and triethanolamine stearate, as emulsifying agent, were used. A weighed amount of mineral oil and surfactant, at 80°C, were added with distilled water at the same temperature in order to obtain 100 g of sample and the mixture was mechanically stirred until room temperature (25°C) was reached. The water content was measured by weighing the sample at room temperature. About 1 g of emulsion was transferred to a test tube of 10 mm external diameter for NMR reading. NMR measurements were performed within 4 hr after the sample preparation.

NMR Measurements

NMR measurements were performed by a pulsed low-resolution spectrometer, Minispec P20, produced by Bruker Co., Karlsruhe, Germany, operating at 20 MHz and equipped with an analog computer B-AC5.

The longitudinal magnetization decay curve was detected by a $180^\circ t/90^\circ$ pulse sequence. The sample, located within a permanent magnet, is first subjected to a 180° RF-pulse (i.e., a pulse which "flips" the equilibrium nuclear magnetization M_0 by 180° with respect to the magnetic field direction). After a variable delay, τ , a 90° RF-pulse is applied which gives rise to a transverse nuclear magnetization, M_T , detected by the transmitter/receiver coil wound around the sample. By plotting the function $\ln(M_0 - M_T)$ vs the time t , the longitudinal magnetization decay curve is obtained. The 90° and 180° pulses are adjusted empirically by varying their respective widths (ca. $4 \mu\text{sec}$ and $8 \mu\text{sec}$ on our instrument). The time delay τ between the pulses was varied from 10 msec to 5 sec. Each measurement was repeated 10 times, the time between 2 consecutive measurements was kept to 10 sec to allow the nuclear magnetization to return to its equilibrium value. The probe temperature was $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Figure 1 shows a typical longitudinal magnetization decay curve for an O/W emulsion (curve a). The curve reported in Figure 1 does not show a single exponential behavior; that can be explained by the presence in the sample of 2 different components having different longitudinal relaxation times, T_{1f} and T_{1s} . In the present case, as it will be described later, the slowly decaying component can be identified with the water and triethanolamine, whereas the fast decaying component can be identified with the oil and the stearic acid. Curve a in Figure 1 can be therefore fitted by the function:

$$M_0 - M_T = C_1 \exp(-t/T_{1f}) + C_2 \exp(-t/T_{1s}) \quad (1)$$

where C_f and C_s are proportional to the content of the 2 components in terms of hydrogen abundance in the sample.

The C_s value can be obtained by a direct extrapolation of the curve at $t = 0$. By subtracting the extrapolated values of the slowly decaying component (dotted line in Fig. 1), the magnetization decay of the fast decaying component is obtained (curve b in Fig. 1) together with the C_f value. The percentage of each component in terms of hydrogen abundance X_i in the sample can therefore be obtained by:

$$X_i = 100 \frac{C_i}{C_f + C_s}, \quad \text{[II]}$$

and compared to the sample composition.

The X_i values of different emulsions with fat content by weight, W_f , in the range 10-70% have been determined by NMR. The results are summarized in Table I, where the sample composition by wt (W_i), the percentage of the fast decaying component in terms of hydrogen abundance (X_f) derived by NMR, the T_{1f} and T_{1s} relaxation times of the 2 components and the correlation coefficients r_f^2 and r_s^2 of the regression analysis on the decay curve of each component are reported. The percentage of the slowly decaying component, X_s , can obviously be obtained as: $X_s = 100 - X_f$. In Figure 2, the fat content, X_f , as determined by NMR vs the fat content by wt, is reported. Figure 2 shows a good correlation between the NMR response and the fat content of the samples; however the X_f and W_f values do not coincide. That can be explained by the different hydrogen abundance (i.e., g of hydrogen/g of component), h_f and h_s , of the 2 components, so that the X_f and W_f values can be related by:

$$W_f = 100 \frac{X_f}{X_f + (100 - X_f) h_f/h_s}, \quad \text{[III]}$$

or, by writing Equation III in a different form, by:

$$\frac{100}{W_f} = \frac{100}{X_f} \frac{h_f}{h_s} + 1 - \frac{h_f}{h_s}. \quad \text{[IV]}$$

Equation IV shows that a plot of $1/W_f$ vs $1/X_f$ gives a straight line for which the slope and intercept both depend

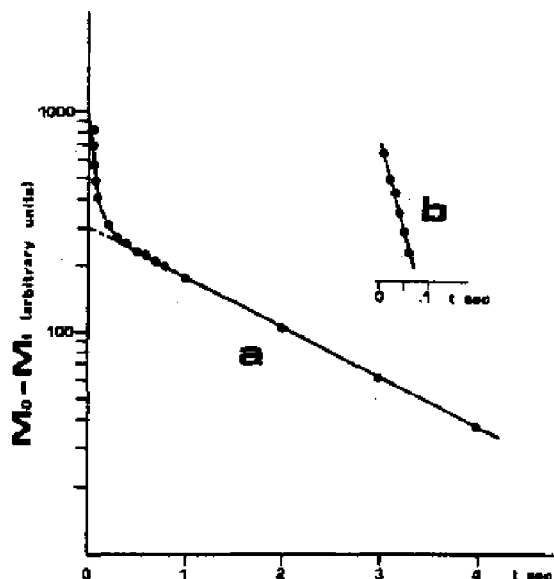


FIG. 1. Curve a: longitudinal magnetization decay curve for an emulsion composed of mineral oil, 66.8%; water, 28.8%; stearic acid, 2.9%; triethanolamine, 1.5%. Curve b: longitudinal magnetization decay of the fast decaying component of the sample; the curve is obtained by subtracting from the overall curve the extrapolated values of the slowly decaying component (dotted line).

on the h_f/h_s ratio. Notice that it is common in the literature to apply linear regression to the $W(X)$ relationships, which is obviously incorrect. A plot of $100/W_f$ vs $100/X_f$ for the emulsions examined is reported in Figure 3; a linear regression analysis on the data of Figure 3 gave a correlation coefficient $r^2 = 0.999$, thus confirming that Equations III and IV fit the experimental data very well. According to that, the fat (or water) percentage by weight can then be directly obtained by Equation III if the relative hydrogen abundance, h_f/h_s , of the 2 components is known a priori and the fat (or water) percentage, in terms of hydrogen

TABLE I

Sample Composition, Percentage of the Fast Decaying Component X_f , Longitudinal Relaxation Times, T_{1f} and T_{1s} , of the Two Components and Correlation Coefficients r_f^2 and r_s^2 of the Regression Analysis on the Decay Curve of Two Components

| Sample | Oil ^a | Stearic acid ^a | Water ^a | Triethanolamine ^a | Oil + stearic acid (W_f) ^a | X_f ^b | T_{1f} (sec) | r_f^2 | T_{1s} (sec) | r_s^2 |
|--------|------------------|---------------------------|--------------------|------------------------------|---|--------------------|----------------|---------|----------------|---------|
| 1 | 9.9 | 3.0 | 85.5 | 1.6 | 12.9 | 14.1 | 0.045 | 0.991 | 2.488 | 0.999 |
| 2 | 9.1 | 4.6 | 84.0 | 2.3 | 13.7 | 15.1 | 0.060 | 0.999 | 2.280 | 0.998 |
| 3 | 12.0 | 3.0 | 83.5 | 1.5 | 15.0 | 16.0 | 0.056 | 0.981 | 2.256 | 0.998 |
| 4 | 13.8 | 3.0 | 81.7 | 1.5 | 16.8 | 17.5 | 0.037 | 0.998 | 2.210 | 0.995 |
| 5 | 14.5 | 2.8 | 81.3 | 1.4 | 17.3 | 17.9 | 0.046 | 0.994 | 2.353 | 0.999 |
| 6 | 23.9 | 3.1 | 71.4 | 1.6 | 27.0 | 28.5 | 0.031 | 0.996 | 2.206 | 0.999 |
| 7 | 24.9 | 3.0 | 70.6 | 1.5 | 27.9 | 29.1 | 0.021 | 0.995 | 2.375 | 0.999 |
| 8 | 26.8 | 3.1 | 68.6 | 1.5 | 29.9 | 31.4 | 0.060 | 0.992 | 2.832 | 0.986 |
| 9 | 30.7 | 3.1 | 64.7 | 1.5 | 33.8 | 36.3 | 0.033 | 0.996 | 2.172 | 0.999 |
| 10 | 35.5 | 3.1 | 59.9 | 1.5 | 38.6 | 41.0 | 0.050 | 0.999 | 2.277 | 0.999 |
| 11 | 40.0 | 3.0 | 55.5 | 1.5 | 43.0 | 45.1 | 0.035 | 0.999 | 2.130 | 0.999 |
| 12 | 43.2 | 3.1 | 52.1 | 1.6 | 46.3 | 49.1 | 0.034 | 0.995 | 2.132 | 0.999 |
| 13 | 45.7 | 3.2 | 49.5 | 1.6 | 48.9 | 51.8 | 0.035 | 0.993 | 2.330 | 0.999 |
| 14 | 45.6 | 8.0 | 42.4 | 4.0 | 53.6 | 55.9 | 0.040 | 0.999 | 1.680 | 0.999 |
| 15 | 50.7 | 3.0 | 44.8 | 1.5 | 53.7 | 56.0 | 0.037 | 0.997 | 2.070 | 0.999 |
| 16 | 50.5 | 3.1 | 37.7 | 3.9 | 58.4 | 61.4 | 0.060 | 0.997 | 1.696 | 0.999 |
| 17 | 58.3 | 3.1 | 37.0 | 1.6 | 61.4 | 63.0 | 0.038 | 0.999 | 2.100 | 0.999 |
| 18 | 58.8 | 3.0 | 36.7 | 1.5 | 61.8 | 64.8 | 0.050 | 0.985 | 2.220 | 0.999 |
| 19 | 62.6 | 3.1 | 32.7 | 1.6 | 65.7 | 68.4 | 0.050 | 0.998 | 2.419 | 0.999 |
| 20 | 66.8 | 2.9 | 28.8 | 1.5 | 69.7 | 71.8 | 0.057 | 0.989 | 1.977 | 0.999 |
| 21 | 68.5 | 2.6 | 27.6 | 1.3 | 71.1 | 72.6 | 0.041 | 0.971 | 1.787 | 0.999 |

^aPercentage by wt.

^bPercentage of the fast decaying component in terms of hydrogen abundance determined by NMR.

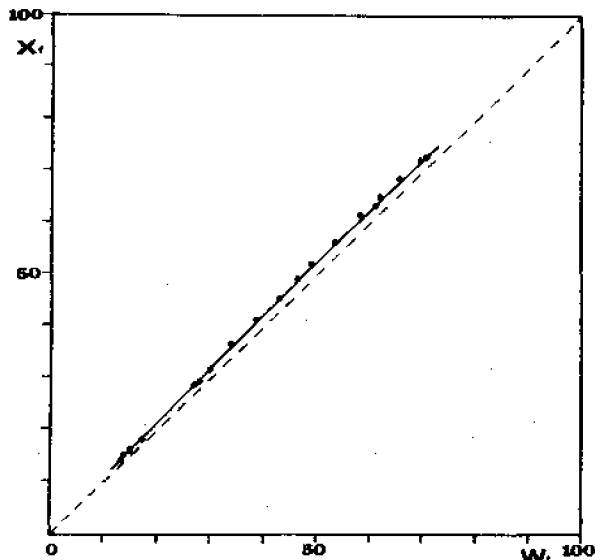


FIG. 2. Percentage of the fast decaying component in terms of hydrogen content, X_f , as obtained by NMR, vs the oil and stearic acid percentage by weight, W_f . The dotted line represents the $X_f = W_f$ function.

content, X_f , is measured by the analysis of the longitudinal magnetization decay curve. On the contrary, if the h_f/h_s ratio is unknown, a correlation curve, as shown in Figure 3, must be derived and the h_f/h_s ratio must be evaluated.

In the present case, the h_f/h_s ratio of 1.085 was found by regression analysis. Assuming this h_f/h_s ratio, the fat content by weight, W_f , was calculated with Equation III and the standard deviation between these values and those given by the sample composition reported in Table I was calculated, obtaining an SD of ± 0.5 .

From these results, it can be concluded that pulsed low-resolution NMR is a suitable technique for oil and water determination in emulsions. Finally, it can be noted that the time required for the analysis is about 20-30 min if 6 points, each of them obtained by the average of 10 measurements, are taken to detect the longitudinal magnetization decay.

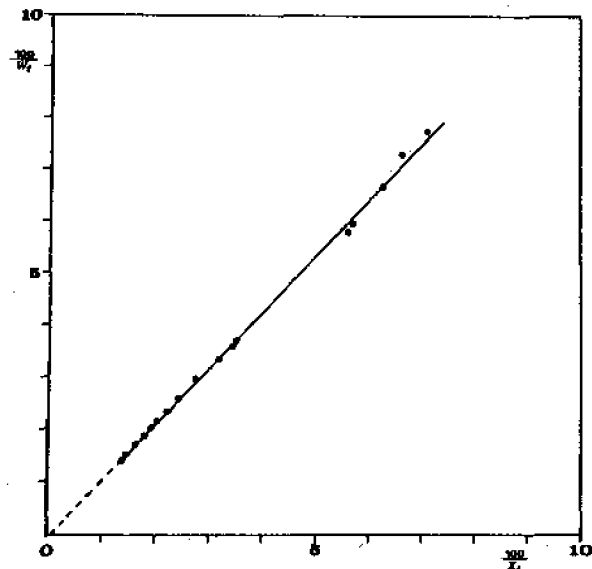


FIG. 3. $100/W_f$ vs $100/X_f$ plot.

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ERRATUM

In "Effect of Degumming Conditions on Removal and Quality of Soybean Lecithin," by G.R. List, J.M. Avelaneda and T.L. Mounts (*JAACS* 58:892, 1981), the captions to Figures 3 and 4 should be transposed to read: FIG. 3. Recovery of acetone insolubles from crude soybean oil. ● Theory, acetone-insoluble content crude oil. □ Calculated from phosphorus content of degummed oil. △ Experimental acetone-insoluble content of hexane solubles. FIG. 4. Effects of degumming parameters on phosphorus removal and acetone-insoluble content of gums.