

The Use of NMR in Quantitative Determination of Oil and Water in Emulsions

Salleh Harun

Physics Department

Faculty of Science and Environmental Studies

Universiti Pertanian Malaysia

43400 UPM, Serdang, Selangor, Malaysia.

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ABSTRAK

Teknik resonans magnet nukleus digunakan untuk menentukan kuantiti air dan minyak di dalam beberapa emulsi minyak/air. Kaedah ini menggunakan urutan denyut perolihan songsangan untuk menghasil dan mengukur amplitud gema-gema spin pada sela masa tak linear. Suhu dan frekuensi yang digunakan ialah pada 24.5°C dan 2.5MHz. Kuantiti tiap-tiap komponen diperolehi daripada pepadanan data kepada model tak linear yang mengandungi satu atau pun dua eksponen. Bagi n-hexadecane/air dan minyak paraffin/air relaksasi bersesuaian dengan model dua keadaan tak bertukaran. Amaun setiap bahagian boleh ditentukan dengan baik daripada amplitud-amplitud signal. Walau bagaimanapun, minyak zaitun menunjukkan relaksasi berlainan dan lebih kompleks. Perbezaan nisbah amplitud signal dengan yang diperolehi dari kaedah timbangan dibincang.

ABSTRACT

Nuclear magnetic resonance techniques have been used to determine quantitatively the amount of water and oil in several oil/water emulsions. The technique utilizes the inversion recovery pulse (IR) sequence to produce and measure the amplitude of the spin echoes at non-linearly spaced time intervals. In this study, the temperature and the operating frequency were 24.5°C and 2.5MHz respectively. The quantity of each component was determined by fitting the data to non-linear models consisting of either one or two exponentials. For n-hexadecane/water and paraffin oil/water, the relaxation behaviour conforms to the two-state non-exchange model. The amount of each constituent could be estimated fairly accurately from the signal amplitudes. Olive oil emulsion, however, appears to be more complex. The difference between signal amplitude ratio and that obtained by weighing is discussed.

Keywords: emulsion, relaxation, nuclear magnetic resonance.

INTRODUCTION

The last twenty years have witnessed a tremendous development in pulsed nuclear magnetic resonance (NMR) techniques in various fields of research and applications. The relaxation times and the proton density have been measured and applied under various conditions to elucidate the state of water in tissues and industrial products (Mathur-De Vre 1984). Fat and

water content as well as their distribution in biological samples have been determined by NMR methods (Smith 1986).

Conventionally, fat or oil content is determined by solvent extraction, and water content by drying method. Both processes are obviously tedious and time-consuming. In this paper, a pulsed NMR technique to estimate the quantity of oil and water in emulsions is described. Previously, oil and water components in an emulsion were determined from the spin-spin relaxation signal (Jones 1988). In the present report, the quantity of each component was obtained through computer analysis of the data taken from the spin-lattice relaxation measurements.

MATERIALS AND METHODS

Sample Preparation

Emulsions of various composition were prepared from paraffin oil/water, n-hexadecane/water and olive oil/water. A small amount of Cu^{2+} ions (about 1×10^{20} per cc) was added to the water phase to reduce the relaxation times of pure water from about 3 seconds (Krynicky 1966) to about 200 millisecond. A mixture of emulsifying agents - Tween 20 (polyoxyethylene sorbitan monolaurate) and Span 80 (sorbitan monooleate) - was used to stabilise the emulsions. Independent experiments indicated that at a concentration of 5% (v/v), the mixture had no profound effect on the relaxation times T_1 and T_2 .

Experimental

All measurements were carried out on a home-built pulsed NMR spectrometer at the Department of Bio-Medical Physics and Bio-Engineering, University of Aberdeen. The resonance frequency and temperature were 2.5MHz and 24.5°C respectively. The signal intensity consisting of echo amplitude was obtained by using the modified inversion recovery pulse sequence [180° - τ - 90° - 180° -Echo-]. The delay time τ was varied non-linearly from 2 ms to 200 ms, with 31 data points. Since the signal originates from two kinds of non-exchangeable spins, the most appropriate expression for the signal decay is

$$S(\tau) = A + Q_1 e^{-\tau/T_{11}} + Q_2 e^{-\tau/T_{12}}$$

This equation is a solution of the phenomenological Bloch equations (Bloch 1946) with suitable initial conditions (Salleh 1991); Q_1 and Q_2 correspond to the quantities of each spin, while T_{11} and T_{12} are their respective relaxation time constants. The constant A is added to take into account the errors arising from field offset, base line shift and from electronic noise (Sass and Ziesson 1977; Weiss and Ferreti 1985).

Data Analysis

The method of least-squares, using the Gauss-Newton algorithm (Gill 1978) was used to fit the data to the above equation. The fitting procedure simulta-

neously yielded Q_1 , Q_2 , T_{11} and T_{12} including the estimation of the error. The fractional amplitude

$$k = \frac{Q_1}{Q_1 + Q_2} \quad \text{or} \quad k = \frac{Q_2}{Q_1 + Q_2}$$

was calculated and compared with the fractional amount

$$F = \frac{W_1}{W_1 + W_2} \quad \text{or} \quad F = \frac{W_2}{W_1 + W_2},$$

where W_1 and W_2 were the weights of each component obtained by physical method.

RESULTS

Fig. 1 shows the relaxation intensity decay curve for the n-hexadecane/water emulsion at 50%. The solid line is the fitted curve, while the cross signs are the experimental data points. *Fig. 2* illustrates the same data but fitted to the single component decay. It is obvious that fitting the data to the two-component equation is better than fitting it to a single decay equation.

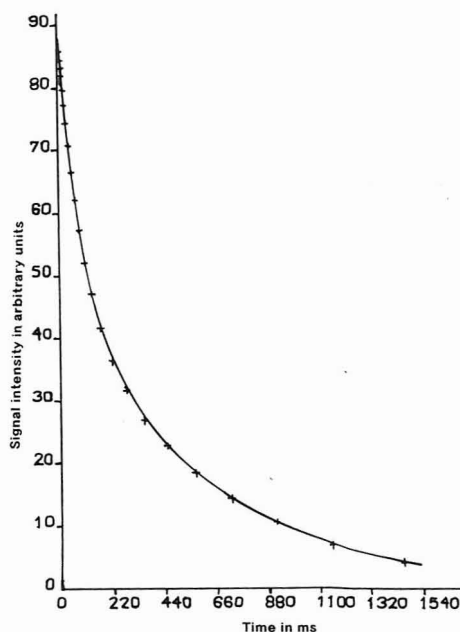


Fig. 1. Signal intensity decay curve of n-hexadecane emulsion. The solid line is the fitted curve according to the equation in the text

Table 1 shows the fractional amount of water obtained experimentally compared with that from weighing.

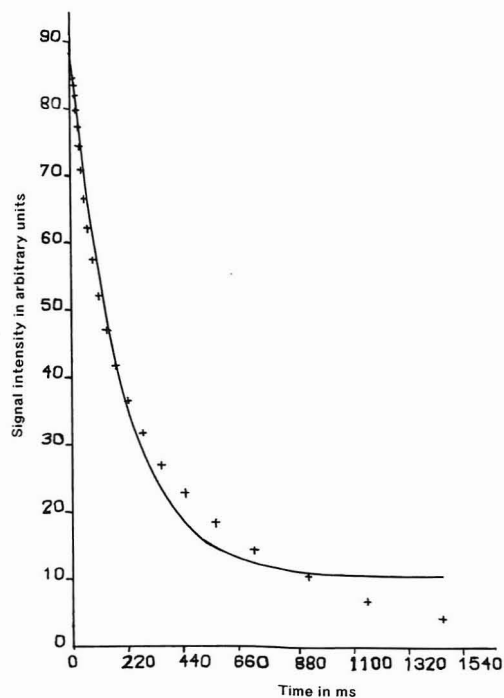


Fig. 2. Signal intensity decay curve of the same n-hexadecane emulsion. The solid line is the fitted curve according to monoexponential expression

TABLE 1
F and k values of n-hexadecane emulsions

Emulsion	$F = \frac{W_1}{W_1 + W_2}$	$k = \frac{Q_1}{Q_1 + Q_2}$
E75	0.80	0.78 ± 0.06
E76	0.70	0.70 ± 0.05
E77	0.60	0.60 ± 0.03
E81	0.55	0.46 ± 0.02
E68	0.50	0.47 ± 0.02
E8	0.45	0.47 ± 0.03
E78	0.40	0.39 ± 0.01
E79	0.30	0.27 ± 0.02

W_1 = amount of water, W_2 = amount of oil

Fig. 3 illustrates the k values plotted against F . The slope and the coefficient of regression were found to be 1.01 and 0.99 respectively. The intercept is almost zero. Thus, a k value can be used as an estimate of F with an error of 2%. Table 2 shows the results obtained from paraffin oil emulsions. A linear relationship is again observed between k and F (Fig. 4). The slope and the coefficient of regression were 0.96 and 0.99 respectively.

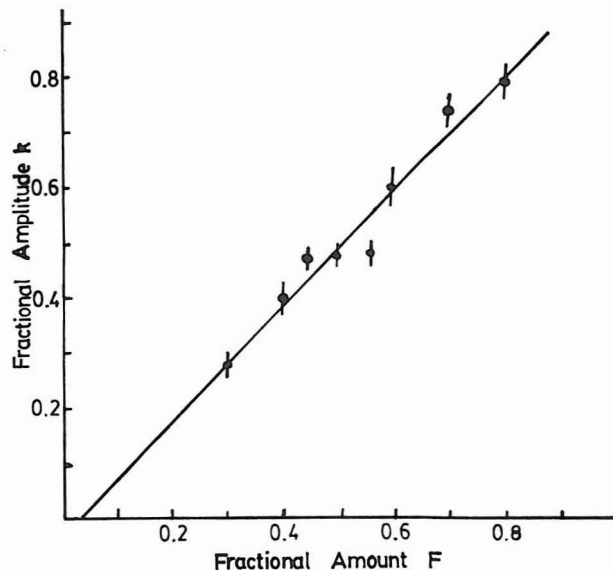


Fig. 3. Fractional amplitude k plotted against the fractional amount F for *n*-hexadecane emulsion

TABLE 2
F and k values of paraffin oil emulsions

Emulsion	$F = \frac{W_1}{W_1 + W_2}$	$k = \frac{Q_1}{Q_1 + Q_2}$
E90	0.80	0.82 ± 0.19
E91	0.70	0.68 ± 0.19
E92	0.60	0.69 ± 0.22
E93	0.55	0.48 ± 0.06
E94	0.50	0.49 ± 0.09
E95	0.45	0.43 ± 0.10
E96	0.40	0.37 ± 0.06
E97	0.30	0.29 ± 0.05
E98	0.20	0.18 ± 0.02

From the above observations it was concluded that the spin-lattice relaxation of *n*-hexadecane and paraffin oil emulsions obeys the model

expressed by the equation. In this situation, protons of the oil and those of the water relax independently, giving rise to two signals which can be separated through the decomposition procedure. Such a phenomenon is an indication of a two-state-non-exchange model.

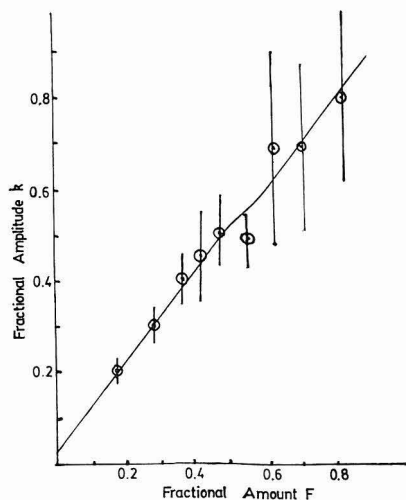


Fig. 4. Fractional amplitude k plotted against the fractional amount F for paraffin oil emulsion

The linearity of the graph, with the coefficient of regression of ≈ 1 , shows that the method may provide an efficient means of estimating the amount of each constituent in the emulsions with reasonable accuracy.

Table 3 shows the results of the analysis of olive oil emulsions. The T_1 of olive oil and water are 116.6 ± 3.1 ms and 256.9 ± 4.6 ms respectively.

TABLE 3
F and k values of olive oil emulsions

Emulsion	$F = \frac{W_1}{W_1 + W_2}$	$k = \frac{Q_1}{Q_1 + Q_2}$
E210	0.20	0.21 ± 0.10
E211	0.30	0.32 ± 0.13
E212	0.40	0.32 ± 0.09
E213	0.45	0.38 ± 0.11
E214	0.50	0.40 ± 0.01
E215	0.55	0.48 ± 0.09
E216	0.60	0.49 ± 0.05
E217	0.70	0.52 ± 0.08
E218	0.80	0.58 ± 0.17

Pure oil $T_{11} = 45.8 \pm 3.0$ (ms); $T_{12} = 161.1 \pm 9.0$ (ms); $k = 0.56 \pm 0.12$

It was observed that the variation of k with F for olive oil emulsions is also linear (not shown) with the coefficient of regression of 0.97. However, it does not follow a 1:1 correspondence. The slope is 0.62. The unexpectedly low k values, especially at high oil composition, may be due to the existence of two classes of spins in the oil itself, slow and fast. This is indicated in the last row of the table where, in pure form, the oil reveals two components with equal amplitudes ($k = 0.56 \pm 0.12$). The time constant of the slow component ($T_{12} = 161.1 \pm 9.0$ ms) is not sufficiently far from that of water ($T_1 = 256.9 \pm 4.6$ ms) for the analysis to resolve. Consequently, the slow component is lumped with the water component. In this situation, F cannot be determined directly from the k value. It can, however, be used to prepare a calibration curve for independent work.

CONCLUSION

The NMR method presented in the present report proved to be a reliable and fast technique. With the help of a standard graph, the technique may be extended for quantitative determination of other products. The method is found to be less tedious, easier to operate and faster than the traditional procedure.

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REFERENCES

- BLOCH, F. 1946. Nuclear induction. *Phys. Rev.* **70**: 460-465.
- GILL, P.E. 1978. Algorithms for the solutions of the nonlinear least-squares problems. Society for Industrial and Applied Mathematics. 977-991.
- JONES, S.A. 1988. Determination of the components in oil/water emulsions by means of pulsed NMR Bruker minispec application note 23.
- KRYNICK, K. 1966. Proton spin-lattice relaxation in pure water. *Physics* **32**:167-178.
- MATHUR-DE VRE, R. 1984. Biomedical implications of the relaxation behaviour of water related to NMR imaging. *British J. Radiobiology* **57**: 955-976.
- SALLEH, H. 1991. Nuclear magnetic resonance (NMR), theory and applications. *Jurnal Sains Nuklear Malaysia* **9(1)**: 1-12.
- SASS, M. and D. ZIESSON. 1977. Error analysis for optimized inversion recovery spin-lattice relaxation measurement. *J. Magn. Reson.* **25**: 263-276.

- SMITH, F.W. 1986. The clinical application of NMR imaging at 1.7 and 3.5 MHz. D.Sc. thesis, University of Aberdeen.
- WEISS, G.H and J.A. FERRETI. 1985. The choice of optimal parameters for measurement of spin-lattice relaxation times IV. Effects of non-ideal pulses. *J. Magn. Reson.* **61**: 499-515.