EVALUATION OF EMULSION STABILITY BY THERMOGRAVIMETRIC ANALYSIS (TG)

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ABSTRACT

A rapid and simplified method for the determination of phase inversion temperature (PIT) and the stability of oil in water emulsions, stabilized by nonionic emulsifiers, is described. The method is based on the use of any thermogravimetric apparatus from which the rate of loss of water can be measured as a function of linear increase in the emulsion temperature. A DTG peak is obtained at the PIT: the emulsion in which the lowest PIT is observed is also the less stable one.

INTRODUCTION

The relationship between the hydrophilic—lypophilic balance (HLB) values of various emulsifiers and the emulsion stability, i.e. kinetics of globule coalescence, has been studied by several investigators using a variety of methods and techniques [1—4].

It is also well known that an oil in water emulsion, stabilized by nonionic emulsifiers, can be inverted into a water in oil emulsion (resulting in a change in the nature of the emulsion) by increasing the emulsion temperature to a critical phase inversion temperature (PIT). The PIT of a given emulsion is influenced by the HLB value of the given emulsifier [5—8].

Sherman et al. [9,10] first realized that causing phase inversion of an emulsion will alter its thermal properties, e.g. thermal conductivity, heat capacity, and heat of vaporization. Thus, they assumed that any technique which will provide information about the dependence of thermal behaviour on temperature will be suitable for determining the PIT of a given emulsion and will be further correlated to its stability (globule coalescence). It has therefore been assumed that measurement of the inversion temperature, by the DTA technique, will provide information about emulsion stability [10].

In the course of our studies on emulsion globule coalescence, we realized that the correlation between the HLB values, PIT and emulsion stability can be examined using a rapid and simplified method, namely a thermogravimetric analysis which is based on measuring differences in rates of water vaporization from the emulsion before reaching the PIT and after passing it [11]. Thus, we found that it is possible to examine the loss of weight of a

given emulsion while heating the system instead of measuring its DTA profile.

The present study investigates the use of thermogravimetric measurements along with DTA in order to illustrate that a DTG profile is sufficient for the required information on the emulsion PIT and stability.

EXPERIMENTAL

The PIT values of the oil in water emulsions were measured from TG, DTG and DTA profiles obtained on a Mettler thermoanalyzer in which all curves were recorded simultaneously with the temperature increase.

An oil in water emulsion of commercial soya bean oil was studied. Each freshly prepared emulsion was heated in an open platinum crucible to facilitate evaporation and removal of water. A stream of dry nitrogen (5 l h^{-1}) was passed over the sample, which was heated at $2°C$ min^{-1}. In the control samples (in cases where DTA and TG measurements were carried on simultaneously) a pure soya bean oil served as a reference.

Each emulsion contained $10-40\%$ by weight of the dispersed phase ($\phi =$ $0.1-0.4$). The emulsifying agents were commercial grade Spans and Tweens from Atlas-Europol S.p.A. and ethoxylated castor oil (ECO) from Berol (Sweden).

The emulsifiers were weighted and blended together so as to provide the required HLB value and concentration ($2-20\%$), and added to the oil phase prior to emulsion preparation.

The emulsions were prepared at room temperature by slow addition of the oil to the water phase while stirring and passing it through a Silverson Laboratory homogenizer (Standard Laboratory Model) for 5 min.

Samples from the prepared emulsion were examined under a Zeiss optical microscope (Large Universal Model).

RESULTS

Figure 1 presents typical DTA, TG and DTG curves for the oil in water emulsion prepared with any emulsifier blend. The DTA curve shows an endothermic peak which corresponds to the PIT (also measured separately by visual observation).

Water evaporation occurs right from the beginning of the heating process. The rate at which water is lost increases gradually with temperature up to a point at which there is a drastic decrease in its vaporization and a change in the TG slope. The DTG curve shows a peak at exactly the same temperature where the DTA peak was measured.

Figure 2 demonstrates typical DTG curves for O/W emulsions prepared with three different emulsifier blends having exactly the same HLB value (11.5).

It can be seen that for ethoxylated castor oil and Span 80 blend the PIT value is $40°C$. The PIT value for ethoxylated castor oil and Span 60 blend is
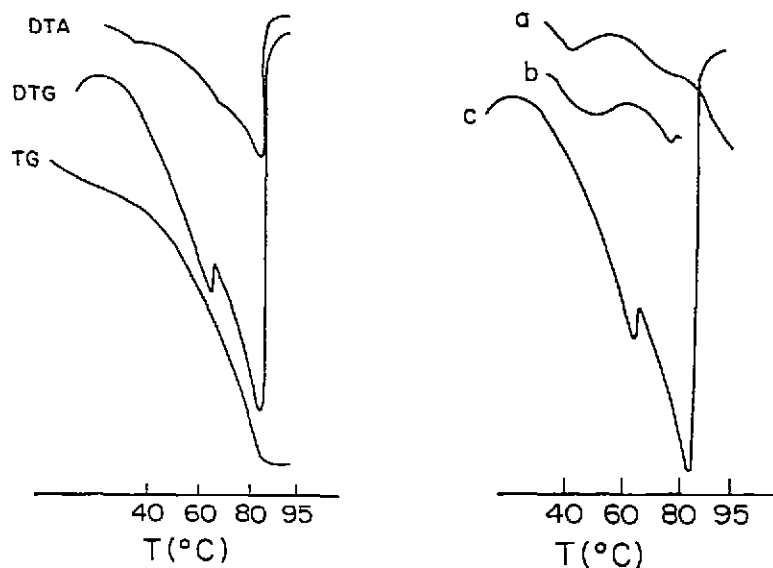
Fig. 1. DTA, TG and DTG curves for soya bean oil in water emulsion. Heating rate = $2°C$ min^{-1}; $\phi = 0.2$; 10% emulsifier (ECO + Span 20; HLB = 11.5).

Fig. 2. DTG curves for soya bean oil emulsion prepared at a constant HLB value (11.5). Heating rate = $2°C$ min^{-1}; $\phi = 0.2$; 10% emulsifer. (a) ECO + Span 80 (b); ECO + Span 60; (c) ECO + Span 20.

$46°C$, while a blend of ethoxylated castor oil and Span 20 forms an emulsion with a PIT of $80°C$.

The emulsion oil droplets were photographed as observed under the microscope. Figure 3 illustrates the particles' dimensions of three emulsions.
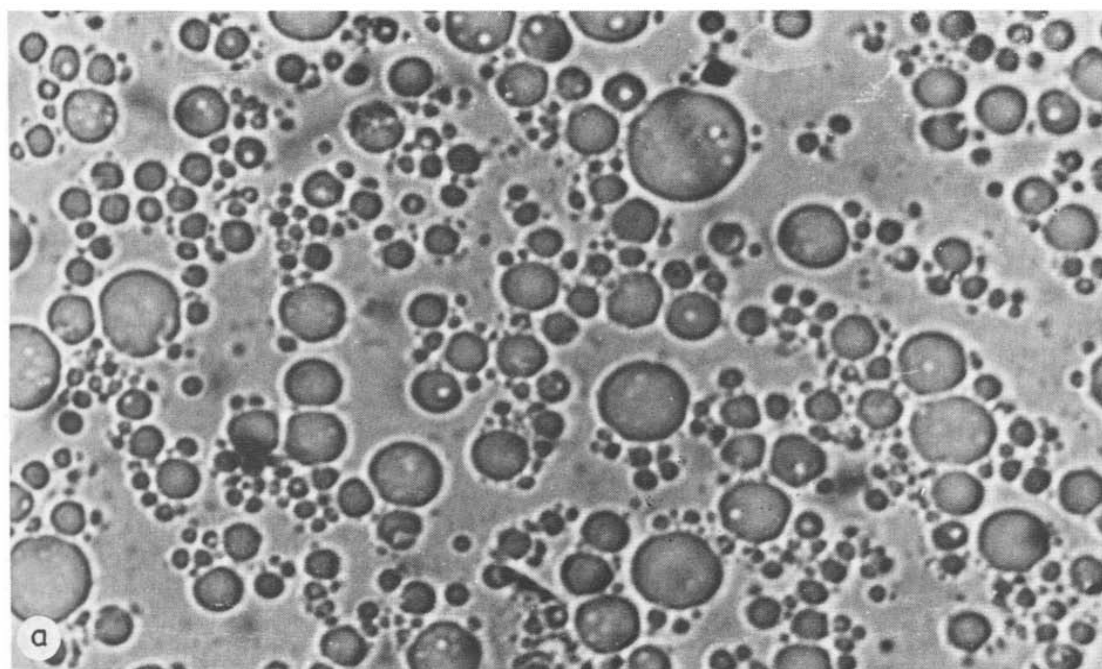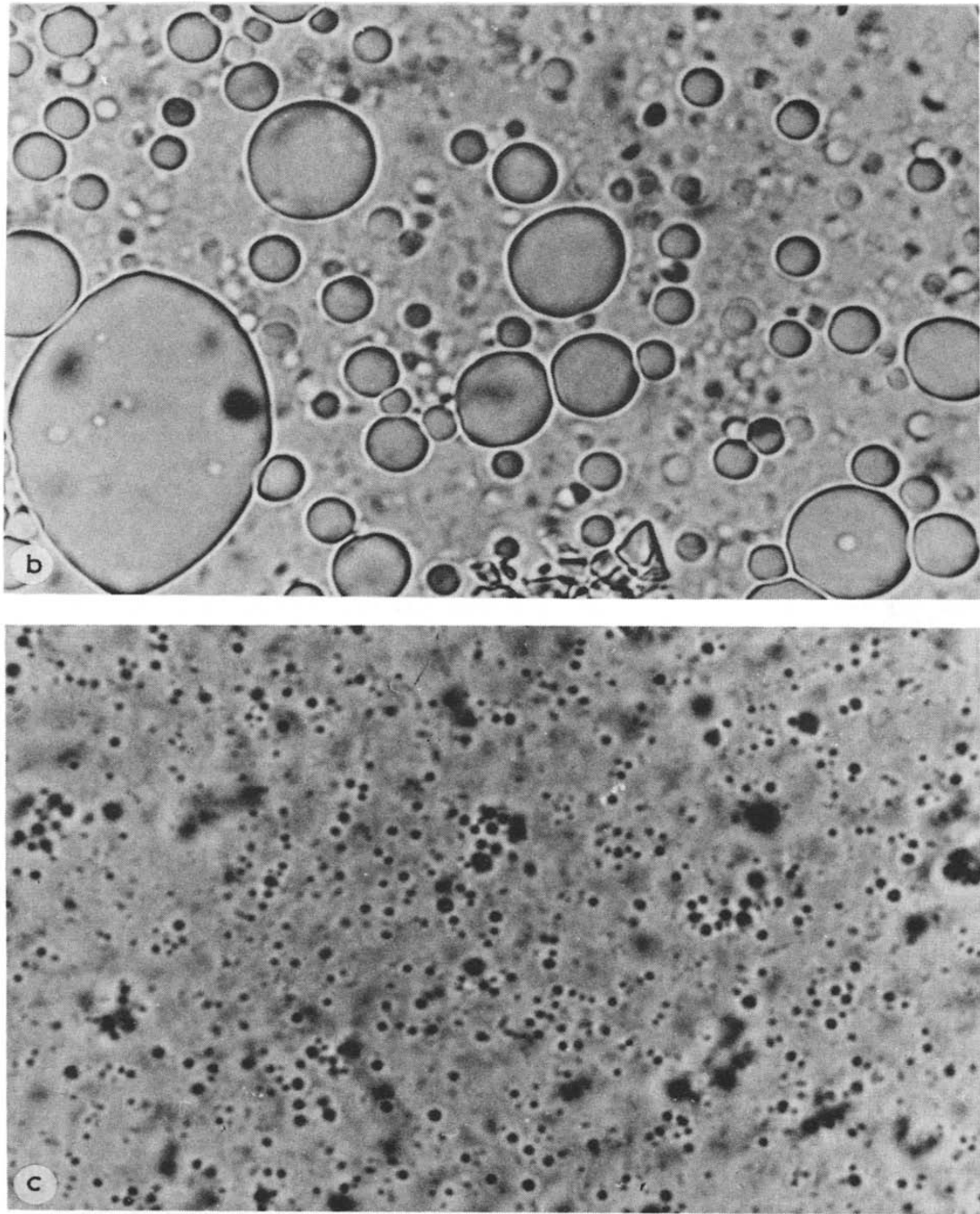
Fig. 3. Emulsion droplets as photographed from an optical microscope (×1000). (a) ECO + Span 80; (b) ECO + Span 60; (c) ECO + Span 20.

It can be seen that there is a direct correlation between the PIT values and the particle size distribution. The smallest particles were detected for emulsions having highest PIT values.

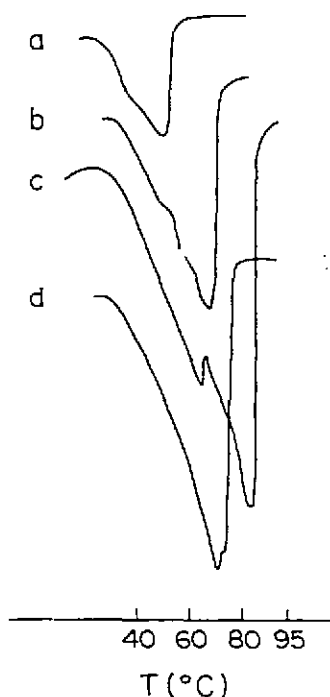Several combinations of one particular emulsifier blend were used in order

Fig. 4. Influence of the emulsifier's HLB value on the PIT of the emulsion as recorded from DTG curves. Heating rate = $2°C$ min^{-1}; $\phi = 0.2$; 10% ECO + Span 20. (a) HLB = 10.5; (b) HLB = 11.0; (c) HLB = 11.5; (d) HLB = 12.0.

to prepare emulsions with different HLB values. Figure 4 demonstrates the DTG curves obtained for such combinations. The PIT varies from $48°C$ to $80°C$. It can be seen that the best HLB combination for the soya bean oil emulsion was 11.5 while emulsifiers with higher and lower HLB values gave lower PITs and less stable emulsions.

Additional confirmation of those observations was found when particle size distribution was examined under the microscope (Fig. 5). The emul-

TABLE 1

PITs of emulsions of soya bean oil in water in which the concentration of emulsifiers and the oil phase has been varied; the emulsifier was a blend of ethoxylated castor oil and Span 20 at HLB = 11.5

% Emulsifier	% Oil	PIT ($°C$)
2	20	42
5	20	56
10	20	80
15	20	82
20	20	84
10	10	82
10	20	80
10	30	60
10	40	<50

sions with the high PIT values had small oil droplets while unstable emul-
sions had large particles.

The concentration of the oil phase was also changed from 10 to 40% caus-
ing a decrease in the observed PIT values (Table 1). In addition, it can be
demonstrated that emulsions prepared with higher concentrations of emulsi-
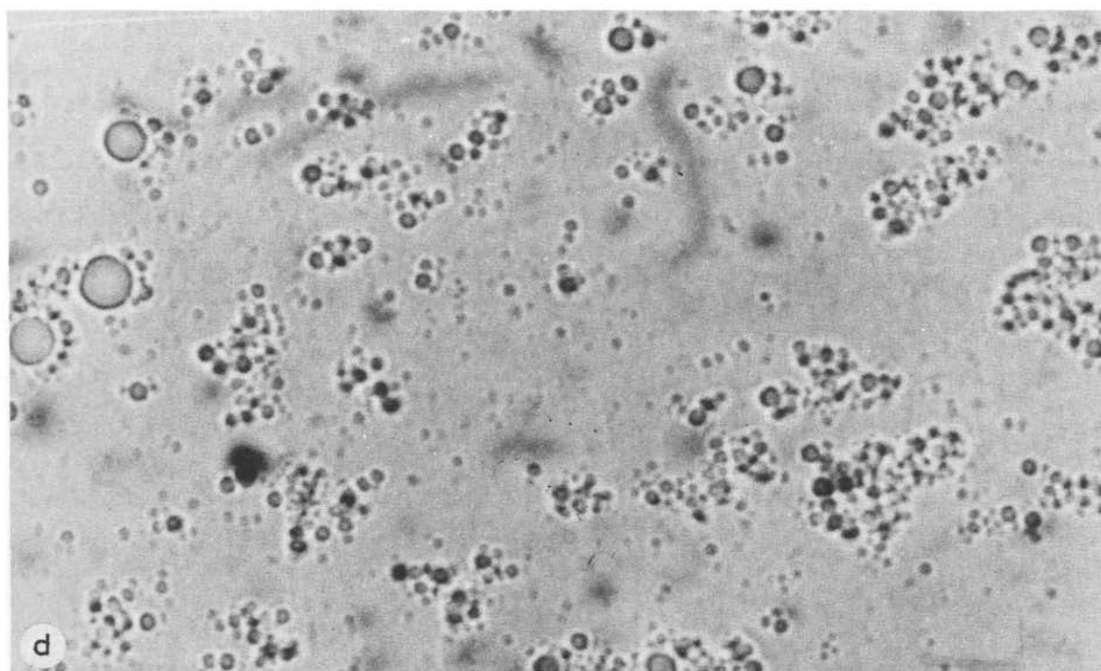fiers will have high PIT values and increasing stability. When the emulsifer
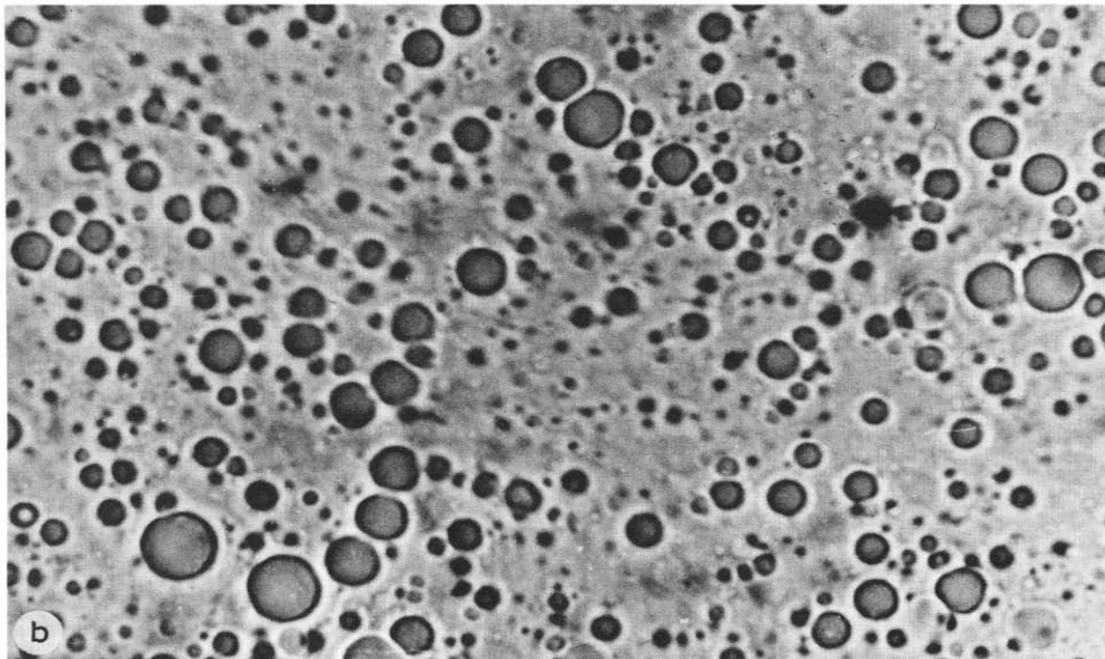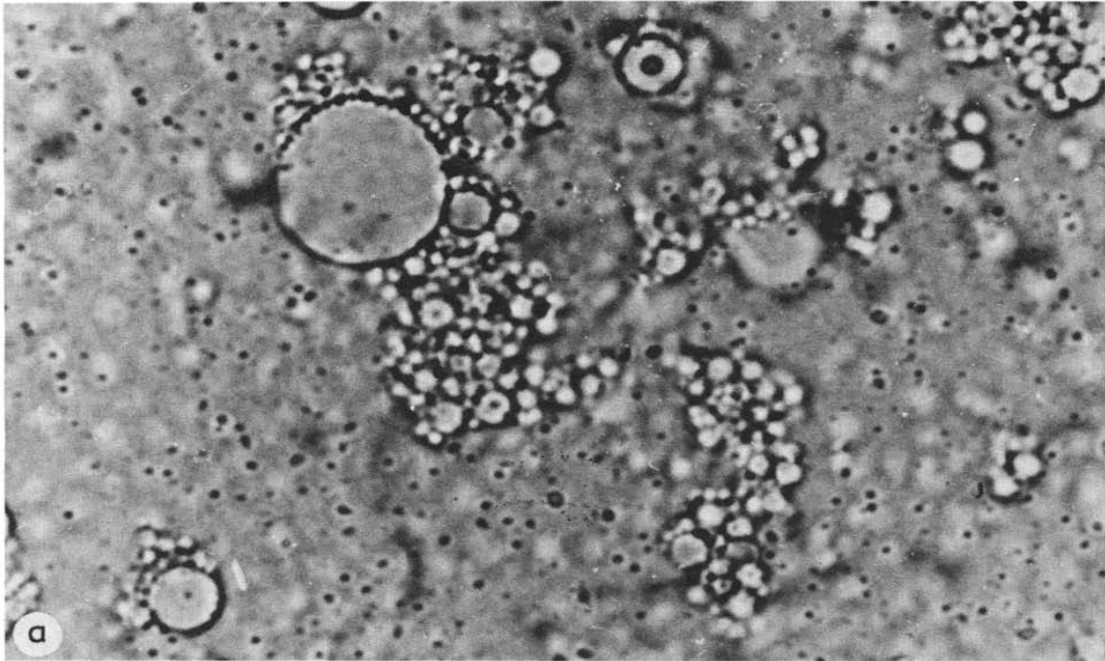
Fig. 5. Droplets of emulsion prepared from different emulsifiers' HLB. (a) HLB = 10.5; (b) HLB = 11.0; (c) HLB = 11.5; (d) HLB = 12.0. Emulsions as described in Fig. 4 (×1000).

concentration was only 2% of the total formulation low PIT values were detected, while when 20% emulsifer was used high PIT values were observed (Table 1).

DISCUSSION AND CONCLUSIONS

The data presented in this study suggest a rapid and simple method for measuring PIT values of oil in water emulsions. The DTG curves are more accurate than the DTA profiles and can be obtained using less complicated techniques. Furthermore, the proposed method measures loss of water which is easier for interpretation than change in the DTA during the heating process [11].

The experimental data can also contribute to the understanding of factors affecting PIT and emulsion stability. Among those parameters are the nature of the emulsifier's blend, the optimal HLB value, concentration of emulsifier and concentration of the oil phase.

ACKNOWLEDGEMENT

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