# Investigation of Phase Transitions in Glyceride/Paraffin Oil Mixtures Using Ultrasonic Velocity Measurements

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**A pulse echo technique has been used to measure the ultrasonic velocity of a number of 15% w/w glyceride/paraffin oil mixtures with increasing temperature (0-70 C). At the lower temperatures the glycerides are completely solid and there is a fairly steady decrease in velocity with temperature (ca. $-3.8$ ms$^{-1}$C$^{-1}$). As the temperature rises the glycerides become increasingly soluble in the paraffin oil and the velocity decreases more rapidly. Once the glyceride is completely soluble in the paraffin oil, a fairly steady decrease in velocity with temperature (ca. $-3.3$ ms$^{-1}$C$^{-1}$) resumes. The dependence of ultrasonic velocity on the amount of solid glyceride present means the technique can be used to investigate phase transitions in binary glyceride/oil mixtures.**

Ultrasonics has been used to investigate a number of the properties of fat/oil systems. These include solid fat content (SFC) determinations (1-5), estimation of crystal compressibilities (5), investigation of equilibrium properties of phase transitions (6) and characterization of liquid oils (7-12). The majority of these investigations have concentrated on naturally occurring animal or vegetable fats, whose principle constituents are the glycerides. Glycerides vary in type and proportion between different fats and determine many of their physical and chemical properties (13).

In order to appreciate the factors which influence the propagation of ultrasound in fatty materials it is necessary to understand the properties of their glyceride constituents. Previous workers have investigated the dependence of ultrasonic velocity on SFC for a number of triglyceride/oil mixtures (2,3), the dependence of velocity on temperature for tristearin and for triolein (5) and the relationship between the velocity and molecular formula of many liquid triglycerides and fatty acid methyl esters (7,8,11,12). In this work the variation of ultrasonic velocity with temperature is examined for a number of glyceride/paraffin oil mixtures which undergo phase transition. The factors which influence the velocity in these mixtures also are discussed. The glycerides were diluted to 15% w/w with paraffin oil to prevent vacuole formation (14), which can cause large attenuation of an ultrasonic signal.

## MATERIALS AND METHODS

*Materials.* Tristearin (SSS); tripalmitin (PPP); trilaurin (LLL); distearin (SS); glycerol 1,3 dipalmitate-2-oleate (POP); glycerol 1,3 distearate-2-oleate (SOS); glycerol 1,3 dipalmitate-2-stearate (PSP), and glycerol 1-palmitate-2-oleate-3-stearate (POS) were supplied by Unilever Research Laboratories (URL), Colworth House, England. Stearic acid (SA) was obtained from BDH Chemicals Ltd., United Kingdom. The purity of the mono-acid saturated triglycerides was determined at URL using high pressure liquid chromotography (HPLC) of the fatty acid methyl esters (FAME), and was better than 96% (2). Paraffin oil was obtained from Boots Company, Nottingham, England.

*Sample preparation.* The physical properties of fat/oil mixtures depend on their thermal and shear history (15); thus, samples were prepared using a constant tempering procedure. Fat and oil were weighed into a small glass cuvette, mixed thoroughly, and melted at 80 C in a vacuum oven to remove any air. The mixture was then placed in a 5 C water bath where it was left overnight, to ensure complete crystallization, before measurements were made. Sedimentation in the samples was negligible due to the formation of a matrix of interlinking needle-like crystals (as observed by light microscopy). X-ray diffraction patterns of the crystallized mono-acid saturated triglycerides corresponded to the $\beta$-polymorphic form. The rapid transformation of triglycerides to their most stable form in binary triglyceride/oil mixtures has been noted elsewhere in the literature (16-18).

*Ultrasonic measurements.* The ultrasonic velocity of the samples was measured with increasing temperature using a pulse echo technique described in an earlier paper (2). Using this technique, the velocity can be determined to within 0.7 ms$^{-1}$. However, there are ultrasonic instruments available commercially that are accurate to 0.1 ms$^{-1}$ which may be adapted for this type of measurement.

## RESULTS AND DISCUSSION

The ultrasonic velocity with increasing temperature for the 15% w/w glyceride/paraffin oil mixtures investigated is shown in Figures 1-5. The results for paraffin oil (which is liquid across the whole temperature range) and for 15% w/w tristearin in paraffin oil are shown in Figure 1. The curves drawn through the experimental results were calculated using a cubic polynomial, and are included in Figures 2-5 for comparative purposes.

The velocity versus temperature profiles of all the mixtures follow a similar trend represented diagramatically by Figure 6. The glyceride is completely solid at lower temperatures, and there is a fairly constant decrease of velocity with increasing temperature (region I). As the temperature rises further the glycerides melt and the velocity decreases more rapidly (region II). Once the glyceride reaches a temperature where it is completely liquid, the decrease in velocity with temperature is again fairly constant (region III). The exceptions to this trend are the POS and POP in paraffin oil mixtures because their triglyceride components are still partially soluble at the lower temperatures (Figs. 3,4). The ultrasonic velocity is higher in solid than in liquid glyceride due to the greater elastic modulus of the solid phase (5).

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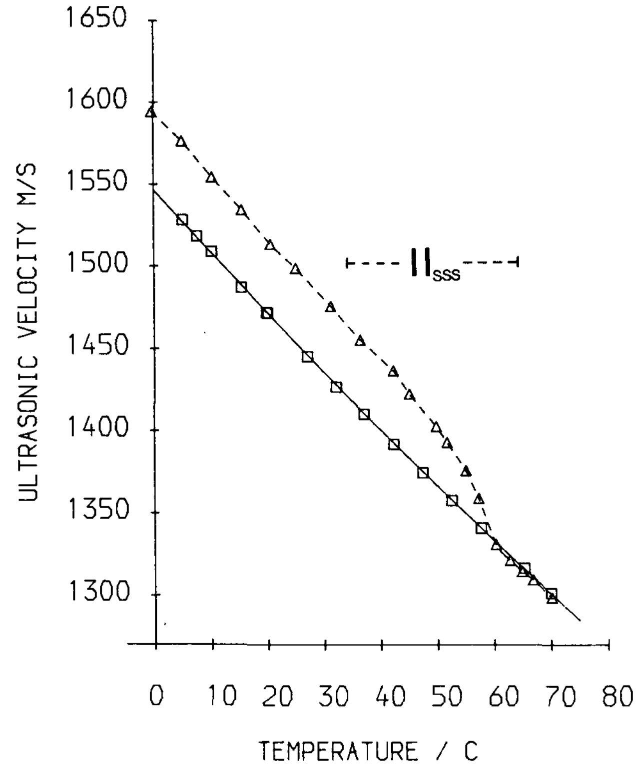

FIG. 1. Variation of ultrasonic velocity with increasing temperature for paraffin oil (□) and 15% w/w tristearin in paraffin oil (△). Curves drawn using cubical polynomial. II indicates the temperature range of region II as calculated by Equation 2 in the text.

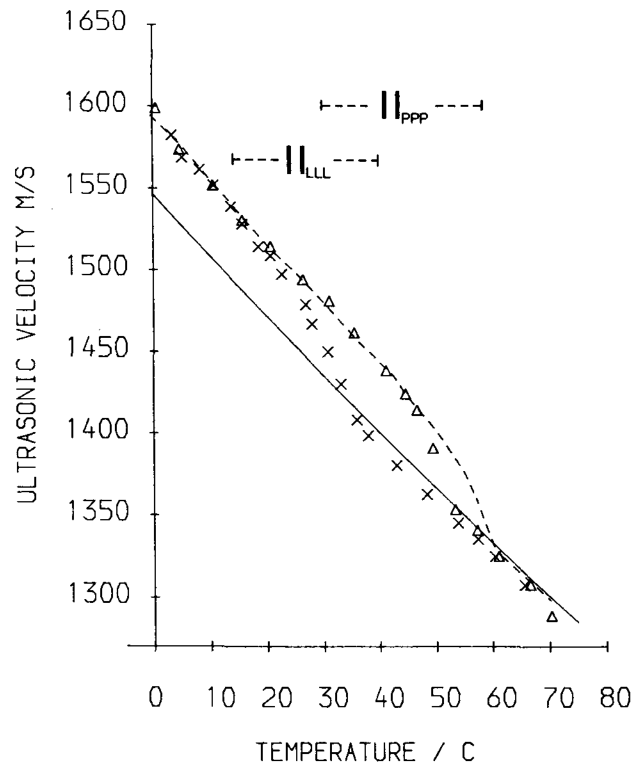

FIG. 2. Variation of ultrasonic velocity with increasing temperature for 15% w/w tripalmitin in paraffin oil (△) and 15% w/w trilaurin in paraffin oil (X). II indicates the temperature range of region II as calculated by Equation 2 in the text.

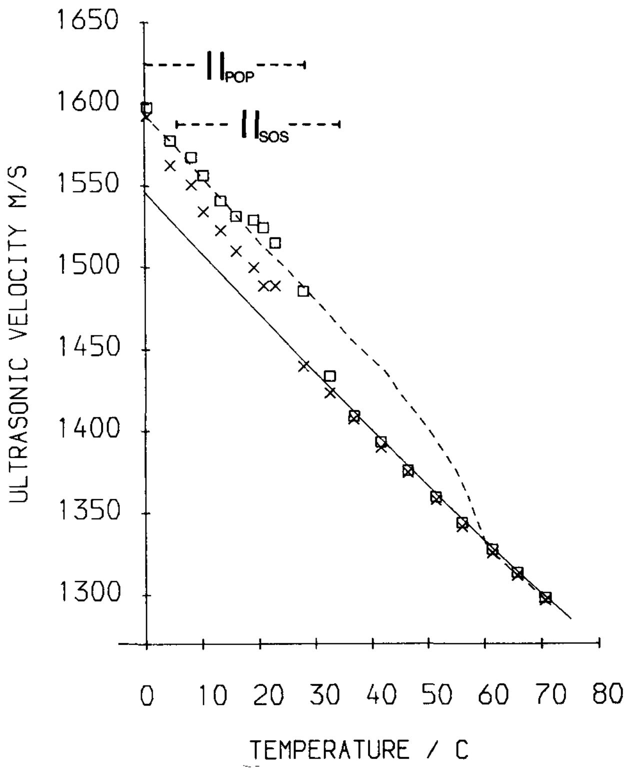

FIG. 3. Variation of ultrasonic velocity with increasing temperature for 15% SOS in paraffin oil (□) and 15% w/w POP in paraffin oil (X). II indicates the temperature range of region II as calculated by Equation 2 in the text.

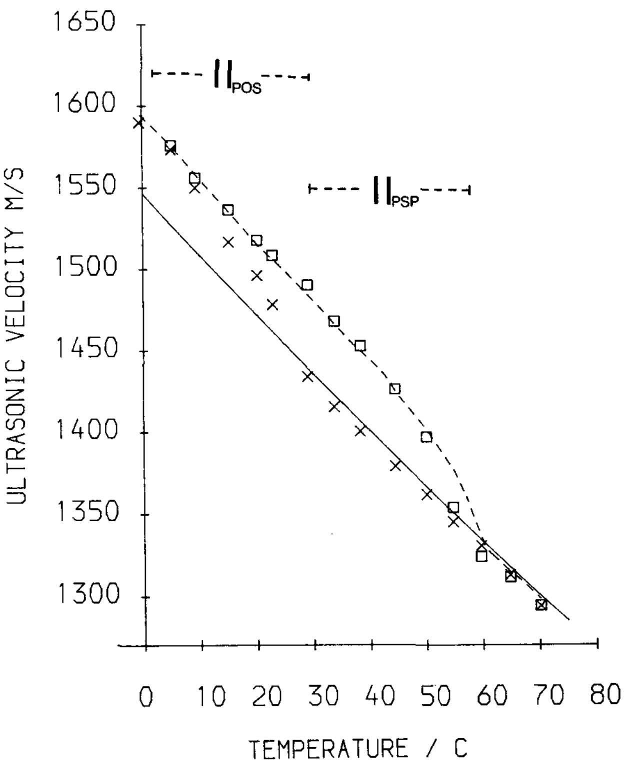

FIG. 4. Variation of ultrasonic velocity with increasing temperature for 15% w/w POS in paraffin oil (X) and 15% w/w PSP in paraffin oil (□). II indicates the temperature range of region II as calculated by Equation 2 in the text.

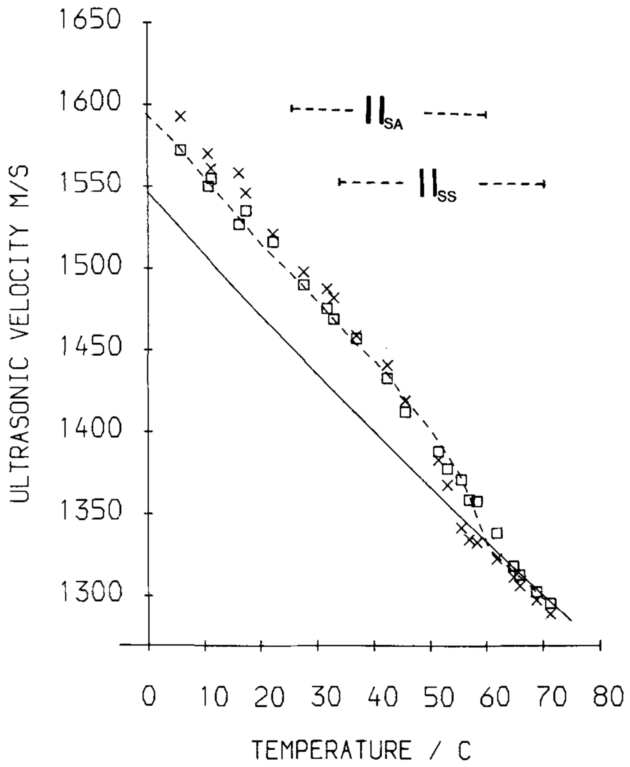

**FIG. 5. Variation of ultrasonic velocity with increasing temperature for 15% w/w distearin in paraffin oil (□) and 15% w/w stearic acid in paraffin oil (X). II indicates the temperature range of region II as calculated by Equation 2 in the text.**

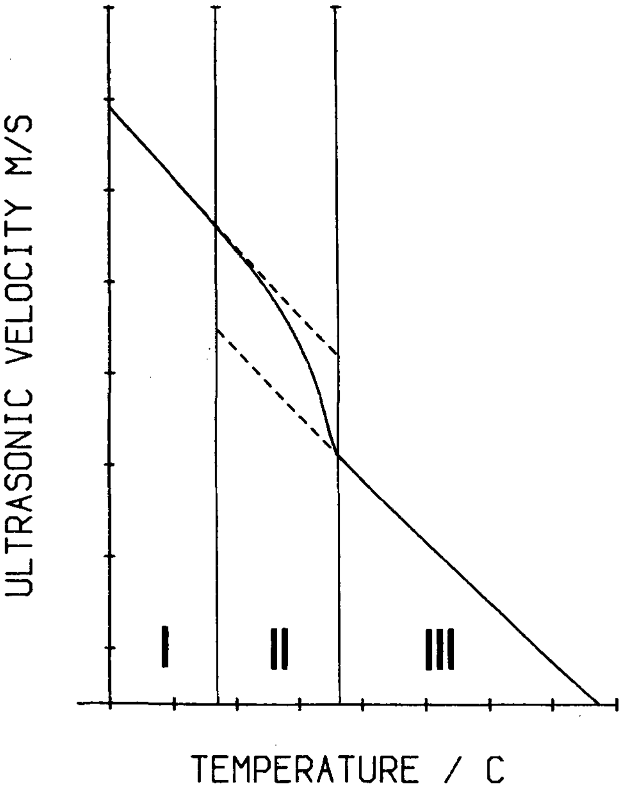

**FIG. 6. Diagrammatic representation of the variation of ultrasonic velocity with temperature for a glyceride/paraffin oil mixture. In region I the triglyceride is completely solid, in region III it is completely liquid and in region II it is part solid and part liquid.**

In the following sections the factors which influence the ultrasonic velocity of the glyceride/paraffin oil mixtures in the three regions are discussed.

*Region I.* The variation of velocity with temperature in region I can be described using Taylor series expansions (1). However, a better fit to our results was obtained using an exponential function of the form:

$$v = a.\exp(bT) \qquad [1]$$

where v is the velocity, T is the temperature and a and b are constants which are determined using least squares regression analysis of experimental measurements. The values of a and b, calculated from the measurements shown in Figures 1-5, are listed in Table 1 for those mixtures where there was sufficient data.

An examination of region I in Figures 2-4 and Table 1 indicates that the type of solid triglyceride present does not greatly influence the velocity through the sample; all the triglyceride mixtures investigated have similar variations of velocity with temperature (ca. $-3.8\ ms^{-1}C^{-1}$). However, Figure 5 and Table 1 show that the velocities of the distearin and stearic acid in paraffin oil mixtures are significantly larger than those of the triglyceride mixtures. This is important because when the technique is used for determining SFC in fatty materials it is usually assumed that each component, in relation to its amount, yields a linear contribution to the solid content (15). Triglycerides, however, make up a large proportion of most fats, and therefore it does seem reasonable to assume that the ultrasonic velocity is independent of the type of solid fat present.

*Region III.* In region III the variation of ultrasonic velocity with temperature can also be described by Equation 1. Table 1 lists the values of a and b calculated using least squares regression analysis of the experimental results shown in Figures 2-5. It can be seen that the temperature coefficient of the velocity of the various glyceride/paraffin oil mixtures is similar (ca. $-3.3\ ms^{-1}C^{-1}$). However, they have significantly different absolute velocities. This is because the various glyceride components have different ultrasonic velocities (8,11,12), and the velocity of an oil mixture depends on the velocities and concentration of its component phases (11,12).

*Region II.* In region II the decrease in ultrasonic velocity with increasing temperature is greater than in regions I and III. This is because the melting of the solid glyceride leads to a decrease in velocity which is superimposed on the decrease due to the temperature coefficients of velocity of regions I and III. The different solubilities of the glycerides in paraffin oil mean that the position of region II in Figures 1-5 depends on the type of glyceride present. The solubility of solid glycerides in oil can be described, to a first approximation, by the following equation, which assumes the mixture follows ideal solubility behavior (18-20):

$$\ln(x) = \Delta H_f/R.(1/T-1/T_{mp})$$

Here x is the mole fraction of glyceride in the liquid phase, $\Delta H_f$ is the enthalpy change per mole of crystallizing material, R is the gas constant, $T_{mp}$ is the absolute melting point of the pure glyceride and T is the abso-

**TABLE 1**

**Variation of Ultrasonic Velocity with Temperature for Regions I and III of the 15% w/w Glyceride/Paraffin Oil Mixtures shown in Figures 1-5**[a]

| | Region I | | | | | Region III | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Glyceride | n | $a/ms^{-1}$ ± 0.5 | $b/C^{-1}$ ± 0.00007 | r | $dV/dT/ms^{-1}C^{-1}$ ± 0.1 | n | $a/ms^{-1}$ ± 0.5 | $b/C^{-1}$ ± 0.00007 | r | $dV/dT/ms^{-1}C^{-1}$ ± 0.1 |
| SSS | 7 | 1594.5 | -0.00247 | -0.999 | -3.8 | 4 | 1545.5 | -0.00248 | -0.999 | -3.3 |
| PPP | 7 | 1595.4 | -0.00246 | -0.997 | -3.8 | 4 | 1545.3 | -0.00249 | -0.997 | -3.3 |
| LLL | 4 | 1593.4 | -0.00247 | -0.999 | -3.9 | 8 | 1534.3 | -0.00244 | -0.999 | -3.3 |
| PSP | 6 | 1594.2 | -0.00243 | -0.999 | -3.7 | - | - | - | - | - |
| POP | - | - | - | - | - | 6 | 1537.9 | -0.00242 | -0.999 | -3.3 |
| SOS | - | - | - | - | - | 6 | 1539.0 | -0.00241 | -0.999 | -3.2 |
| POS | - | - | - | - | - | 6 | 1540.6 | -0.00247 | -0.999 | -3.2 |
| SS | 11 | 1599.1 | -0.00252 | -0.995 | -3.8 | 5 | 1553.6 | -0.00254 | -0.995 | -3.3 |
| SA | 11 | 1614.5 | -0.00260 | -0.993 | -4.0 | 10 | 1540.7 | -0.00249 | -0.998 | -3.3 |
| Paraffin oil | - | - | - | - | - | 15 | 1546.6 | -0.00247 | -1.000 | -3.5 |

[a] Results are presented in the form of exponential equations: v = a.exp(bT), where v is the ultrasonic velocity, T is the temperature, r is the correlation coefficient, n is the number of data points and a and b are constants calculated using least squares regression analysis.

lute temperature. The mass fraction ($\phi_m$) of glyceride in the solid state can then be calculated at any temperature from the relation:

$$\phi_m = [\phi_g - x(1-\phi_g)MWg/MW_o(1-x)]/\phi_g \quad [2]$$

where $MW_g$ and $MW_o$ are the molecular weights of the glyceride and oil phase, respectively, and $\phi_g$ is the total mass fraction of glyceride present in the mixture. The position of region II for a particular glyceride/oil mixture therefore depends primarily on the melting point and heat of fusion of the glyceride component.

*Investigation of phase transitions.* The dependence of the ultrasonic velocity on the amount of solid glyceride present suggests that the ultrasonic technique may prove a useful tool for investigating phase transitions (1,5). To do this it is necessary to relate the ultrasonic velocity of a mixture to the amount of solid glyceride present.

This can be done using a method similar to that suggested by Miles et al (1).

In region I the glyceride is completely solid, in region III it is completely liquid, in the intermediate region it is partly solid, partly liquid (region II). To estimate the amount of solid glyceride in region II it is assumed that the mixture consists of a 'solid' and a 'liquid' phase whose velocities and densities are the same as those found by extrapolation from regions I and III, respectively. Thus, the variation of velocity with temperature of the 'solid' and 'liquid' phases in region II is described by Equation 1 and the values of the constants a and b, given in Table 1 (Fig. 6). The variation of density with temperature for the 'solid' and 'liquid' phases can be described in a similar manner using the relation:

$$\varrho = c.\exp(dT) \quad [3]$$

where $\varrho$ is the density, T is the temperature and c and d are constants calculated using least squares regression analysis of experimental density measurements.

The velocity of a mixture can then be related to the ratio of solid to total glyceride at any temperature using the Equation (1-4):

$$v = [(\phi\varrho_I + (1-\phi)\varrho_{III})(\phi/\varrho_I v_I^2 + (1-\phi)/\varrho_{III} v_{III}^2)]^{-1/2} \quad [4]$$

Where the subscripts I and III represent the extrapolated values of the relevant parameters from regions I and III, respectively, and $\phi$ is the ratio of solid to total glyceride (v/v). This equation assumes that the component phases do not dissolve in one another (i.e., $\Sigma\,\phi = 1$), that the fat crystals are much smaller than the ultrasonic wavelength, that no scattering of the ultrasound occurs and that interaction between the fat crystals is negligible (3,4). Equation 4 has been used by a number of workers to model the ultrasonic velocity through triglyceride/oil mixtures, and good agreement has been found between theory and experiment for SFC up to 15% (2-4); therefore, it should be applicable to the systems used in this work. However, it must be appreciated that this equation is only a limiting case of more general formulations, and that significant deviations from it may occur when ultrasonic scattering is important, i.e., in emulsions (4).

If the densities of the 'solid' and 'liquid' phases are similar (i.e., $\varrho_I \approx \varrho_{III}$), then a simpler form of Equation 4 can be used which depends on velocity measurements only (1):

$$v = [\phi/v_I^2 + (1-\phi)/v_{III}^2]^{-1/2} \quad [5]$$

*Predictions of solid content in the tristearin/paraffin oil mixtures.* Using this technique, the variation of solid glyceride with temperature was calculated for the 15% w/w tristearin in paraffin oil mixture. The variation of velocity with temperature for the 'solid' and 'liquid' phases was calculated using Equation 1 and the parameters given in Table 1. The densities were calculated from the volume averaged values of experimentally measured paraffin oil densities and values of the density of tristearin found in the literature (23). Least squares

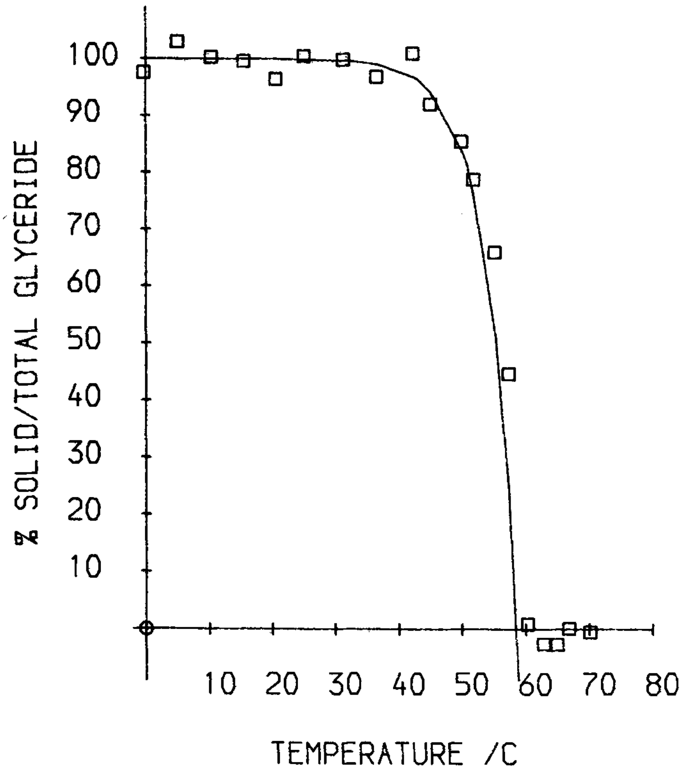

**FIG. 7.** Variation of percentage solid to total triglyceride with increasing temperature for a 15% w/w tristearin in paraffin oil mixture (1 MHz). □, values estimated using the ultrasonic technique; ——, values calculated from the ideal solubility equation (Equation 2).

regression analysis gave the constants $c = 907.2\ kgm^{-3}$, $d = -0.00063\ C^{-1}$ for region I and $c = 893.0\ kgm^{-3}$, $d = -0.00072\ C^{-1}$ for region III. The variation of solid tristearin with temperature was then calculated from the experimental velocity measurements shown in Figure 1 using a rearranged form of Equation 4 (1) (Fig. 7). For comparison, the solid tristearin content predicted using the ideal solubility equation (Equation 2) was also plotted on Figure 7 (using the values $T_{mp} = 74.0$ C, $\Delta H = 180 Jg^{-1}$ (18) and $MW_{paraffin\ oil} = 440$ (16)). The values of solid glyceride content determined by the ultrasonic technique are slightly above those predicted by the ideal solubility equation. This phenomena has also been observed by other workers (18), who attributed it to demixing.

Predictions of the solid tristearin content calculated using Equation 3 and those calculated using Equation 5 agreed to within 1%, and so Equation 5 may prove a more practical means of relating the ultrasonic velocity to the solid content because it requires velocity measurements only.

The relationship between the amount of solid glyceride present and ultrasonic velocity means that the ultrasonic technique should prove a useful means of examining phase transitions in binary glyceride/oil mixtures.

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