$C_{16}H_{32}O_2$. Its IR spectrum gave bands at 1740 cm^{-1} ($\underline{C}OOCH_3$). The NMR signals are at δ3.6s (3H, $COOC\underline{H}_3$), 2.25m (2H, $-C\underline{H}_2-COOCH_3$), 1.25br,s (chain $-C\underline{H}_2$) and 0.9t (3H, terminal $C\underline{H}_3$).

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A Study of Dilatation and Acoustic Propagation in Solidifying Fats and Oils: I. Theoretical

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ABSTRACT

A theoretical relationship is presented relating acoustic velocity to dilatation in two-phase systems. The theory is based on studies of seismic propagation by Kuster and Toksöz, who include acoustic propagation in a fluid matrix containing spherical or spheroidal solid inclusions as a special case of their theory. The relationship presented in this paper applies in the long wavelength limit and predicts a linear relationship between acoustic dilatation and volume dilatation in crystallizing liquids, when the acoustic dilatation is much less than unity. I anticipate that this theory may lead to the application of acoustics in the assessment of a wide range of crystallizing systems such as oils.

INTRODUCTION

A number of workers have studied the propagation of ultrasound in liquid oils (1,2,3), in milk (4) and in solidifying coconut oil (5). In addition, ultrasonics have been widely used to study phase transitions in other systems, and a number of workers have applied ultrasonics to the measurement of compressibility and other parameters in a wide variety of biphasic materials (7,8,9). In this paper I will concern myself solely with a two-phase system where the liquid forms the continuous matrix in which the solid phase is suspended. However, the theory on which I base my conclusions is general enough to allow extension to other situations.

THEORY

The treatment in this paper is based on the work of Kuster and Toksöz (7), who in turn developed their treatment of the subject from Ament (10). The problem may be stated as solving the equations of motion for acoustic waves in two-phase media. A number of alternative formulations of the problem exist (9) but that of Kuster and Toksöz is the most convenient for my purpose. Although Kuster and Toksöz's formulation applies to seismic waves in 2-phase media, propagation in a fluid matrix with spherical or spheroidal solid inclusions is included as a special case. In this case, a shear wave cannot be supported and a bulk compressive wave propagates in the liquid matrix. The solid inclusions are assumed to have a mean diameter of much less than one acoustic wavelength. Definitions of the symbols used in the treatment described below are given in Table I.

The starting equations are in Table II. Equations 1-4 are identical to equations 24-26 of Kuster and Toksöz. Note that equation 1 can be obtained by assuming that the effective compressibility of the system is simply the volume average of the compressibilities of the solid and liquid phases and that in equation 2, the ordinary composition rule for densities, equation 5, is modified by the motion of the solid inclusions, relative to the fluid. In addition, v* is the acoustic velocity that is actually measured for the complete system.

The following equations may be derived from equations 1-4 and 6:

$$K = K^*(1 - \epsilon\kappa) \qquad [7]$$

where $\kappa = 1 - K/K'$.

$$\rho^* = \rho(1 + \epsilon R)/(1 - 2\epsilon R) \qquad [8]$$

where $R = (\rho' - \rho)/(\rho + 2\rho')$.

$$\Delta v/v^* = 1 - \sqrt{K\rho^*/K^*\rho} \qquad [9]$$

We call this parameter the acoustic dilatation.

We can substitute for K* and ρ^* in equation 9, from equations 7 and 8 to obtain:

$$(1 - \frac{\Delta v}{v^*})^2 = (1 - \epsilon\kappa)(1 + \epsilon R)/(1 - 2\epsilon R) \qquad [10]$$

The above equation can be reduced under the following assumptions. If $\Delta v/v^* \ll 1$ and $\epsilon R \ll 1$ then

$$\epsilon = \frac{\Delta v}{v^*}\, 2/(\kappa - 3R) \qquad [11]$$

The problem of relating ϵ, the volume fraction of solid, to the dilatation D, as measured in conventional oil dilatometry, is discussed by Hannewijk et al. (11). They state that the volume fraction of solid, ϵ, is given by:

$$\epsilon = \frac{D}{D_s},$$

provided (a) that the solubility of the solid fraction in the liquid phase is negligible and (b) that the melting dilatations for all the solidifying components are the same. Under these conditions we can relate the dilatation D to the acoustic dilatation.

$$D \doteqdot \frac{\Delta v}{v^*} \frac{2D_s}{(\kappa - 3R)} \qquad [12]$$

The parameter $\alpha = 2D_s/(\kappa - 3R)$ may be taken as a constant if the temperature dependence of the quantities it is composed of is much less than that of D. In this case D will be linearly dependent as the acoustic dilatation.

DISCUSSION

Note from equation 9 that since the maximum acoustic dilatation occurs on complete solidification when $K^* = K'$ and $\rho^* = \rho'$, $(\Delta v/v^*)$ max $= 1 - \sqrt{(K\rho'/K'\rho)}$.

To estimate the values likely to be obtained in triglyceride mixtures for $(\Delta v/v^*)_{max}$, take a mixture of tristearin and triolein as an example. Triolein differs from tristearin by one double bond, otherwise, they are chemically similar. At 20 C tristearin is solid and completely insoluble in triolein and can, therefore, be expected to form a solid phase within a liquid matrix composed entirely of triolein, at low enough solid contents. From Figure 3 of Hussin and Povey (12), the velocity of sound in tristearin is 1950 ms^{-1} at 20 C; the density of tristearin is 856 kg m^{-3} at this temperature and the corresponding data for triolein are 1450 ms^{-1} and 899 kg m^{-3}. From equation 3, I therefore obtain .58 for K/K' and .95 for ρ'/ρ. Thus $(\Delta v/v^*)_{max}$ = .26.

In Figure 1, the relationship between ϵ and $\Delta v/v^*$ is plotted over the range of possible values for κ and R. The limits on the quantities in equation 10 are: $0 \leqslant \epsilon \leqslant 1$, $-1 \leqslant R \leqslant ½$ for $0 \leqslant (\rho,\rho') \leqslant 00$. In practice $K' > K$ for a crystallizing system, so the limits $0 \leqslant \kappa \leqslant 1$ and $-1 \leqslant R \leqslant ½$ have been taken in Figure 1.

Equation 10 (Fig. 1) is unlikely to be valid for values of ϵ near 1 because of multiple scattering and the need for a continuous liquid matrix in which the diameter of the included phase is much less than 1 acoustic wavelength. For values of $\kappa \doteqdot 3R$, $\Delta v/v^*$ is given by equation 10 and for $\kappa < 3R$, $\Delta v/v^*$ will be negative. The line for tristearin/triolein has the values $\kappa = 0.42$, $R = -.016$. For small values of R, $(1 - \Delta v/v^*)^2$ will be linearly dependent on ϵ over the entire range of ϵ.

In conclusion, the preceding development of the theory of Kuster and Toksöz indicates that the measurement of acoustic dilatation may provide a method for measuring solid content in a wide range of crystallizing systems. Its applicability in any particular case will depend on κ and R, on the relationship between the acoustic wavelength and inclusion diameter and on the existence of a continuous liquid matrix.

TABLE I

Definitions of Quantities

K	– Matrix bulk modulus
K'	– Inclusion bulk modulus
K^*	– Effective bulk modulus
ρ	– Matrix density
ρ'	– Inclusion density
ρ_g	– Static sample density
ρ^*	– Effective bulk density
V	– Matrix volume
V'	– Inclusion volume
m	– Sample mass
v	– Compressional wave velocity in the matrix
v*	– Effective compressional wave velocity
v'	– Compressional wave velocity in the inclusions
ϵ	– Volume fraction of inclusions
$\Delta v/v^* = 1 - v/v^*$	– Acoustic dilatation
D	– Dilatation
D_s	– Melting dilatation

TABLE II

Starting Equations

$$\frac{K - K^*}{K^*} = \epsilon \frac{K - K'}{K'} \qquad [1]$$

$$\frac{\rho - \rho^*}{\rho + 2\rho^*} = \epsilon \frac{\rho - \rho'}{\rho + 2\rho'} \qquad [2]$$

$$v^* = \sqrt{(K^*/\rho^*)} \qquad [3]$$

$$v = \sqrt{(K/\rho)} \qquad [4]$$

$$\rho_g = \epsilon\rho' + (1 - \epsilon)\rho \qquad [5]$$

$$\epsilon = \frac{V'}{V + V'} \qquad [6]$$

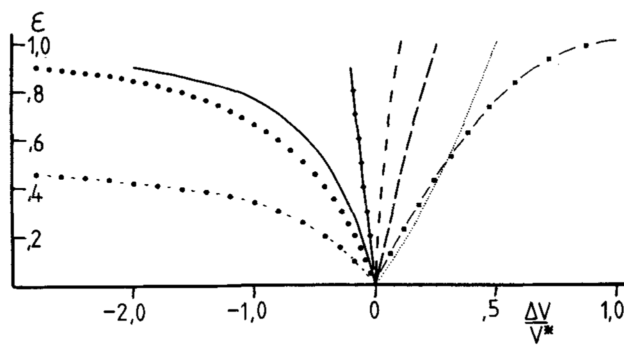

FIG. 1. The solid content, ϵ, plotted as a function of $\Delta v/v^*$ for ••• κ = 0,R = .5; .... κ = 0,R = −.5; ____ κ = .42,R = .5; __ __ __ κ = .42,R = 0; ____ ____ κ = .42,R = −.016; —▪—▪— κ = 1,R= 0; —♦—♦— κ = 1,R= .5

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