Migration of Dioctylphthalate and Dioctyladipate Plasticizers from Polyvinylchloride Films into Olive Oil

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ABSTRACT

The migration of dioctylphthalate (DOP) and dioctyladipate (DOA) plasticizers from food grade polyvinylchloride (PVC) films into commercial olive oil has been studied. Olive oil was chosen as a fat simulant. Experiments were carried out at 6, 22 and 30°C with and without agitation as a function of time (0–100 h). Two different PVC films were used containing 31·5% DOA and 29·5% DOP, respectively. Results showed a significantly higher amount of plasticizer migration into oil with agitation than without (30% versus 22·2% for DOP after 100 h). The equilibrium amount of DOA migrated was found to be higher than the respective amount of DOP whereas diffusion coefficients determined were slightly higher for DOP than DOA. These findings were related to solubility, compatibility and molecular weight of plasticizer. Data were fitted to the Arrhenius equation and activation energies for diffusion of plasticizers in PVC were calculated.

INTRODUCTION

Commercial plastics materials contain, besides the polymeric component, various processing aids, mainly plasticizers, and, to a lesser extent, antioxidants, lubricants, stabilizers, colorants, etc., which significantly improve chemical and mechanical properties of plastics such as flexibility, stability, tensile strength. (Crompton, 1979; Sears *et al.*, 1985). These

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additives are usually low molecular weight compounds possessing high mobility as a result of which they often migrate from the polymer matrix by diffusion into a liquid or solid contacting medium. Factors which influence potential migration of plasticizers include: (a) structure of the polymeric material, (b) method of plasticizer addition to the polymer, (c) compatibility of plasticizer/polymer, (d) nature of food contacting phase and (e) nature of plasticizer and external experimental conditions (temperature, time, agitation).

Among the most widely used plasticizers in food applications are DOP and DOA which have been the focus of many studies because of their potential toxicity to man.

Several studies on laboratory animals fed with diets containing such plasticizers, have reported symptoms such as reduced weight gain, enlargement of the liver, neuromuscular and skeletal abnormalities, reduction in incidence of pregnancies, etc. (Baker, 1978; Lawrence, 1978; Pollack et al., 1985). It has also been reported that the metabolite of DOP, mono(2-ethylhexyl)phthalate (MEHP) causes inhibition of growth and mutagenesis in several microorganism cultures (Ruuska et al., 1987).

The process of migration for most plasticizers obeys, only in certain cases, Fick's law of diffusion (Vergnaud, 1983). Usually Fick's law applies to polymers possessing a flexible rather than a stiff backbone (Little Inc., 1983). Diffusion in an isotropic medium is given by eqn (1):

$$\frac{dc}{dt} = \frac{d}{dx}\left(D\frac{dc}{dx}\right) \tag{1}$$

where D is the diffusion coefficient.

If the amount of plasticizer migrated at time t is M_t and M is the respective amount at equilibrium, then M_t will be given by eqn (2):

$$\frac{M - M_t}{M} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp - D\frac{(2n+1)^2\pi^2}{4L^2}t \tag{2}$$

where L is the film thickness.

Agitation, given by the Reynolds number, has also proved to be a very important factor in migration (Messadi et al., 1981).

The mathematical treatment of the phenomenon of migration becomes very complicated if one considers the simultaneous migration of the contacting liquid medium to the plastic material as well as the migration of the plastics components to the liquid medium.

The amount of plasticizer migrating can be determined either as the amount found in the liquid medium or by difference from the amount remaining in the polymeric material (Rossi, 1977).

There are several methods reported in the literature for the determination of migrating plasticizers such as radiolabelling, GC and HPLC methods (Kampouris *et al.*, 1975; Kampouris, 1976; Daun & Gilbert, 1977; Mori, 1976; Otsuki, 1977).

In the present work the migration of DOP and DOA plasticizers from food grade PVC wrapping films into olive oil at 6, 22 and 30°C has been studied. Experiments were carried out, with and without agitation, to determine its effects on migration. Olive oil was chosen both as a fat simulant of solid foods such as fat-rich meat products, wrapped in PVC films, and as a common liquid food. Diffusion coefficients and activation energies of diffusion for both plasticizers were also calculated.

MATERIALS AND METHODS

Materials

Two types of PVC film were used in all experiments; namely, RMF-61 containing 31·5% DOA and VF-71 containing 29·5% DOP of $13 \mu m$ (5×10^{-4} in) thickness. Both films were donated by Borden Chem. Division, N. Andover, MA, USA. Analytical grade DOA and DOP were purchased from Fluka AG, Buchs, Switzerland.

Migration experiment

Rectangular strips of each film were placed on a stainless steel screen of area $400 \, cm^2$. The film/screen combination was placed inside glass mason jars of 500 ml capacity. The jars were filled with olive oil and sealed (Fig. 1). At predetermined intervals, known aliquots of oil were removed from the jars and analyzed for plasticizer content. Migration experiments were carried out at 6, 22 and 30°C to simulate open refrigerator and room temperatures as well as 'extremely' hot day supermarket temperatures. Jars were sampled at 6, 18, 30, 50, 75 and 100 h (about 4 days). This period of 4 days corresponds to a typical holding time for fresh meat products before consumption. All experiments were carried out in triplicate.

Sample treatment for plasticizer analysis

Five millilitres of contaminated oil were saponified with 40 ml of KOH 2M in methanol for 3 h. After saponification methanol was removed by evaporation. Then the residue was acidified with HCl solution (1:1 v/v) and subjected to steam distillation until 200 ml of distillate were collected. The

Fig. 1. Cell assembly for migration studies of plasticizers from PVC film into olive oil.

distillate was shaken with 50 ml portions of diethyl ether and the extraction was repeated four times. The combined ether extracts were left overnight with 30 g of anhydrous sodium sulphate. Ethyl ether was separated from Na_2SO_4 and evaporated. The residue was redissolved in carbon disulphide and this solution was used for gas chromatographic analysis.

Gas chromatographic (GC) analysis

The alcoholic component of the plasticizer (2-ethyl hexanol) was determined under the following conditions.

Instrument
A Varian 3700 GC unit was used, equipped with a flame ionization detector. Column: Aluminium. 1·90 m long, 6·35 mm od. Stationary phase: 10% SE-30 on Anachrom ABS, 60–80 Mesh. Temperatures: Column, 165°C, injection port, 220°C, detector, 220°C.

Quantitation was made using an appropriate standard curve. The recovery factor of the above method was obtained by preparing olive oil samples with known amounts of DOA and DOP and determining the plasticizer content following the same course as for experimental samples. Recovery factors of 74·8% for DOA and 68·2% for DOP were obtained.
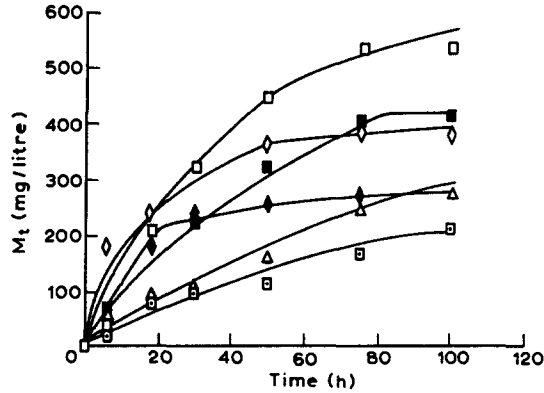
Fig. 2. Migration of DOA into olive oil at 6°C without agitation (⊡), with agitation (◆), at 22°C without agitation (△), with agitation (◇), and 30°C without agitation (■), with agitation (□).

RESULTS AND DISCUSSION

The amounts of DOA and DOP migrated to olive oil with and without agitation at 6, 22 and 30°C are given in Figs 2 and 3, respectively. It is clear from both figures that the amount of plasticizer migrated with agitation is significantly higher than that without agitation. As expected, agitation reduces the concentration of the migrating plasticizer in the boundary layer between film and oil resulting in the further migration (desorption) of the plasticizer, due to a higher concentration gradient of plasticizer between the two media.
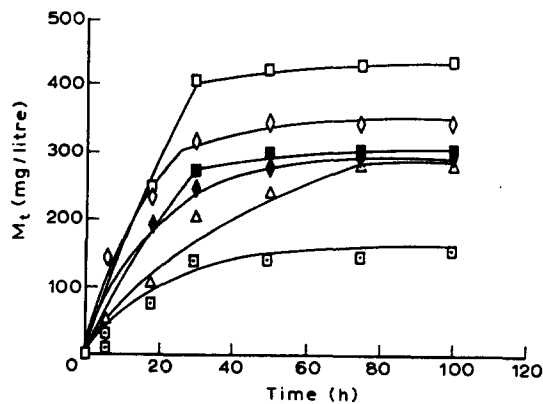

Fig. 3. Migration of DOP into olive oil at 6°C without agitation (⊡), with agitation (◆), at 22°C without agitation (△), with agitation (◇), and 30°C without agitation (■), with agitation (□).

The effect of temperature is also significant. For example, it is shown in Fig. 2 that, for an increase in temperature from 6 to 30°C, in the system without agitation, the amount of DOA migrated increases from approximately 200 mg/litre to over 400 mg/litre. Increase in temperature increases the mobility of the plasticizer molecules which desorb from the PVC film into the oil more freely.

Comparison of data in Figs 2 and 3 shows that equilibrium was attained faster in the system PVC film/DOP/olive oil than in the system PVC film/DOA/olive oil while the total amount of DOA migrated after 100 h was higher than that of DOP. This last observation can be possibly attributed to the higher solubility of DOA in the oil, as well as to the lower molecular weight of DOA versus DOP. Furthermore, the initial concentration of DOA in the film was slightly higher than the respective DOP concentration. The diffusion coefficients were also calculated for both systems with and without agitation.

Assuming long migration times and a diffusion coefficient independent of concentration, eqn (2) can be reduced to (Till *et al.*, 1982; Papaspyrides, 1986):

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right)\exp\left(-\pi^2 Dt/L^2\right) \tag{3}$$

Equation (4) can be used instead of eqn (3) for the initial stages of migration:

$$M_t = 2C_{p0}(Dt/\pi)^{1/2} \tag{4}$$

where M_t is the amount of plasticizer migrated in time t, expressed in mg/cm^2 and C_{p0} is the initial concentration of plasticizer in the film expressed in mg/cm^3.
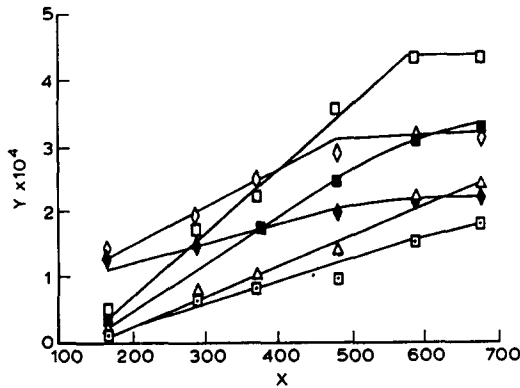

Fig. 4. Plot of $x = 2(t/\pi)^{1/2}$ versus $y = (Mt/C_{p0})$ for DOA at 6°C without agitation (⊡), with agitation (◆), at 22°C without agitation (△), with agitation (◇) and 30°C without agitation (■), with agitation (□).
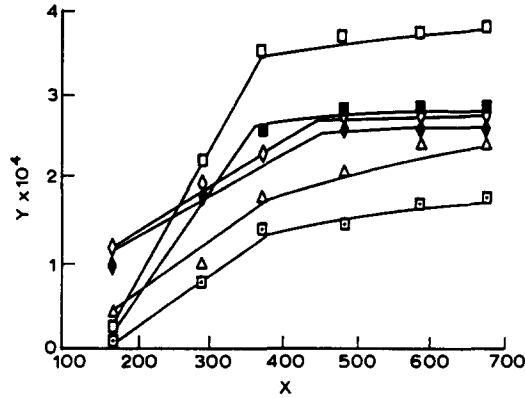
Fig. 5. Plot of $x = 2(t/\pi)^{1/2}$ versus $y = (Mt/C_{p0})$ for DOP at 6°C without agitation (⊡), with agitation (◆), at 22°C without agitation (△), with agitation (◇), and 30°C without agitation (■), with agitation (□).

A plot of M_t/C_{p0} against $2(t/\pi)^{1/2}$ is initially linear and has a slope of $D^{1/2}$ (Figs 4 and 5). Diffusion coefficient values for both systems are given in Table 1.

From Table 1 and Figs 2 and 3 it is clear that, even though the total amount of DOA migrated is higher than the respective amount of DOP, the diffusion coefficient values for DOA are lower than those for DOP. It seems possible that the mechanism of plasticizer migration during the initial stages of migration—stages for which diffusion coefficient values were calculated—is different from that during the later stages. It seems that the PVC film containing DOP is rapidly attacked by olive oil and thus releases significant amounts of plasticizer during the initial stages of migration (high D value). In contrast, the PVC film containing the DOA is slowly attacked by the oil and thus releases DOA in smaller amounts (lower D value). As a result migration of DOP from the first film reaches equilibrium in approximately 30 h while

TABLE 1

Diffusion Coefficient Values of DOA and DOP at Various Temperatures with and without Agitation

T °C	DOA		DOP	
	w/o agitation	*w/agitation*	*w/o agitation*	*w/agitation*
	$D\,(cm^2/s)$		$D\,(cm^2/s)$	
6	$3{\cdot}0 \times 10^{-14}$	$0{\cdot}6 \times 10^{-13}$	$1{\cdot}5 \times 10^{-13}$	$2{\cdot}5 \times 10^{-13}$
22	$1{\cdot}4 \times 10^{-13}$	$2{\cdot}5 \times 10^{-13}$	$4{\cdot}5 \times 10^{-13}$	$7{\cdot}0 \times 10^{-13}$
30	$0{\cdot}5 \times 10^{-12}$	$1{\cdot}0 \times 10^{-12}$	$1{\cdot}6 \times 10^{-12}$	$2{\cdot}6 \times 10^{-12}$

migration of DOA from the second film approaches equilibrium after 100 h. The explanation is possibly related to the specific way in which the plasticizers are retained in the polymer matrix (plasticizer/polymer compatibility).

Table 1 also shows that, for a given plasticizer system and temperature, the diffusion coefficient values approximately double with the introduction of agitation in the system while, for a given system and conditions of agitation, a five-fold increase in temperature results in an approximately 10-20-fold increase in diffusion coefficient values. This shows the relative effect of temperature and agitation on diffusion coefficient values.

Our diffusion coefficient values, approximately 2×10^{-13} for DOA and 6×10^{-13} for DOP in the presence of olive oil at 22°C, are significantly lower than those of Messadi and Vergnaud (1981) and Messadi et al. (1981) who reported D values for DOP in the range of 10^{-8} in the presence of benzyl alcohol and in the range of 10^{-7} in the presence of n-heptane at 30°C (initial concentration of plasticizer = 25% w/w; sample thickness = 3·4 mm). They are also significantly lower than those of Papaspyrides (1986), who reported D values for DOP: 4×10^{-9}, 1×10^{-8} and $9·5 \times 10^{-9}$ in the presence of methanol, n-propanol and n-butanol, respectively, at room temperature (initial concentration of DOP = 50%, samples thickness = 2·5 mm). Differences reflect the higher extraction potential of organic solvents versus edible oils as well as the significantly larger thicknesses of PVC samples used by these authors.

Our D value (approximately $0·5 \times 10^{-13}$ for DOA at 6°C) correlates rather well with that of Till et al. (1982) who estimated a value of approximately $2·3 \times 10^{-12}$ cm²/s in the presence of corn oil at 4°C (initial DOA concentration 24% w/w, sample thickness 66 μm), considering the larger film thickness of PVC sample used by these authors.
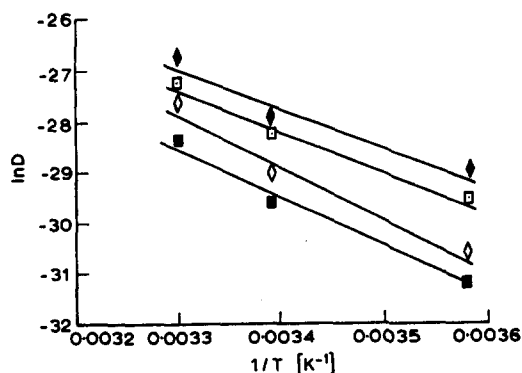

Fig. 6. Arrhenius plots of lnD versus $1/T$ for DOP without agitation (□), with agitation (◆) and DOA without agitation (■), with agitation (◇).

TABLE 2
Activation Energy Values for Diffusion of DOP and
DOA with and without Agitation

System	Ea (kcal/mol)
DOP w/o agitation	16·5
DOP w/agitation	15·7
DOA w/o agitation	19·4
DOA w/agitation	19·1

Finally, our value of 5×10^{-13} for DOA at 6°C is significantly below that extrapolated from Quackenbos' (1954) data (2×10^{-10} cm^2/sec) in the presence of mineral oil (initial DOA concentration = 45% w/w; sample thickness = 40 μm). The difference can be again attributed to a significantly higher DOA initial content as well as film thickness resulting in increased D values.

Changes in diffusion coefficient values with temperature (Table 1) were found to obey an Arrhenius type equation:

$$D = A \exp(-Ea/RT) \tag{5}$$

where A is the preexponential factor and Ea is the activation energy for diffusion. Using the Arrhenius plot (Fig. 6), the activation energy for diffusion for both systems was calculated. Values are given in Table 2.

Table 2 shows that, in the case of agitation, slightly lower Ea values (enhanced diffusion) are calculated than those without agitation. It is also clear that Ea values for DOA are higher than those for DOP, which is in general agreement with the above data on diffusion coefficient values.

It is obvious that olive oil used as a simulating solvent for fatty foods will extract a higher amount of plasticizer than would the solid food. In this respect present data should be used with caution. They are, however, perfectly valid when used to estimate the diffusion coefficient of the plasticizers in the PVC film. The study of migration of DOP and DOA in solid fatty foods will be the objective of a forthcoming paper.

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