Evaluation of a Mathematical Model of Diocyl Phthalate Plasticizer Migration from PVC Discs into Colza Oil

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ABSTRACT

Results of long time tests are given for migration of diocyl phthalate (DOP) from solid PVC discs into well-stirred colza oil. The following factors were examined: time, plasticization level (from 20 to 50 wt%), and temperature (30 and 50°C). The use of labelled DOP and radioactivity measurements in conjunction with weight loss give quantitative information on the mass exchanged (plasticizer migration and colza oil penetration) and lead to DOP concentration profiles that are developed through the bulk of polymer during the process. Mathematical model investigated in this study takes into account the following conditions: (1) the concentration of colza oil in the polymer matrix was neglected; (2) the diffusion in transient conditions through the PVC mass with DOP concentration-dependent diffusivity was considered. Statistical analysis shows that this self-consistent model is able to reproduce, to a good approximation for the DOP, the concentration profiles in the polymer, and the kinetics of transfer into the oil.

INTRODUCTION

Properties of poly(vinyl chloride) (PVC), an important commodity industrial polymer, are modified by compounding with a compatible plasticizer.

Generally, plasticizers are incorporated into plastic materials to improve their workability through the decrease of the characteristic temperature of glass-to-rubber transition, $T_g$ [1] and increase of flexibility.

Plasticized PVC is often used in the packaging industry for liquid foods [2]. In all applications, the
plasticized PVC is in contact with the surrounding medium and the plasticizer may migrate with the following results [3-10]:

(i) Because of plasticizer loss, the polymer deteriorates its mechanical properties.

(ii) The surrounding medium is contaminated by the plasticizer. This problem is complicated by several factors:

(a) In a variety of contexts, there is a simultaneous transport of the liquid into, and the plasticizer out of the PVC. However, the amount of liquid transported into PVC often follows a more complex phenomenon. This amount increases rapidly to a maximum value; then, the liquid comes out partially (counterdiffusion) [11].

(b) For both these transfers, the diffusivity is concentration-dependent.

(c) Many factors may affect the migration process, including the nature of the polymer and plasticization process, the surrounding medium, the nature and amount of plasticizer, and the conditions of migration process, i.e., stirring, time, and temperature.

The migration is a slow process which can take several months at storage temperatures, thus shorter time tests at higher temperatures were proposed. On the other hand, the problem of identifying migrating species in the presence of chemically complex structures led very quickly to the simulation of real foodstuffs by pure products. However such simulations are, not conclusive.

Some authors[12] consider it better to derive mathematical models rather than change the conditions of the experiments. Sophisticated theoretical models, concerned with transfer of plasticizer into pure solvents, have been referred to in the literature and they must be adjusted to real foodstuffs.

In this paper, the results of long time tests are given for migration of the plasticizer (dioctyl phthalate: DOP) from solid PVC discs into well-stirred (Reynolds number is about 2000) colza oil, using a method based on labelled plasticizer and measurements of the radioactivity of the two in-contact phases. The following factors were examined: time, plasticization level (ranging from 20 to 50 wt%) and temperature (30 and 50°C). The transport kinetics in the liquid foodstuff are completed by the study of the migratory phenomenon developed through a particular disc matrix.

Low penetration advantage of the edible oil within the PVC samples in order to test a simplified mathematical model is considered. Calculated and measured DOP concentrations in colza oil, as well as calculated and measured DOP concentration profiles that are developed through PVC matrix are compared by using the one-way analysis of variance.

**THEORY**

The following assumptions were made:

(1) PVC discs are used and the case of one dimensional diffusion in a medium bounded by two parallel planes is considered, e.g., the planes \(x = \pm L\).

(2) Concentration of colza oil in bulk polymer is neglected.

(3) The transfer of DOP through PVC mass is obtained by diffusion in unsteady state, as the diffusivity is dependent on the plasticizer concentration.

(4) The concentration of the plasticizer on the PVC surface reaches the equilibrium value as soon as the PVC sample is soaked in the colza oil.

It has been generally assumed that diffusion under transient conditions is as described by Fick's equation [13]:

\[
\frac{\partial C}{\partial t} = \frac{1}{D} \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)
\]  

(1)

where \(t, x,\) and \(D\) are the time, abscissa measured through the thickness \((=2L)\) of the disc, and diffusivity, respectively, the latter depends on the concentration of the diffusing plasticizer according to the relationship:

\[
D(x,t) = D_0 \exp (-A/C)
\]

(2)

The values of the coefficients \(A\) and \(D_0\) depend on the nature of the liquid foodstuff and the temperature.

**Mathematical Analysis of Short Tests**

Equation (1) is analytically intractable with the above conditions. However, for very short times, the small amount of matter transferred at time \(t\) is very low, so that the concentration of the plasticizer is almost constant. In this case, the value of \(M_t\), as a fraction of the quantity transported after infinite time \(M_{\infty}\), can be expressed in terms of the square root of the time [12, 13]:

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**Note:** The above text contains a mathematical equation that requires specialized knowledge to interpret fully. Further assistance may be needed to fully comprehend its implications and significance.
This equation is very useful for determining the diffusivity which corresponds to the concentration of plasticizer in the PVC at the beginning of this short test.

**Numerical Analysis for Long Tests**

In this case, the problem is solved using a numerical explicite method with finite differences. The numerical analysis [14] applied to eqn 1 leads to:

\[
M = \left( \frac{L}{\pi} \right)^{0.5} t^{0.5} \text{D}^{0.5} \]

(3)

This equation is very useful for determining the diffusivity which corresponds to the concentration of plasticizer in the PVC at the beginning of this short test.

The total amount of plasticizer transferred at time \( t \) can be obtained by integrating the profile of concentrations with respect to time.

\[
C(x, t + \Delta t) = \frac{1}{M} \left[ C(x - \Delta x, t) + C(x + \Delta x, t) \right]
\]

(4)

with the dimensionless modulus \( M \):

\[
M = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{1}{D(x, t)}
\]

(5)

**EXPERIMENTAL**

**Synthesis of Labelled DOP**

Labelled phthalic anhydride [74mg, \(^{7-14}\)C; 0.5mCi; CEA (Paris)] was transferred to a four necked flask and mixed with 5g of unlabelled phthalic anhydride dissolved in 50 mL of acetone. The flask is equipped with a thermometer, an inlet tube, a dropping funnel, a magnetic stirrer and a side condenser. The mixture is heated with continuous stirring until all the acetone is evaporated. 45g phthalic anhydride is added with 200 mL octanol, 60 mL toluene to promote the removal of water, and 0.6 mL conc. H\(_2\)SO\(_4\). The mixture is heated in an oil bath for 200 min. while the temperature is gradually raised to 170\(^\circ\)C. All the phthalic anhydride is dissolved after 80 min. After 110 min., the temperature of the vapor is stabilized at ca 82\(^\circ\)C for 50 min., then increases again to indicate the end of the reaction. During this period, a slow N\(_2\) stream is passed and an equimolecular mixture of octanol and toluene is periodically added.

At the end of the experiment, the mixture is cooled and diluted with 2 \( \times \) 500 mL (10%) aqueous sodium carbonate solution and dried for 12 h over anhydrous CaCl\(_2\). The solution is then filtered and finally evaporated to remove diethylether, toluene and unreacted octanol. The diester is purified using vacuum distillation and yields 92%. Products with lower radioactivity are obtained by dilution with pure unlabelled DOP.

**Sample Preparation**

Commercial PVC [Sicron 540 HV (Sonatrach Algeria); K70] is blended at 80 C with the calculated amounts of labelled DOP (20, 30, 40 and 50 wt\%) and a fixed amount of barium-cadmium-zinc stabilizer [Irgastab BC 447 (ENPC-Algeria)]. The resulting dry blend is plasticized in a plastograph (Haake) working at 135 C, 35 rev/min, for 10 min. The plasticized mass is pressed using a steel mould operated by a power press at 150 C for 10 min. under 50 bars, to form a sheet of ca 3 mm thick. Several discs are cut, having nearly the same characteristics (18 mm in diameter, and 3 mm thick); those with a weight difference not exceeding 5% are selected for use and distributed into groups of 20 samples.

**Mass Transfer Study**

All experiments were carried out with 20 PVC solid discs immersed in 200 mL of colza oil contained in a 250 mL flask, kept at a temperature fixed to 0.1\(^\circ\)C, using a controlled rate of stirring. At intervals, PVC samples and colza oil were taken for analysis, so that the PVC-liquid ratio remains constant. Each PVC disc is weighted, and the concentration of the plasticizer in the oil is measured, so that the amounts of DOP and colza oil transferred can be determined. Then, each disc is peeled off into 15 slices of 0.200 mm thick using a lathe with a knife at the end of it. These slices are parallel to each other and to the flat faces of the discs (Figure 1). This operation works properly when the PVC disc is hardened with liquid N\(_2\).

**Measurements**

The variations of the DOP contents of the two phases in contact are monitored using the radioactive tracer tech-
nique, with automatic quenching correction and the external standard technique. The method is proved simple and reproducible, and is, therefore, used to find the amounts of the DOP in complex mixtures prepared in the laboratory. The accuracy was 3% for the least successful test and the reproducibility was 0.25%.

The radioactivity of the liquid medium, removed at a given time after immersion, is measured by transferring 0.5 mL of colza oil to a plastic measuring vial containing 10 mL of the scintillation solution (Ready-solv. NA-Beckman). The mixture is shaken to ensure complete solubilization; the radioactivity is measured by means of a Beckman β-LS 2800 spectrophotometer over a period of 10 min. The analyses were carried out in duplicate; thus each quoted result represents the average of six measurements.

The following operations were carried out successively in order to measure the concentration of plasticizer mixture inside every PVC disc, for different x values of abscissa along the thickness of disc: (1) weighting of peeled slices; (2) dissolution of slices in 3mL of THF; (3) analysis on 0.5mL of the obtained solution as described previously.

RESULTS AND DISCUSSION

Study of DOP Transfer into Colza Oil

The curves in Figure 2 show the influence of temperature and the effect of initial DOP concentration in PVC discs on plasticizer migration into stirred colza oil. The operational conditions are respectively: (1) [DOP] = 50% for 30 and 50°C; (2) T=30°C for 20 and 50% DOP.

The curves indicate the importance of temperature for the migration rate. Any rise in temperature favours the physical process and increases drastically the amount of migrated plasticizer. On the other hand, the

![Figure 1. Diffusion of the DOP through the plane disk.](image)

![Figure 2. Variation in plasticizer migration (g/L) from PVC disk into colza oil vs. time under isothermal conditions (30 and 50°C) for various plasticizer concentrations in PVC, with the vegetable oil being stirred (Re=2000).](image)

initial DOP concentration influences strongly the migration process. The migration increases as a result of increasing PVC plasticization which involves both a greater DOP concentration gradient between the plastic disc and the liquid foodstuff (driving force of the transfer) and a reduction of the resistance to transfer. These two parameters (temperature and initial DOP concentration) affect the amount of the plasticizer transferred into colza oil at equilibrium (M∞).

The effect of time in all the above cases indicates that there is no linear relation between the amount of migrated DOP and the square root of time. Generally, the desorption curves are sigmoid in shape with a point of inflexion at ca 50% equilibrium desorption. Such anomalous diffusion [13] occurs when the diffusion and polymer relaxation rates are comparable.

The influence of time was found to be of importance when it is < 120 h. For longer periods (>120 h), the migration process becomes practically unaffected by time. This behaviour is common for low migration rates and when the loss of plasticizer is coupled with a very low entry of liquid into the PVC samples (see below).

Colza Oil Transfer in PVC Discs

Chemically, the used colza oil is a complex mixture of triacylglycerols which comprise ca 98% of the oil and other minor components such as sterols, ketones, alde-
hydres, hydrocarbons and pigments. The triacylglycer- 

erols with acyl groups containing 12 or more carbon 
atoms cannot diffuse into the plastic [15]. Thus, the role 
of the minor components may be important.

The curves on Figure 3, obtained under various 
experimental conditions, show a weak penetration of 
the colza oil into the PVC samples, at small rates.

Profiles of DOP Concentration through PVC Discs

According to the process described above, PVC discs 
are removed from colza oil at different times, and every 
disc was peeled off in to fifteen layers of 200 µm thick.
The DOP concentration is measured in every layer and 
is referred to the position of the centre plane of every 
layer in the PVC disc. This position was expressed by 
the relative abscissa x, where -7 ≤ x ≤ 7 (Figure 1). 
Point 0 on the abscissa is taken for the centre plane of 
the PVC disc, parallel to the faces, and ±7 the abscissa 
at the centre plane of the two layers close to each disc 
face. The problem is symmetric with respect to x = 0, 
so the data are given only for 0 ≤ x ≤ 7, when T = 30°C; 
[DOP] = 30% (Table 1), and T = 50°C; [DOP] = 20% 
(Table 2).

Modelling and Simulation

The parameters D0 and A (equation (2)) are determined 
under isothermal conditions (30 and 50°C) in the liquid 
in motion using PVC discs with plasticization levels 
ranging from 20 to 50 wt%. Diffusivities of DOP are 
calculated from the slopes of the straight lines obtained 
by plotting the DOP values transferred at short times 
against the square root of time. As the logarithm of dif- 
fusivities of the DOP are found to be related to the 
reciprocal of the initial plasticizer level, it is easy to 
 obtain the following equations:

For: T = 30°C and [DOP] = 30%

D = 2.15 \times 10^{-7} \exp(-94.5/C) \quad (6)

For: T = 50°C and [DOP] = 20%

D = 2.15 \times 10^{-7} \exp(-63/C) \quad (7)

The amount of plasticizer transferred at equilibrium 
M∞ is obtained from long test experiments (over 500 h)

Table 1. Measured (m) and calculated (th) DOP concentration profiles developed through a PVC disc vs. time; T=30°C; initial plasticizer concentration = 30%.

<table>
<thead>
<tr>
<th>Relative abscissa x</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC disc thickness (mm)</td>
<td>1.5</td>
<td>1.3</td>
<td>1.1</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>72 h m</td>
<td>28.40</td>
<td>27.10</td>
<td>26.60</td>
<td>25.90</td>
<td>23.10</td>
<td>21.60</td>
<td>20.40</td>
<td>18.00</td>
</tr>
<tr>
<td>72 h th</td>
<td>29.08</td>
<td>29.07</td>
<td>28.18</td>
<td>27.26</td>
<td>25.35</td>
<td>23.41</td>
<td>20.71</td>
<td>18.00</td>
</tr>
<tr>
<td>120 h m</td>
<td>26.60</td>
<td>25.30</td>
<td>24.00</td>
<td>22.50</td>
<td>21.90</td>
<td>20.10</td>
<td>18.60</td>
<td>16.50</td>
</tr>
<tr>
<td>120 h th</td>
<td>29.60</td>
<td>26.88</td>
<td>25.90</td>
<td>24.89</td>
<td>23.06</td>
<td>21.19</td>
<td>18.85</td>
<td>16.50</td>
</tr>
<tr>
<td>240 h m</td>
<td>22.40</td>
<td>22.30</td>
<td>21.00</td>
<td>20.10</td>
<td>19.50</td>
<td>18.00</td>
<td>17.10</td>
<td>15.90</td>
</tr>
<tr>
<td>240 h th</td>
<td>22.48</td>
<td>22.45</td>
<td>21.83</td>
<td>21.15</td>
<td>20.00</td>
<td>18.81</td>
<td>17.36</td>
<td>15.90</td>
</tr>
<tr>
<td>360 h m</td>
<td>18.90</td>
<td>18.60</td>
<td>18.30</td>
<td>18.00</td>
<td>17.40</td>
<td>16.80</td>
<td>16.20</td>
<td>15.30</td>
</tr>
<tr>
<td>360 h th</td>
<td>19.44</td>
<td>19.41</td>
<td>19.03</td>
<td>18.60</td>
<td>17.88</td>
<td>17.13</td>
<td>16.22</td>
<td>15.30</td>
</tr>
</tbody>
</table>
that were made under the same conditions as for determining the diffusivities.

The profiles of the plasticizer concentration developed through the PVC discs are calculated at various times by using the model (lines $C_{th}$ in Tables 1 and 2).

The regression lines:

$$C_{th} = a + b C_m$$ (8)

fitting the pairs of values $C_m$ and $C_{th}$ were found by the method of the least squares. The calculation of parameters $a$ and $b$ and the subsequent variance analysis [16] were worked out for each experiment and considering the combined results (Table 3).

The standard deviations $SE(a)$ and $SE(b)$ measure the precision with which the parameters $a$ and $b$ have been obtained if one takes into account the number of degrees of freedom ($N-2$) where $N$ is the number of paired values of $C_m$ and $C_{th}$.

$$F_{obs.} = \frac{s_1^2}{s_2^2}$$

$s_1^2$ is the variance due to the regression line (variation of $C_{th}$ with $C_m$), and $s_2^2$ is the residual variance about the regression line (measures the scatter of the $C_{th}$ values about the regression line). The table gives for a confidence level of 99.9%, a limit $F_{0.999}$ (1,$N-2$) in each case substantially less than the $F_{obs}$ value (Table 3).

### Table 2. Measured (m) and calculated (th) DOP concentration profiles developed through a PVC disc vs. time; $T=50^\circ$C; initial plasticizer concentration = 20%.

<table>
<thead>
<tr>
<th>Relative abscissa $x$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC disc thickness(mm)</td>
<td>1.5</td>
<td>1.3</td>
<td>1.1</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>72 h</td>
<td></td>
<td>19.30</td>
<td>18.60</td>
<td>18.00</td>
<td>17.60</td>
<td>16.50</td>
<td>15.40</td>
<td>13.60</td>
</tr>
<tr>
<td>th</td>
<td></td>
<td>19.47</td>
<td>19.46</td>
<td>18.94</td>
<td>18.40</td>
<td>17.29</td>
<td>16.15</td>
<td>14.58</td>
</tr>
<tr>
<td>120 h</td>
<td>m</td>
<td>18.00</td>
<td>17.60</td>
<td>16.40</td>
<td>16.20</td>
<td>15.00</td>
<td>13.80</td>
<td>12.60</td>
</tr>
<tr>
<td>th</td>
<td></td>
<td>18.28</td>
<td>18.27</td>
<td>17.72</td>
<td>17.16</td>
<td>16.14</td>
<td>15.11</td>
<td>13.80</td>
</tr>
<tr>
<td>240 h</td>
<td>m</td>
<td>15.70</td>
<td>15.40</td>
<td>15.00</td>
<td>14.80</td>
<td>14.00</td>
<td>13.40</td>
<td>12.30</td>
</tr>
<tr>
<td>th</td>
<td></td>
<td>15.74</td>
<td>15.72</td>
<td>15.36</td>
<td>14.98</td>
<td>14.30</td>
<td>13.65</td>
<td>12.83</td>
</tr>
<tr>
<td>360 h</td>
<td>m</td>
<td>13.40</td>
<td>13.40</td>
<td>13.10</td>
<td>12.90</td>
<td>12.40</td>
<td>12.10</td>
<td>11.50</td>
</tr>
</tbody>
</table>

### Table 3. Determination of the parameters $a$ and $b$ (regression lines (8)) and variance analysis. (1): $T = 30^\circ$C and [DOP] = 30%; (2): $T = 50^\circ$C and [DOP] = 20%.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>a</th>
<th>b</th>
<th>SE (a)</th>
<th>SE (b)</th>
<th>N</th>
<th>$F_{obs}$</th>
<th>$F_{0.999}(1, N-2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>1</td>
<td>-1.008</td>
<td>1.094</td>
<td>1.969</td>
<td>0.082</td>
<td>8</td>
<td>177.873</td>
</tr>
<tr>
<td>120</td>
<td>2</td>
<td>-0.473</td>
<td>1.068</td>
<td>5.103</td>
<td>0.307</td>
<td>8</td>
<td>286.270</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-1.425</td>
<td>1.114</td>
<td>1.226</td>
<td>0.055</td>
<td>8</td>
<td>160.617</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.182</td>
<td>0.979</td>
<td>1.454</td>
<td>0.094</td>
<td>8</td>
<td>107.419</td>
</tr>
<tr>
<td>240</td>
<td>1</td>
<td>1.521</td>
<td>1.014</td>
<td>1.332</td>
<td>0.074</td>
<td>8</td>
<td>224.538</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.438</td>
<td>0.987</td>
<td>0.709</td>
<td>0.050</td>
<td>8</td>
<td>2536.569</td>
</tr>
<tr>
<td>360</td>
<td>1</td>
<td>-2.461</td>
<td>1.166</td>
<td>0.677</td>
<td>0.039</td>
<td>8</td>
<td>112.480</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.364</td>
<td>1.036</td>
<td>0.294</td>
<td>0.020</td>
<td>8</td>
<td>1349.398</td>
</tr>
<tr>
<td>combined results</td>
<td>1</td>
<td>-1.552</td>
<td>1.114</td>
<td>0.733</td>
<td>0.035</td>
<td>32</td>
<td>1467.917</td>
</tr>
</tbody>
</table>
3). Hence, calculated profiles of DOP concentration correlate well with the measured ones.

Figure 4 shows that the model is self-consistent (that is, the diffusion is well concentration-dependent as indicated above), since the logarithm of DOP diffusivities are related to the reciprocal of local concentration of plasticizer according to a linear relation, with a regression parameter equal or close to unity.

The integration of the concentration profiles provide the quantities of DOP transferred into colza oil at different times for the following condition:

[DOP] = 20% and T=50°C

[DOP] = 30% and T=30°C

Table 4 compares the theoretical masses ($M_{th}$) and the measured ones ($M_m$).

The parameters $a$ and $b$ for the regression line:

$$M_{th} = a + b M_m$$

are calculated for each experiment and considering the combined data (Table 5). The statistical results show that the calculated masses correlate with measured ones (with a P-value $\leq 0.01$).

**CONCLUSION**

When plasticized PVC discs are immersed in colza oil, two phenomena take place simultaneously: plasticizer migration and liquid penetration. DOP transfer is strongly enhanced when the initial plasticizer concentration and/or the test temperature increases. The influence of time is of importance when it is lower than 120 h. The transport kinetics in the liquid food were completed by the study of the migratory phenomenon in PVC itself, leading to the profiles of the DOP concentration developed through the polymer bulk during the process. Colza oil penetrates into PVC discs with difficulty, resulting in weak rates of sorption and small amounts of sorbed oil.

A mathematical analysis was undertaken by neglecting the small amounts of colza oil transferred into the polymer matrix. The simplified model was found (analysis of variance for one-way) to be available for determining the DOP concentration profiles, which integration provided correct values for transferred mass DOP into colza oil (P-value $\leq 0.01$).
The model is self-consistent; that is, the data obtained verify the assumption of an exponential concentration-dependent diffusivity.

REFERENCES