Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1544-1552

Modelization of Dioctyl Phthalate Transfer from Plasticized PVC Disks Dipped into Sunflower Oil

NADIA FERTIKH* and DJELLOUL MESSADI
Pollution laboratory, Badji Mokhtar Unversity, B.P 12, 23200, Annaba, Algeria
Tel / Fax: 0021338876560
E-mail: n_fertikh@ yahoo.fr

Plasticized PVC packaging of liquid foodstuffs leads to a simultaneous diffusion: additives (plasticizer in particular) - liquid. The temperature used currently higher than the PVC glass transition temperature Tg. In such circumstances the diffusion is generally Fickian, with a diffusion depending on the concentration of the liquid and plasticizer. Nevertheless, when the liquid is an edible oil this dependence may be adjusted by neglecting the small amounts of oil which diffuse into the polymer. A simplified predictive mathematical model of dioctyl phthalate (DOP) plasticizer migration from PVC into sunflower oil was tested. The statistical results show that the computed DOP concentrations into the edible oil, as well as computed profiles of DOP concentration developed through PVC matrix correlate with measured ones, with a P-value = 0.001. Diffusivities at various thicknesses inside the PVC disk vary exponentially in term of reciprocal plasticizer local concentration.

Key Words: Dioctyl phthalate, Plasticizer, Polymer, Interaction, Diffusivity, Packaging.

INTRODUCTION

Putting into contact a solid polymer and a liquid, is an usual practice in packaging. It involves generally mass exchanges between the two phases, which constitute a major drawback, especially when the liquid is a foodstuff [1-6]. In all applications, the plasticized PVC is in contact with the surrounding medium and the plasticizer may migrate with the following results[7-11]: (i) Because of plasticizer loss, the polymer deteriorates its mechanical properties, (ii) The surrounding medium is contaminated 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)[12], (b) For both these transfers, the diffusivity is concentration-dependent and (c) Many factors may affect the migration process, including the nature of 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[13] 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 the present paper, migration of dioctyl phthalate (DOP) from solid polyvinyl chloride (PVC) discs into sunflower oil in contact was studied for several plasticization levels and temperature testing. Quantitative analysis in such a complex mixture and in polymer matrix itself was made easy by using radioactive tracer technique (the choice technique for migration studies on a large scale).

No analytical solution can be found when the diffusivity is not constant. A theoretical model based on a second-order partial differential equation solved by an explicit finite-difference numerical method, was built by neglecting the small amounts of foodstuff liquid transferred into the bulk polymer and tested on limited volume of well-stirred sunflower oil.

Theoretical approach

The following assumptions were made:

(1) We used PVC discs and considered unidimensionnal diffusion in a medium bounded by two parallel planes, *e.g.*, the planes $x = \pm L$.

(2) The small amount of oil transferred in the bulk polymer is negligible.

(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 sunflower oil.

It has been generally assumed that diffusion under transient conditions is as described by Fick's equation[14]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right), \text{ for } -L < x < L \tag{1}$$

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

$$D(x,t) = D_O \exp(-A/C) \tag{2}$$

The values of the coefficients A and D_O depend on the nature of the liquid foodstuff and the temperature.

The boundary conditions were:

$$t = 0 \quad \begin{array}{ll} C(x,0) = C_0, & -L \leq x \leq L \\ C(x,0) = 0, & x \;\overline{\wedge}\; -L \text{ and } x\phi L \end{array} \tag{3}$$

$$t > 0 \quad C(-L,t) = C(+L,t) = C_\infty \tag{4R}$$

D(x,t) and C(x,t) denote the diffusivity and the concentration of DOP measured at abscissa x and time t, 2L is the thickness of a particular disc, C_∞ is the equilibrium concentration of plasticizer and C_0 is its initial concentration.

Mathematical analysis of short tests

Equation (1) is analytically intractable with the above conditions. However, for very short times, the small amount of substance transferred at times 't' was very low, so that the concentration of the plasticizer is almost constant. In this case, the value of Mt, as a fraction of the quantity transported after infinite time M_∞, can be expressed in terms of the square root of the time[13,14]:

$$\frac{M_t}{M_\infty} = \frac{2}{L}\sqrt{\frac{D_t}{\overline{\wedge}}} \tag{5}$$

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

Since eq. 1 cannot be analytically solved under the above conditions, the problem is solved using a numerical explicit method with finite differences. The numerical analysis[14,15] applied to eq. 1 allows to write:

$$\frac{C(x,t+\Delta t) - C(x,t)}{\Delta t} = D\left(x + \frac{\Delta x}{2}, t\right)\frac{C(x+\Delta x,t) - C(x,t)}{\Delta x^2} - D\left(x - \frac{\Delta x}{2}, t\right)\frac{C(x,t) - C(x-\Delta x,t)}{\Delta x^2} \tag{6}$$

by assuming:

$$D\left(x + \frac{\Delta x}{2}, t\right) = D(x,t) = D\left(x - \frac{\Delta x}{2}, t\right)$$

it follows:

$$C(x,t+\Delta t) = \frac{1}{M}\left[C(x-\Delta x,t) + C(x,t)(M-2) + C(x+\Delta x,t)\right] \tag{7}$$

where M is the dimensionless modulus:

$$M = \frac{(\Delta x)^2}{\Delta t, D(x,t)} \quad (8)$$

We can then calculate the concentration within the disc at the abscissa x and time (t +Δt), when we know the concentration at time t and at the abscissa (x -Δx), x and (x +Δx).

From this concentration profile we can deduce, the total quantity of plasticizer transferred for a given time; we shall calculate the mean concentration of the DOP remaining in the polymer disc using the trapezium rule.

$$M_t = 2\Delta x\left[\frac{3}{8}C_p(0) + \frac{9}{8}C_p(1) + C_p(2) + C_p(3) + \ldots\ldots + C_p\left(\frac{N}{2} - 1\right) + \frac{1}{2}C_p\left(\frac{N}{2}\right)\right] \quad (9)$$

EXPERIMENTAL

Synthesis of labelled DOP

The plasticizer was prepared from labelled phthalic anhydride [74 mg; (7-^{14}C); 0.5 mCi, CEA (Paris)]. The synthesis conditions were defined and best parameter for optimum yields (92%) specified[16]. Products with lower radioactivities were obtained by dilution with pure unlabelled DOP.

Sample preparation

Commercial PVC [Sicron 540HV (Sonatrach-Algeria); K70] was blended at 80°C with the calculated amounts of labelled DOP (20-30-40 and 50% by weight) and a fixed amount of barium-cadmium-zinc stabilizer was plasticized in a plastograph (Haake) working at 135°C, 35 rpm, for 10 min under a pressure of 50 bars, to form a sheet *ca.* 3 mm thick. A number of discs were cut, having nearly the same characteristics (18 mm dia; 3 mm thickness); those discs with a weight difference not exceeding 5% were selected for use and distributed into groups of 20 samples.

Method for studying the transfer

All experiments were carried out by using 20 PVC solid discs dipped into a closed glass reactor of 250 mL capacity, kept at a temperature fixed to 0.1°C, using a controlled rate of stirring. At intervals, PVC samples and sunflower oil were taken for analysis, so that the PVC-liquid ratio remains constant. Each PVC disc is weighed, and the concentration of the plasticizer in the oil is measured, so that the amounts of DOP and sunflower oil transferred can be determined. Then, each disc was wiped quickly and peeled off into 15 slices (0.200 mm) by using a lathe with a knife at the end of it. These slices were parallel to each other and to the flat faces of the discs. This operation works properly when the PVC is hardened with liquid nitrogen.

Measurement

The variations of the DOP contents of the two phases in contact were separately monitored by using the radioactive tracer technique, with automatic quenching correction and the external standard technique. The method is simple and reproducible. It was 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 after given time of immersion is measured by transferring 0.5 mL of sunflower oil to a plastic measuring vial containing 10 mL of the scintillation solution (ready-solv. NA-Beckman) shaking to ensure complete solution and measuring the radioactivity by means of a Beckman β-LS 2800 Spectrophotometer over a period of 10 min. The analyses were done six times, 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 the abscissa along the thickness of disc: (1) weighing of peeled slices; (2) dissolution of slices in 3 mL of THF; (3) analysis on 0.5 mL of the obtained solution as described previously.

RESULTS AND DISCUSSION

Diffusion coefficient variation with concentration

Experiments were performed under isothermal conditions (20, 30 and 50°C) in the well-stirred sunflower oil, by using PVC discs plasticized with various DOP percentages (20-30-40 and 50% by weight). Diffusivities of DOP were calculated from the slopes of straight lines obtained by plotting the values of the amount of DOP transferred at short times *vs.* the square root of time. Since the logarithm of diffusivities of the DOP were found to be related to the reciprocal of the initial plasticizer level, it was easy to obtain the coefficients D_0 and A (Table-1) appearing in eq. 1.

TABLE-1
VARIATIONS OF THE DIFFUSIVITY [EQ.(1)] WITH THE RECIPROCAL OF THE DOP CONCENTRATION

T(ºC)	$10^7 D_0$	A
20	1.12	193
30	2.15	100
50	2.15	63

Profiles of DOP concentrations developed through PVC disks

According to the process described before, PVC discs were removed from sunflower oil at different times, and every disc was peeled off in fifteen 200 μm-thick layers. The DOP concentration was measured in every layer. This concentration was related to the position of the centre plane of every layer in the PVC disc before cutting; this position was expressed by the relative abscissa x, where $-7 \leq x \leq 7$. the 0 point on the abscissa was 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, we give the data only for $0 \leq x \leq 7$.

The computation of DOP concentration profiles was carried out with the help of an Unisys micro-computer, utilizing Turbo-Basic language.

Following parameters realize the best possible compromise between calculus precision and stability. (1) space increment: $\Delta x = 0.01$ cm. (2) Disc thickness: 2L = 0.30 cm. (3) time increment: $\Delta t = 3600$ s.

The model was found to be useful for determining the profiles of DOP concentration. The calculated concentrations (Cth) *vs*. the time for different positions in the disc and various experimental conditions, compared to the corresponding measured concentrations (Cm) are shown in Table-2.

TABLE-2
EVALUATION OF CONCENTRATION PROFILES MEASURED (m) AND CALCULATED(th) WITHIN DISK WHEN: (1) % DOP = 30; T = 30°C (2) % DOP = 20; T = 50°C.

Relative abscissa x			0	1	2	3	4	5	6	7
Disc thickness (mm)			1.5	1.3	1.1	0.9	0.7	0.5	0.3	0.1
120 h	1	m	28.00	27.70	26.10	25.50	24.30	22.10	21.60	20.40
		th	28.48	28.30	27.75	26.85	25.61	24.08	22.35	20.50
	2	m	14.88	14.71	14.53	14.20	13.95	13.45	12.80	12.25
		th	18.16	18.15	17.57	16.97	15.88	14.78	13.39	12.00
240 h	1	m	24.90	24.60	24.00	23.40	22.50	21.30	20.10	18.30
		th	24.69	24.52	24.00	23.23	22.17	20.90	19.49	18.00
	2	m	13.81	13.71	13.65	13.44	13.23	12.72	12.43	11.91
		th	15.68	15.67	15.31	14.92	14.26	13.58	12.75	11.91
360 h	1	m	20.40	20.10	19.50	18.60	18.00	17.10	16.20	15.00
		th	20.49	20.35	19.95	19.29	18.42	17.38	16.22	15.00
	2	m	12.97	12.86	12.70	12.54	12.00	11.91	11.52	11.06
		th	13.57	13.56	13.32	13.06	12.63	12.17	11.62	11.06

The regression lines:

$$Cth = a + b\ Cm \qquad (10)$$

fitting the N pairs of values Cm/Cth were found by the method of least squares.

The calculation of the parameters a and b and the subsequent variance analysis were done for every experiment and by considering the combined data.

The standard deviations SE (a) and SE(b) can be used as a measure of the precision with which the parameters a and b have been obtained, if the degree of freedom (N-2) is taken into account.

$F_{obs.} = s_1^2/s_2^2$; s_1^2 is the variance due to the regression (variation of Cth with Cm) and s_2^2 the residual variance around the regression straight line (measures the scatter of the values of Cth around the regression straight line). The values of calculated F (Table 3) are higher than the corresponding values given by the Fisher-Snedecor's F(1; N-2) table, for a probability P = 0.999. Therefore the test is meaningful and there is a correlation between Cth and Cm.

TABLE-3
COMPARISON OF THEORETICAL AND MEASURED CONCENTRATION PROFILES. DETERMINATION OF PARAMETERS a AND b [EQ. 11] AND VARIANCE ANALYSIS. EXPERIMENTAL AND THEORETICAL DOP CONCENTRATIONS PRESENTED IN TAB.2

		a	b	r	SE(a)	SE(b)	SE(c)	N	$F_{obs.}$	$F_{0.999\ (1\ ;\ N-2)}$
72 h	1	-2.29	1.14	0.985	2.10	0.08	0.57	8	193.33	35.51
	2	-6.21	1.46	0.979	1.97	0.12	0.54	8	140.37	35.51
120 h	1	0.90	1.00	0.976	2.26	0.09	0.69	8	119.43	35.51
	2	-17.75	2.43	0.997	1.06	0.08	0.19	8	1001.00	35.51
	3	5.51	0.97	0.958	4.61	0.11	3.06	8	66.75	35.51
240 h	1	-1.53	1.06	0.998	0.55	0.02	0.15	8	1839.40	35.51
	2	-12.53	2.04	0.996	1.02	0.08	0.14	8	685.94	35.51
360 h	1	-0.64	1.05	0.994	0.85	0.05	0.24	8	509.46	35.51
	2	-3.88	1.35	0.992	0.87	0.07	0.13	8	362.30	35.51
	3	6.90	0.84	0.973	3.16	0.08	1.91	8	106.48	35.51

Diffusivity dependence on local concentration of migrating species is characteristic of diffusion in bulk polymer. The diffusion coefficient values of plasticizer in PVC were found to vary with the plasticizer concentration (Fig. 1) according to eq. 1, rewritten as follows:

$$\text{Ln } D = \ln D_0 - A/C \quad (11)$$

The correlation coefficients ($0.99523 \leq r \leq 0.99999$) near 1 showed close agreement. Thus by contrast with another model tested previously[12], the present model is self-consistent.

Kinetics of the DOP transfer in the oil

The integration of the concentration profiles provides the quantities of DOP transferred into sunflower oil at different times, for the following conditions: (% DOP = 20- T = 50°C) and (%DOP = 30- T= 30°C).

Table-4 compares the theoretical masses (Mth) to the measured ones (Mm). The statistical analysis (Table-5) shows that these two parameters are in correlation, with a P-value= 0.001.

TABLE-4
MEASURED (m) AND CALCULATED (th) MASSES (g) OF DOP TRANSFERRED IN THE OIL AS FUNCTION OF TIME

C_O (%)	T (°C)		t (h)						
			6	24	48	72	120	240	360
20	50	m	0.0270	0.1092	0.1161	0.1210	0.1297	0.1383	0.1494
		th	0.0781	0.0869	0.0927	0.0973	0.1047	0.1139	0.1236
30	30	m	-	0.1197	0.1205	0.1262	0.1500	0.1723	0.1919
		th	-	0.1268	0.1332	0.1382	0.1620	0.1665	0.1891

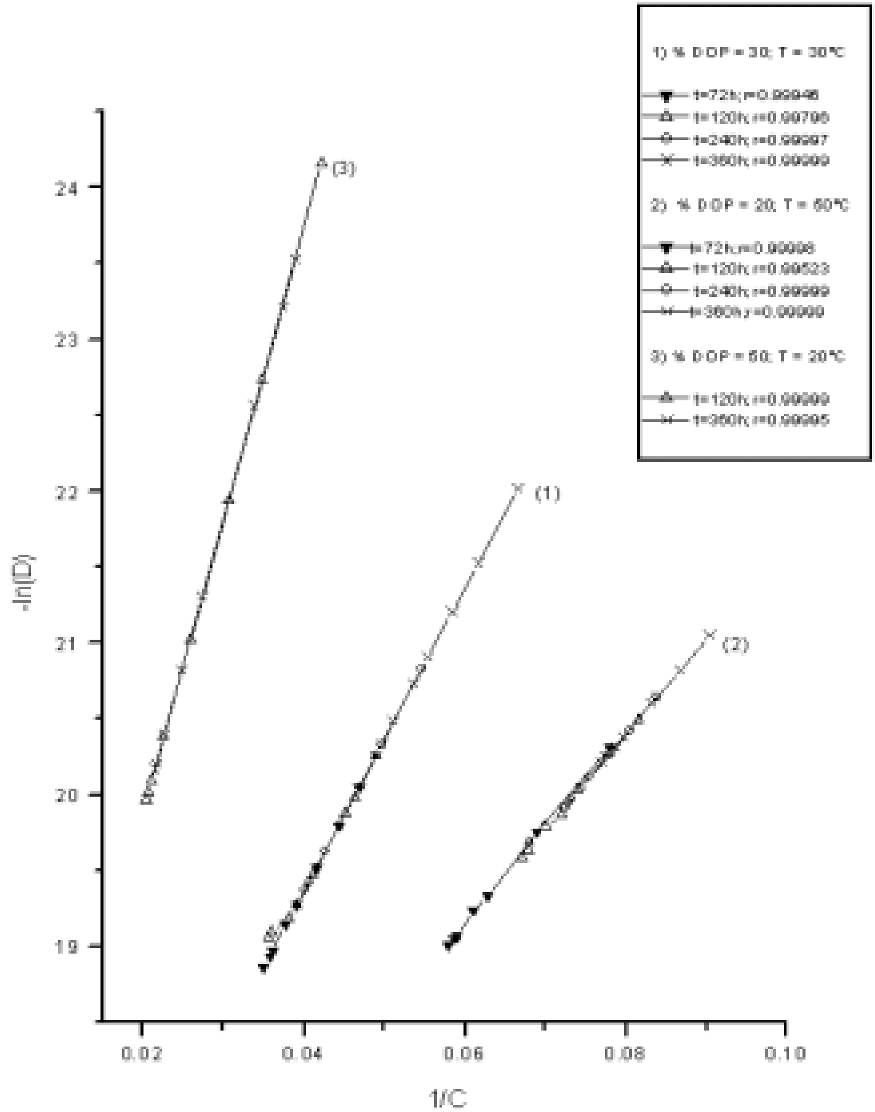

Fig. 1. The variation of Ln D in term of reciprocal plasticizer local concentration (1/C)

TABLE-5
TRANSFER KINETICS: PARAMETERS AND VARIANCE ANALYSIS. C_0 IS THE PLASTICIZED LEVEL (WEIGHT %) OF SAMPLE

C_0	T(°C)	a	b	SE(a)	SE(b)	N	$F_{obs.}$	$F_{0.999}$ (1; N-2)
20	50	0.063	0.327	0.0113	0.095	7	11.673	6.869
30	30	0.037	0.767	0.0112	0.075	6	104.84	8.610
Combined results		0.036	0.677	0.0195	0.146	13	21.472	4.437

Conclusion

The results of long time tests were given for migration of dioctyl phthalate from solid PVC discs into sunflower oil, using a method based on labelled plasticizer and measurements of the radioactivity of the two phases in contact. The following factors were examined: time, plasticizing level (20, 30, 40 and 50% by weight), temperature (20, 30 and 50°C). The transport kinetics in the liquid foodstuff were completed by studying of the migratory phenomenon developed through the matrix of a particular disc. The model described in this paper took into account two different points: the concentration of sunflower oil in the polymer matrix was neglected; diffusion in transient conditions through the PVC mass with concentration-dependent diffusivities was considered. Using this self consistent model, it was possible to reproduce the experimental results with a good approximation.

REFERENCES

1. A. Gheid, N. Fertikh, A. Mansour and D. Messadi, *Eur. Polym. J.*, **26**, 409 (1990).
2. D. Messadi, N. Fertikh and A. Gheid, *Eur. Polym. J.*, **27**, 1187 (1991).
3. D. Messadi and A. Gheid, *Eur. Polym. J.*, **30**, 167 (1994).
4. A. Gheid and D. Messadi, *J. Soc. Alg. Chim.*, **6**, 151 (1996).
5. D. Messadi and S. Djilani, *Eur. Polym. J.*, **34**, 815 (1998).
6. S. Djilani, A. Toubal and D. Messadi, *J. Chim. Phys.*, **95** 1951 (1998).
7. C.D. Papaspyrides and S.G. Tingas, *Food Add. Contam.*, **15**, 681 (1998).
8. M.S. Tawfik and A. Huyghebaert, *Food Chem.*, **64**, 451 (1999).
9. S. Djilani, T. Bouchami, F. Krid, N. Boudiaf and D. Messadi, *Eur. Polym. J.*, **36**, 1981 (2000).
10. D. Scholler, J.M. Vergnaud, J. Bouquant, H. Vergallen and H. Feigenbaum, *Pack. Tech. Sci.*, **16**, 209 (2003).
11. M.J. Scotter and L. Castle, *Food Add. Contam.*, **21**, 93 (2004).
12. D. Messadi, Nouvelle méthode d'étude du transfert de matière entre le PVC plastifié et des liquides, Thèse de Doctorat Es-Sciences, *Saint-Etiennne*, **N°25** (1981).
13. J.M. Vergnaud, Liquid Transport Processes in Polymeric Material, Modeling and Industrial Applications-Prentice Hall, Englewood Cliffs, N.J. (1991).
14. J. Crank, The Mathematical of Diffusion-Clarendon Press, Oxford (1976).
15. G.D. Smith, Numerical Solution of Partial Equation-Oxford, University Press, Glasgow 1975.
16. G. Saporta, Probabilité, Analyse de Données et Statistique-Editions Technip, Paris (1990).
17. D. Messadi and J. M. Vergnaud, *Eur. Polym. J*., **33**, 1167 (1997).

(*Received*: 19 April 2006; *Accepted*: 20 September 2006) AJC-5126