

Simultaneous Diffusion of Benzyl Alcohol into Plasticized Poly(vinyl Chloride) and of Plasticizer from Polymer into Liquid

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Synopsis

The diffusion of benzyl alcohol and plasticizer in compression-molded sheets of plasticized poly(vinyl chloride) was studied over the temperature range 30–55°C. A simultaneous diffusion occurred for benzyl alcohol into polymer and for dioctyl phthalate as plasticizer from polymer into liquid when the polymer was soaked in benzyl alcohol. The concentration of benzyl alcohol in polymer increased, rose to a maximum, and then decreased. Diffusion coefficients were measured by considering a nonsteady-state phenomenon for plasticizer concentrations of 25, 38, and 50 wt %, both for dioctyl phthalate and benzyl alcohol. Plasticizer concentration and temperature were found to play an important role.

INTRODUCTION

PVC plays an important role in the plastics industry. The greater part of PVC is used as plasticized PVC, and PVC applications consume approximately 80% of the total production of plasticizers. Thus, any work on migration processes of plasticizers may be of significance for the PVC industry.

In all applications, a plasticized PVC is in contact with some kind of surrounding medium. Under these conditions, the plasticizer may migrate, with the following results:

- (1) Loss of plasticizer; the polymer shows considerable change in mechanical properties.
- (2) The surrounding medium is contaminated by the plasticizer.

Several recent studies have shown that this contamination by plasticizer is a serious problem in liquid foods,^{1–8} drugs, cosmetics, and pure chemicals.^{9–11}

Other works were concerned with the diffusion of a UV stabilizer in plasticized PVC¹² or with the drying of polymer films.¹³

Possible factors which can affect the migration process can be classified in relation to (a) the polymer, i.e., molecular weight; (b) the plasticization process and conditions, and therefore the homogeneity of the system; (c) the surrounding medium, i.e., nature, compatibility with the plasticizer, and effect on polymer; (d) the plasticizer, i.e., nature and amount; (e) the conditions of the test, i.e., time and temperature. The importance of the liquid stirring was pointed out by using the Reynold's number.¹⁴

The present work reports the results of the transfer of DOP as plasticizer from plasticized PVC into benzyl alcohol as solvent. The experiments were carried out within the range 30–55°C, by using plasticized PVC with various concen-

trations of DOP within the range 25–50%. This case happened to be of interest, as the diffusion of benzyl alcohol into the PVC slab and the diffusion and transfer of DOP from PVC into benzyl alcohol took place simultaneously.

THEORETICAL

Plasticized PVC disks were soaked in liquid benzyl alcohol, and the plasticizer diffused from the solid into the liquid. In fact, the benzyl alcohol transfer into the PVC took place simultaneously. It was an unusual observation as such simultaneous diffusion or transfer was not reported in early studies with petroleum oils,⁹ alcohols,¹¹ methanol,¹⁴ *n*-heptane,¹⁵ and liquid foods.^{1–8}

By considering as negligible the transfer resistance through the PVC–liquid interface, the plasticizer was transferred from the PVC into the liquid by a two-step process:^{13,14} (1) Plasticizer transported in the PVC itself by internal diffusion; it was studied by assuming a nonsteady state. (2) Plasticizer diffused into the liquid; it was found to be controlled by a boundary layer phenomenon.¹⁴

Plasticizer Transfer into a Solution of Limited Volume

In most cases, the experiments were performed with a limited volume of liquid, and the concentration of plasticizer in the solution increased as plasticizer was transferred from PVC to the liquid. When the solution was stirred well, the plasticizer concentration in the solution depended only on time and was determined essentially by the condition that the total amount of plasticizer in the solution and in the PVC remained constant as diffusion proceeded.

The following assumptions were made: (a) PVC disks were considered as plane sheets, and the amount of plasticizer diffusing through the edges was negligible in regard to the amount diffusing through the plane faces. (b) The problem was stated mathematically as a nonsteady-state phenomenon. (c) The plasticizer transfer was described by Fick's laws when we included a nonconcentration-dependent diffusion coefficient.

The second Fick's second law is expressed as follows

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where D is the diffusion coefficient taken as nondependent on the plasticizer concentration C , t is time, and x is the coordinate dimension in the direction of the transport.

We assumed that an infinite sheet of thickness $2l$ was placed in the liquid, the PVC sheet occupied the space $-l \leq x \leq l$, while the solution of limited extent occupied the spaces

$$-l - a \leq x \leq -l \quad \text{and} \quad l \leq x \leq l + a$$

The initial condition was

$$\begin{array}{lll} t = 0 & -l < x < l & C = C_0 \quad \text{sheet space} \\ & & C = 0 \quad \text{solution space} \end{array} \quad (2)$$

and the boundary condition expressed the fact that the rate at which plasticizer

left the PVC was always equal to that at which it entered the solution, over the surfaces $x = \pm l$:

$$t > 0 \quad x = \pm l \quad a \frac{\partial C}{\partial t} = D \frac{\partial C}{\partial x} \quad (3)$$

A solution of this problem was obtained¹⁶ in a form expressing the total amount of plasticizer M_t in the liquid at time t as a fraction of M_∞ , the corresponding quantity after infinite time:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_n^2} \exp\left(\frac{-Dq_n^2t}{l^2}\right) \quad (4)$$

where the q_n s are the nonzero positive roots of

$$\tan q_n = -\alpha q_n \quad (5)$$

and $\alpha = a/l$, the ratio of the volumes of liquid and PVC sheet.

Plasticizer Transfer into a Solution of Large Volume

When PVC sheets were suspended in a volume of liquid so large that the concentration of plasticizer in the solution remained constant, the initial and the boundary conditions became

$$\begin{array}{llll} t = 0 & -l < x < l & C = C_0 & \text{sheet space} \\ t > 0 & x = \pm l & C = 0 & \text{sheet faces} \\ t > 0 & -l < x < l & C_t < C_0 & \text{sheet space} \end{array} \quad (6)$$

The solution of the eq. (1) was given¹⁶ in the form of a trigonometric series, for the plasticizer concentration in the PVC space

$$\frac{C_t}{C_0} \frac{\pi}{4} = \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \frac{(2n+1)\pi x}{2l} \exp \frac{-D(2n+1)^2\pi^2 t}{4l^2} \quad (7)$$

and in a form of a series for the total amount M_t of plasticizer which entered the liquid during time t , while M_∞ was the corresponding amount during infinite time:

$$\frac{M_\infty - M_t}{M_\infty} \frac{\pi^2}{8} = \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp \frac{-D(2n+1)^2\pi^2 t}{4l^2} \quad (8)$$

Stirring of Liquid

The stirring rate of the liquid in motion was defined by the value of the Reynold's number:

$$Re = \frac{L^2\rho u}{\mu} \quad (9)$$

where L is the diameter of the reactor, ρ is the liquid density, μ is the dynamic viscosity of the liquid, and u is the number of revolutions of agitator per unit time.

EXPERIMENTAL

Materials

Plasticizer. The plasticizer, dioctylphthlate, used was a commercial sample (Rhone Poulenc France).

Polymer. A commercial PVC resin (Lucovyl, Rhone Poulenc, France) in the form of a white powder was used throughout this work.

Liquid. Pure benzyl alcohol (Rhone Poulenc) was used for the liquid phase.

Formation of the PVC Disks

Sheets of PVC were prepared with DOP as plasticizer at concentrations of 25, 38, and 50 wt %.

The components of the PVC compounds were mixed in a Plastograph for 10 min at a temperature of 140°C. Sheets were prepared by pressing PVC compound in a steel mold operated by a power press at 150°C for 10 min under a pressure of 50 bars. Disks (18 mm in diam, 3.4 mm thick) were cut from the PVC sheets.

Apparatus for Diffusion

The apparatus and procedure have been described earlier.¹⁴ All experiments were carried out with 20 PVC disks soaked in 200 ml benzyl alcohol in a closed flask of 500 ml capacity, using a controlled rate of stirring. Samples were taken at different times; for one PVC disk, 10 ml solution was removed. Thus, the weight ratio between the disks and the benzyl alcohol remained constant.

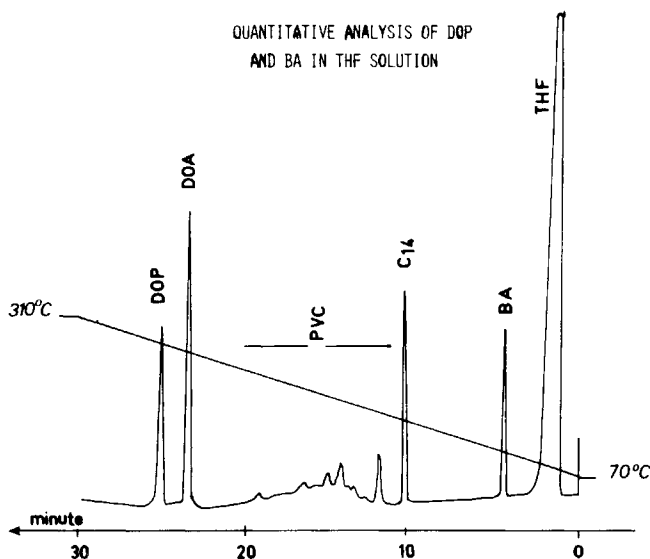


Fig. 1. Chromatogram in gas phase with temperature program. Injection temperature 70°C; heating rate 8°C/min; C14 = tetradecane.

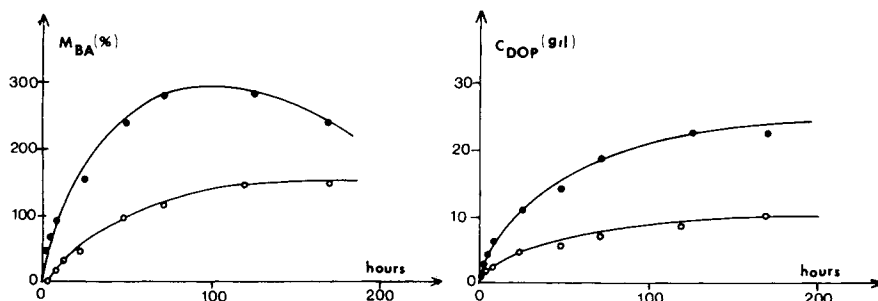


Fig. 2. Left: Transfer of benzyl alcohol (mg in a PVC disk of 1 g) into PVC vs. time: (○) 39°C; (●) 55°C; DOP 25 wt %. Right: Transfer of DOP (g/l. of liquid) vs. time: (○) 30°C; (●) 55°C; DOP 25 wt %.

Analysis of DOP and Benzyl Alcohol in PVC Disks

Each PVC disk was peeled into 17 layers parallel to each other and to the plane faces of the disk by using a lathe with a knife at the end of it and by keeping the disk cool with liquid nitrogen.

Each layer was then weighed and dissolved in an acetone and carbon disulfide mixture. The analysis was performed by gas chromatography after an addition of dioctyl adipate and tetradecane as internal standards (IGC 16, Intersmat, France). Operational conditions were as follows: the column temperature was 70°C at injection time, programmed with a heating rate of 8°C/min. The glass column was 2 m long, and the stationary phase was Chromosorb Q 60/80 mesh and 3% SE 30 silicone rubber (Dow Chemical). A typical chromatogram is shown in Figure 1 while a THF solution is injected.

Analysis of DOP in Liquid

Analysis of DOP in benzyl alcohol was performed by gas chromatography under the same conditions as stated above, by using dioctyl adipate as internal standard.

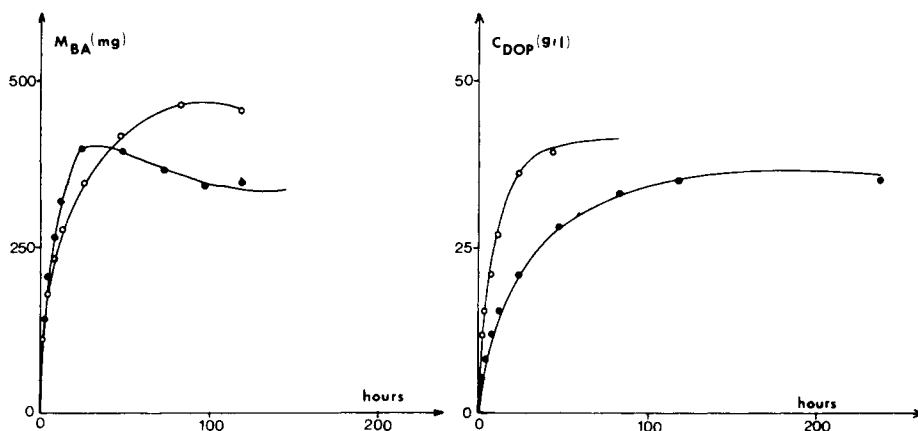


Fig. 3. Left: Transfer of benzyl alcohol (mg in a PVC disk of 1 g) into PVC vs. time: (○) 30°C; (●) 55°C; DOP 38 wt %. Right: Transfer of DOP (g/l. of liquid) vs. time: (●) 30°C; (○) 55°C; DOP 38 wt %.

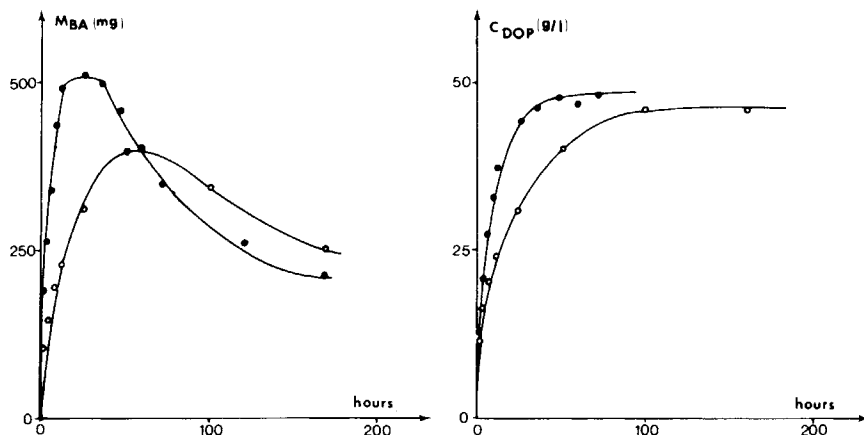


Fig. 4. Left: Transfer of benzyl alcohol (mg in a PVC disk of 1 g) into PVC vs. time: (O) 30°C; (●) 55°C; DOP 50 wt %. Right: Transfer of DOP (g/l. of liquid) vs. time: (O) 30°C; (●) 55°C; DOP 50 wt %.

RESULTS AND DISCUSSION

Previous studies¹⁻¹⁵ reported on the diffusion of plasticizer or additives only from PVC into a liquid, or sometimes on the diffusion from the liquid into PVC¹² when the liquid was a solvent, an additive, or a food. According to the results shown in earlier works, no diffusion of liquid into PVC took place when the liquid was methanol¹⁴ or *n*-heptane.¹⁵

In this article, another experimental fact was pointed out with the simultaneous diffusion of DOP as plasticizer from PVC into liquid and a diffusion of that liquid into PVC when the liquid was benzyl alcohol.

Kinetics of Simultaneous Transfer of DOP from PVC into Liquid and of Liquid into PVC

The importance of several parameters was pointed out in a previous report¹⁴ and these results were taken into account in that work: (1) the stirring of liquid

TABLE I
Diffusion Coefficients $D \times 10^8$ (cm²/s) for DOP Transfer from PVC into Liquid

DOP, wt %	$D \times 10^8$, cm ² /s			E , kcal/mol	D_0
	30°C	40°C	55°C		
25	0.8	2	6	16	2.5×10^{11}
38	8		23	8.3	1.3×10^7
50	12	17	30	6.7	9×10^5

TABLE II
Diffusion Coefficients $D \times 10^8$ (cm²/s) for BA Transfer

DOP, wt %	\bar{D} 30°C	\bar{D} 55°C	\bar{E} kcal/mol	\bar{D}_0	\bar{D} 30°C	\bar{D} 55°C
25	5	10	6.7	3.6×10^4		
38	12	30	9.0	3.4×10^7		1
50	16	68	14	1.7×10^{11}	1.5	2

was found of importance, and all these experiments were carried out with a turbulent flow with a Reynold's number [eq. (9)] of about 3000; (2) the time was also of significance. Diffusion coefficient values were found to decrease with time and to reach a constant value after a time of about 50 h. In this report, only the constant values of diffusion coefficients have been considered.

Experiments were conducted for plasticizer concentration of 25, 38, and 50 wt % at two or three temperatures (30, 40, and 55°C) for each plasticizer concentration.

DOP Transfer from PVC into Liquid

Typical results are shown in Figure 2 (25 wt % for DOP), Figure 3 (38 wt %), and Figure 4 (50 wt %) for the transfer of the plasticizer from PVC into benzyl alcohol at 30 and 55°C.

In every case, the diffusion coefficient values calculated by using both eqs. (4) and (8) were found to be about the same with an accuracy better than 5%. This coincidence can be explained because the ratio of the volumes of liquid and PVC was high enough ($\alpha = 10$). So eq. (8), which is really for the case of an infinite amount of liquid ($\alpha \rightarrow \infty$), was found to be suitable also for our experiment with a good accuracy.

Diffusion coefficient values $D \times 10^8$ (cm²/s) are shown in Table I for dioctylphthalate. The correlation factor of the calculation by the method of least squares was not below 0.97, with a good accord between the experimental values and theory.

The temperature dependence of D has been described by the Arrhenius law:

$$D = D_0 \exp - (E/RT) \quad (10)$$

The increase in the plasticizer concentration was found to produce a decrease

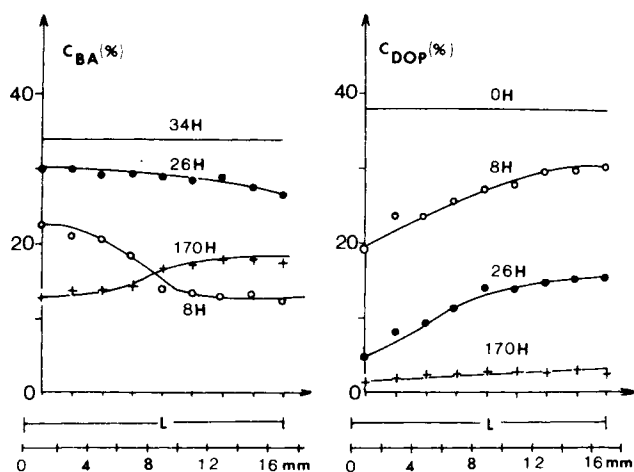


Fig. 5. Left: Concentration profiles of benzyl alcohol (wt % of PVC disk) along PVC disk thickness, at different times: (O) external plane of PVC disk; 1.7 mm center plane of PVC disk; DOP 38 wt %; T 55°C. Right: Concentration profiles of DOP (wt % of PVC disk) along PVC disk thickness, at different times; (O) external plane of PVC disk; 1.7 mm center plane of PVC disk; DOP 38 wt %; T 55°C.

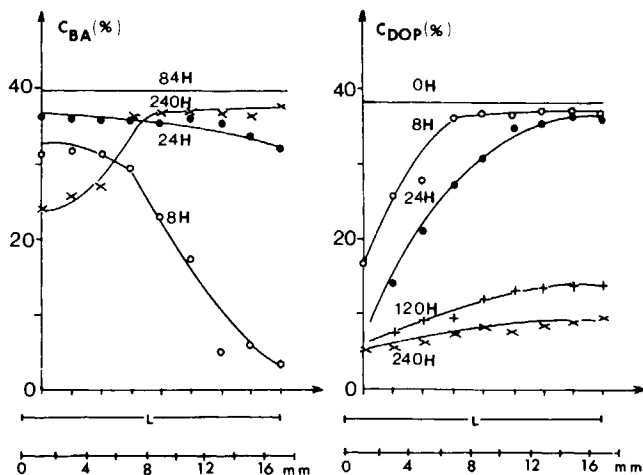


Fig. 6. Left: Concentration profiles of benzyl alcohol (wt % of PVC disk) along PVC disk thickness, at different times; (O) external plane of PVC disk; 1.7 mm center plane of PVC disk; DOP 38 wt %; T 30°C. Right: Concentration profiles of DOP (wt % of PVC disk) along PVC disk thickness, at different times; (O) external plane of PVC disk; 1.7 mm center plane of PVC disk; DOP 38 wt %; T 30°C.

in the activation energy E for diffusion, accompanied by a decrease in the corresponding value of D_0 . This phenomenon was noted previously for other polymer systems.^{12,17} The activation energy values are about the same as those measured for a stabilizer in plasticized PVC.¹²

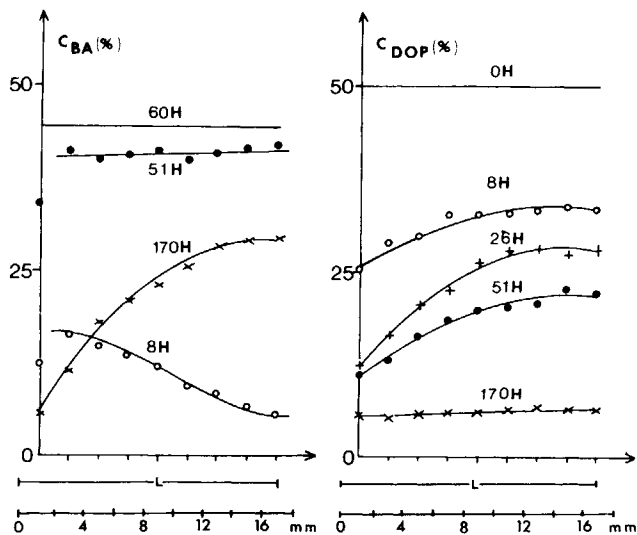


Fig. 7. Left: Concentration profiles of benzyl alcohol (wt % of PVC disk) along PVC disk thickness, at different times; (O) external plane of PVC disk; 1.7 mm central plane of PVC disk; DOP 50 wt %; T 30°C. Right: Concentration profiles of DOP (wt % of PVC disk) along PVC disk thickness, at different times; (O) external plane of PVC disk; 1.7 mm central plane of PVC disk; DOP 50 wt %; T 30°C.

TABLE III
Local Values of Diffusion Coefficients $D \times 10^8$ (cm²/s)

DOP, wt %	T , °C	D (DOP)	\bar{D} (BA)
38	30	2-10	0.5-30
38	55	2-25	1 -90
50	30	2-22	0.3-40

Benzyl Alcohol Transfer in and out of PVC

Diffusion studies were conducted at 30 and 55°C over the wt % range of 25-50 for DOP. Two interesting observations are shown in Figures 2, 3, and 4 for benzyl alcohol: a diffusion of BA into PVC took place coupled with the loss in plasticizer of PVC. The amount of BA transferred into PVC increased at the beginning of the immersion, rose to a maximum value, and then decreased. Thus, it was a two-step phenomenon with a BA transfer into and out of the PVC slab.

Diffusion coefficients were obtained for BA by using eq. (8) for the two steps of the transfer. Correlation factors, not below 0.95, showed that eq. (8) accommodated all the experimental values very well.

As shown in Table II, diffusion coefficients are higher for BA transfer into PVC (noted \bar{D}) than for the loss in weight of DOP. Diffusion coefficients for BA transfer out of PVC (noted \bar{D}) are very low. In contrast to the case of DOP, as the plasticizer concentration increased in PVC, the polymer became less permeable to BA, which produced an increase in the activation energy for the transfer of BA into PVC.

The BA maximum in PVC that appears in curves 2, 3, and 4 (on the left) is dependent on temperature and DOP concentration in PVC. This maximum is of the order of magnitude of the initial amount of DOP in PVC, and it appears when a large value of DOP is extracted. Hence, the degree of swelling of the polymer due to the influx of BA is small when the maximum value of BA in PVC is reached.

Measurements of Additive Concentrations in the PVC Disk Itself

PVC disks were removed at different times and were peeled off in 17 200- μ m-thick layers, as described in the experimental part. In each layer, DOP and BA concentrations were measured.

The concentration of additives (DOP and BA) was plotted against the position of the center plane of every layer in the PVC disk before cutting. As shown in Figure 5, abscissa 0 was taken for the face, and abscissa 1.7 for the center plane of the PVC disk.

The experiments were carried out at different times for the two plasticizer concentration (38 and 50 wt %) at 30 and 55°C. In the curves in Figures 5, 6, and 7, the progression of DOP and BA inside the PVC is clearly shown. For the maximum value of BA transferred into PVC, the concentration of BA appears to be about constant inside the PVC disk along its thickness.

Diffusion coefficients were obtained from these concentration profiles by using eq. (7). They were found to be dependent on the DOP concentration, as is well known. In Table III only the higher and the lower value of diffusion coefficients calculated in a given disk are given, corresponding to the higher and to the lower

value of DOP concentration in PVC, respectively. The values of diffusion coefficients shown in Tables I and II, obtained by using eq. (8), are in the range of the values cited in Table III.

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