

A New Approach to the Study of Plasticizer Migration From PVC into Methanol

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Synopsis

A new approach to the study of the migration rate was attempted for dioctylphthalate as plasticizer from solid PVC into liquid methanol. Two different experiments were carried out: first, a classical one by measuring the increase in the plasticizer concentration in solution; second, a new one by measuring the plasticizer concentration inside the solid PVC itself, for different times and for different depths in that solid. Equations of diffusion in unsteady state were found to correlate well with experiments in both cases. Stirring of the solution measured by Reynold's number was found to be important. Measurements were carried out inside the solid PVC, and the profile of the concentration of dioctylphthalate inside the PVC disc was determined at different times. The diffusion coefficient was calculated inside the PVC disc, and it was found to vary with the DOP concentration.

INTRODUCTION

The migration of plasticizers from plasticized PVC into a liquid is of great interest from two points of view: the loss in weight of PVC compound with the resulting variation of its properties and the increase in the concentration of any undesirable material in the liquid.

The migration of phthalate plasticizers from PVC to several petroleum oils,¹ to several alcohols,² and to other solvents³ was studied quantitatively by a method based on labeled plasticizers and measurements of the radioactivity of the medium. The effects of different factors on the migration process were examined, e.g., the nature of solvent and plasticizer, the amount of plasticizer, and the temperature of solution.

A permeation membrane made of several nylon multilayers stacked one by one was used in a recent work.⁴ At the end of the experiment, the multilayers were peeled into layers for evaluation of the permeate concentration in each of these layers.

Kaufman⁵ reported the kinetics of plasticizer migration between nitrocellulose and ethylcellulose in propellant systems. The concentration dependence of the diffusion coefficient was measured assuming that the concentration is a function of time and distance. Another work of interest⁶ was concerned with the diffusion of a radioactively labeled UV stabilizer in plasticized PVC sheets. The diffusion coefficients were calculated for plasticizer concentrations of 20, 30, 40, and 50%.

Frisch⁷ carried out a mathematical study of simultaneous nonlinear diffusion of a solvent and organic penetrant in a polymer system. Interesting work in this

direction was reported by Hansen,⁸ who studied the drying of polymer films. The drying process by solvent evaporation occurred in two distinct phases. In the first phase, the solvent loss was controlled by boundary layer phenomena. The second phase was controlled entirely by internal diffusion resistance of solvent through the polymer. The division between the two phases was not sharp because a solvent gradient began to develop as soon as internal diffusion became significant relative to boundary layer resistance.

Several other works on diffusion of plasticizers from PVC into liquids are reported in the literature.⁹⁻¹¹ A number of articles deal with the study of the plasticizer diffusion from PVC into food.¹²⁻¹⁷

THEORETICAL

Plasticizer PVC disks were put into liquid methanol and the plasticizer diffused from the solid to the liquid. The plasticizer was transferred from the solid PVC into the liquid phase by a three-step process: (1) plasticizer transport into solid PVC itself, by internal diffusion in nonsteady state; (2) transport phenomena at the interface of PVC and solution, between the two phases; and (3) plasticizer transport into the liquid; it was controlled by boundary layer phenomena.

In this work, the two phases were regarded as balanced at their interface for DOP concentration, and we assumed the transfer resistance to be negligible through that interface.^{8,18} As a result of these assumptions, it was decided to investigate the plasticizer transfer into both the liquid phase and the solid PVC phase.

Plasticizer Transfer into the Solid PVC by Diffusion in a Nonsteady State

The following assumptions were made: (1) We used PVC disks and considered the case of one-dimensional diffusion in a medium bounded by two parallel planes, e.g., the planes $x = \pm l$ (our disks of material were so thin that all the diffusing substance effectively diffused through the plane faces and a negligible amount through the edges). (2) The diffusion was studied as a nonsteady-state phenomenon. (3) At time 0, when solid disks were immersed in a liquid, the concentration of plasticizer was taken as constant in the solid PVC and equal to zero on its faces.

The diffusion in an isotropic medium was defined by Fick's law.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (1)$$

where D depends on the concentration C of diffusing plasticizer, t is time, and x is the abscissa measured through the thickness of the disk.

The boundary conditions were

$$\begin{aligned} t = 0 \quad -l < x < l \quad c = c_0 \text{ (constant)} \\ t > 0 \quad x = \pm l \quad c = 0 \\ t > 0 \quad -l < x < l \quad c_t < c_0 \end{aligned} \quad (2)$$

where $2l$ is the thickness of the PVC disk. The solution of this equation was given¹⁸ in the form of a trigonometric series, where D is constant:

$$\frac{C_0 - C_t}{C_0} = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \frac{(2n+1)\pi x}{2l} \exp \frac{-D(2n+1)^2\pi^2}{4l^2} t \quad (3)$$

Plasticizer Transfer into Liquid Phase

If M_t denotes the total amount of diffusing substance that has left the PVC disk at time t and M^∞ is the corresponding quantity after infinite time, we have the known equation¹⁸

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

A basic fact concerning the transfer rate of plasticizer from solid PVC into liquid is the stirring rate of the liquid in motion. This stirring rate can be defined by the value of Reynold's number, a dimensionless number:

$$Re = L^2 n \rho / \mu \quad (5)$$

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

EXPERIMENTAL

Sample Preparation

Sheets were prepared from commercial PVC (Lucovyl, Rhône-Poulenc, France) and pure plasticizer (dioctylphthalate) by using successively a Plastograph (Brabender) working at 135°C for 10 min and a steel mold operated by a power press at 150°C for 10 min under a pressure of 50 bars. Homogeneity of the sheets was controlled by processing several specimens and titrating plasticizer amount in them by gas chromatography. Several disks were cut and used as samples (18 mm diameter, 3.4 mm thickness, 1.06 g mean weight when DOP is present at 35.5%).

Apparatus for Diffusion

All experiments were carried out by using 20 PVC solid disks soaked in 200 ml methanol as liquid in a closed flask of 500-ml capacity. The experiments were repeated, twice at least, once with controlled stirring and the other time without stirring. Samples were taken at different times; for one PVC disk, 10 ml solution was removed. Thus, the weight ratio between the discs and the methanol solution remained constant. The velocity of liquid in motion was calculated by multiplying the radius value of the flask by the number of stirrer revolutions per unit time.

Analysis of Plasticizer in PVC Disks

Every PVC disk was peeled off into 17 layers by using a lathe with a knife at the end of it. These layers were parallel to each other and to the flat faces of the disks. This operation was found to be possible when the PVC disk was kept cool with the help of liquid nitrogen.

Then, the following operations were carried out successively so as to measure the concentration of plasticizer inside every PVC disk, for different x values of the abscissa taken along the thickness of disk: (1) weighing of peeled sections; (2) dissolution of sections in equimolecular mixture of acetone and carbon disulfide; (3) selective precipitation of PVC by adding 5 ml methanol; (4) extraction of liquid and addition of hexacosane as internal standard for quantitative analysis.

Analyses were performed with a gas chromatograph (Intersmat., France) under isothermal conditions (270°C) with a column (2 m long, 3 mm i.d.) and "OV 17" silicone rubber (2.5%) (Dow Chemical) as liquid phase. The retention times were about 270 sec for hexacosane and 460 sec for DOP, and the response factors for quantitative analysis were found to be equal to 1 for hexacosane and 1.04 for DOP.

Analysis of Plasticizer in Methanol

Analysis of plasticizer in methanol was performed with the gas chromatograph under the same conditions as shown above, by injecting the methanol solution with hexacosane as internal standard.

RESULTS

Study of DOP Transfer into Methanol

The migration of DOP as plasticizer from PVC into methanol was studied by measuring the DOP concentration at different times, while the transfer operation was kept under isothermal conditions.

Effect of Stirring

Measurements for DOP concentration in methanol were made at a temperature of 30°C, while the concentration of DOP in PVC disks was equal to 35.5% (Table I). Experiments for DOP transfer were performed on one hand in a stationary liquid and on the other hand in liquid in motion. The Reynold's number for the experiments with liquid in motion was 3000 ± 500 .

The values in Table I show the significance of stirring on plasticizer transfer from solid PVC into liquid. The effect of stirring was found to be important for short times, when the DOP transport was controlled by boundary layer phenomena.

TABLE I
Effect of Stirring Time in DOP Concentration in Solution

	DOP concentration, g/l.			
	2 hr	12 hr	24 hr	48 hr
Stationary liquid	0.56	1.71	3.26	5.34
Liquid in motion	0.87	2.57	3.75	5.35

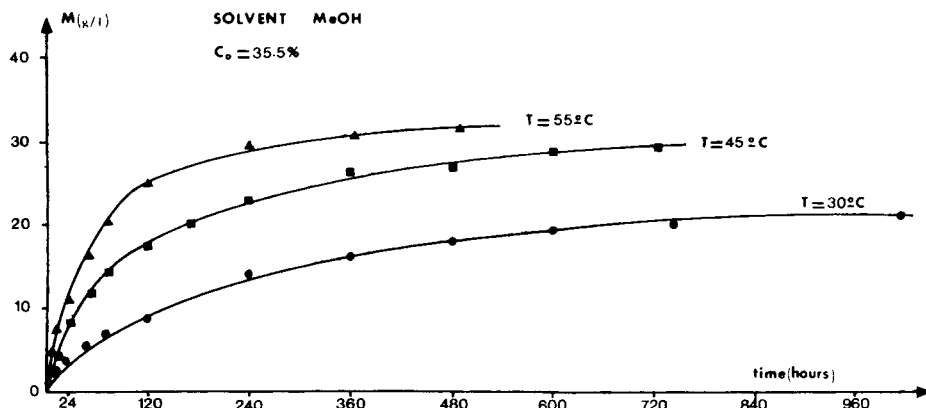


Fig. 1. Variation in plasticizer migration (g/l.) from PVC disk into methanol vs. time, in isothermal conditions at different temperatures, with the liquid in motion. $Re = 3000$.

Influence of Temperature

Several experiments were done at different temperatures (e.g., 30, 45, and 55°C) while the liquid was kept in motion with $Re = 3000$. The concentration of DOP in the PVC disks was equal to 35.5%. The concentration of DOP in methanol, expressed in g/l., was plotted against time of migration for these three temperatures (Fig. 1). The values showed the importance of temperature for the migration rate.

The concentration of DOP in methanol was found to obey a kinetic law according to eq. (4) (this concentration is proportional to the DOP weight M used in this equation). Diffusion coefficients calculated by using this equation and with the help of a computer were found to be only dependent on temperature, and the correlation coefficient r^2 near 1 showed close agreement (Table II).

The time values chosen for these calculations were more than 50 hr, when dependent on time.

By considering that the diffusion coefficient D varies with the temperature according to Arrhenius' law, the activation energy was found to be equal to 9.3 kcal/mole.

Influence of DOP Concentration in the PVC Disks

Experiments were carried out at 55°C with $Re = 3000$ by working with PVC disks of different DOP concentrations, e.g., 25–35.5 and 50% by weight.

Plots of DOP concentration in methanol (g/l.) against time (hr) are shown in

TABLE II
Effect of Temperature on Diffusion Coefficient of DOP Into Methanol^a

	30°C	45°C	55°C
$D \times 10^8, \text{cm}^2/\text{sec}$	1.2	1.7	3.2
r^2	0.99	0.999	0.998

^a DOP in disk = 35.5%; $Re = 3000$.

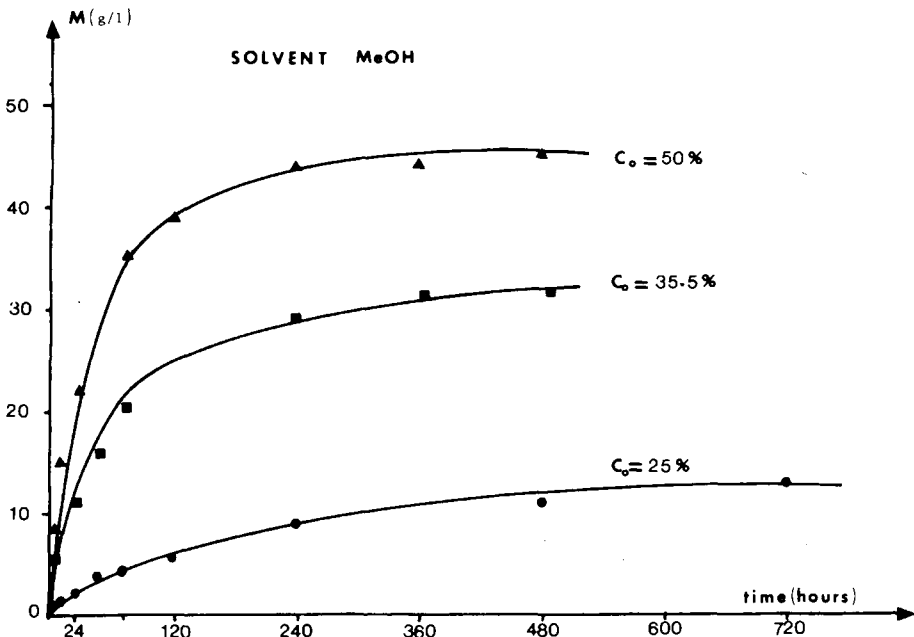


Fig. 2. Variation in plasticizer migration (g/l.) from PVC into methanol vs. time, at 55°C, for different plasticizer concentrations in PVC.

Figure 2. These values were found to obey a kinetic law according to eq. (4). The diffusion coefficients were calculated for times higher than 50 hr. They appeared to vary with the initial DOP concentration in PVC (Table III), as reported in the literature.^{1,4-7,19}

Variation of Diffusion Coefficient with Time

The influence of time was found to be of importance, especially for the lower time values. This fact was investigated by calculating the values of the diffusion coefficient D at different times and by using eq. (4) and our experimental values for M_t . From the values given in Table IV, it was obvious that the effect of time is critical when it is less than 50 hr. For time values higher than 50 hr, D became constant.

When calculating the values of the diffusion coefficients, we chose time values higher than 50 hr, thereby eliminating their dependence on time.

TABLE III
Diffusion Coefficient of DOP From PVC to Methanol Effect of DOP Concentration in PVC^a

DOP, %	25	35.5	50
$D \times 10^8, \text{cm}^2/\text{sec}$	0.8	3.2	4.7
r^2	0.998	0.998	0.988

^a $T = 55^\circ\text{C}$; $Re = 3000$; $t = 100 \text{ hr}$.

TABLE IV
Effect of Time on Diffusion Coefficient of DOP in Methanol^a

	2 hr	12 hr	24 hr	48 hr	100 hr	500 hr
$D \times 10^8, \text{cm}^2/\text{sec}$	7.1	3.7	2.8	2	1.2	1.2

^a $T = 30^\circ\text{C}$; DOP % = 35.5; $Re = 3000$.

Study of Plasticizer Diffusion in the PVC Disk Itself

Effect of Plasticizer Concentration in PVC Disks

According to the process described before, PVC disks were removed from methanol at different times, and every disk was peeled off in seventeen 200-

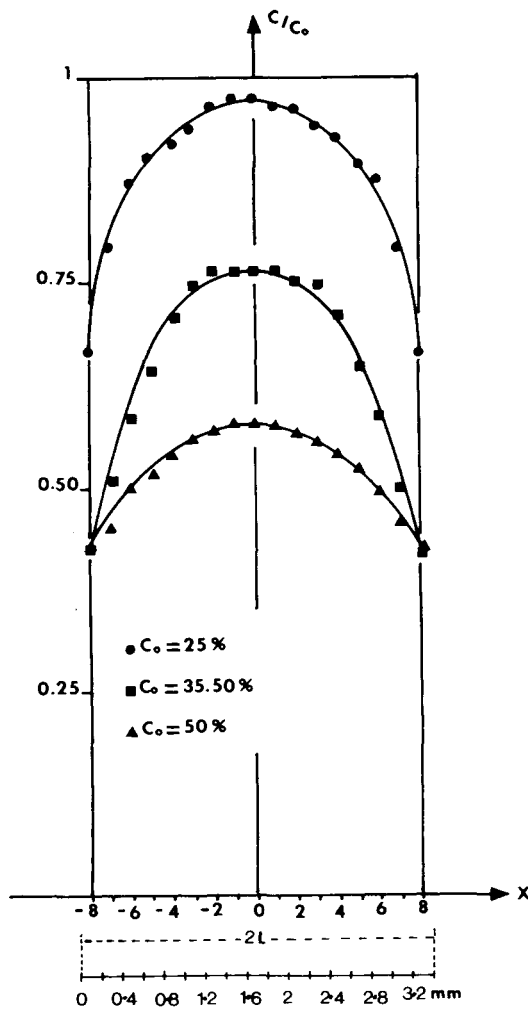


Fig. 3. Variation in relative plasticizer concentration along the PVC disk thickness, after 50 hr, for different initial plasticizer concentration in PVC. C_0 = plasticizer concentration at time 0. On the abscissa are shown the 17 layers parallel to the faces of the PVC disk. Abscissa 0 was taken for the center plane of the PVC disk, and abscissas ± 8 for the center plane of the two layers close to the disk faces.

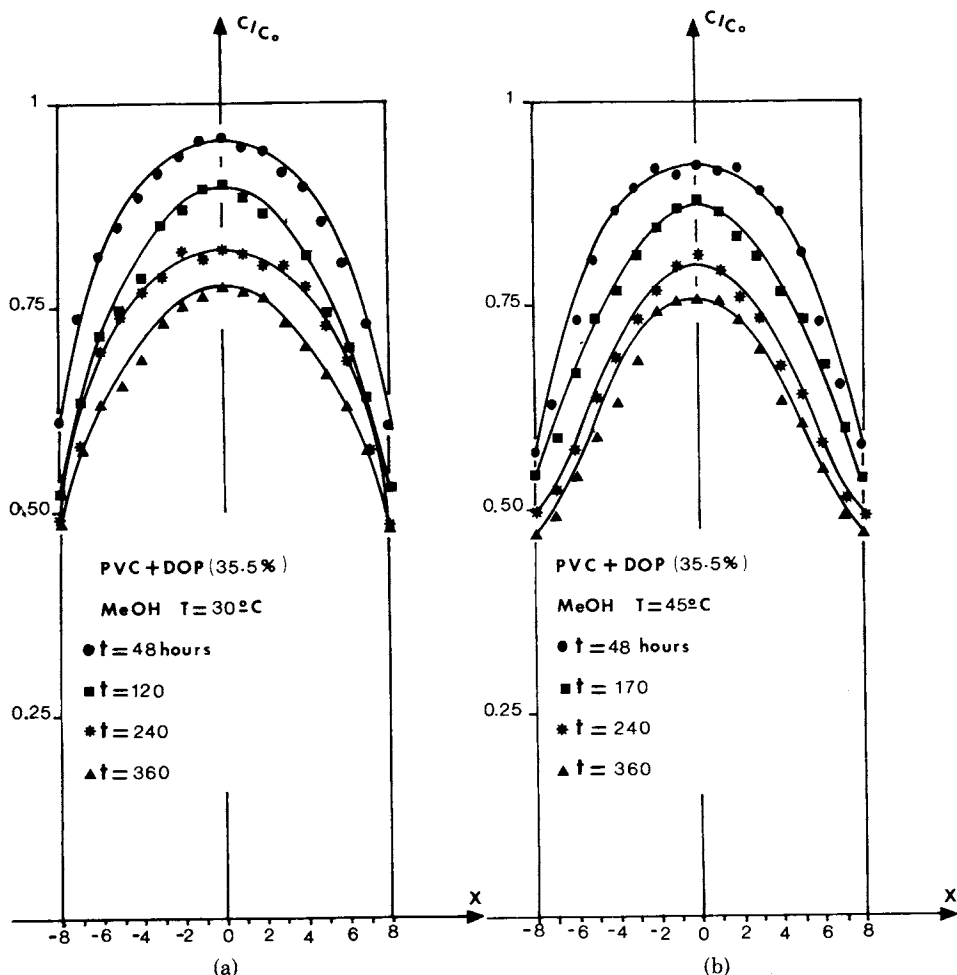


Fig. 4. Variation in relative plasticizer concentration along the PVC disk thickness for different times, at different temperatures: (a) 30°C; (b) 45°C; (c) 55°C; initial DOP concentration = 35.5%.

μm -thick layers. The DOP concentration was measured in every layer. This concentration was plotted against the position of the center plane of every layer in the PVC disk before cutting; this position was expressed by x on the abscissa, as shown in Figure 3, where $-8 < x < 8$. The 0 point on the abscissa was taken for the center plane of the PVC disk, parallel to the faces, and ± 8 the abscissa at the center plane of the two layers close to each disk face.

The experiments were performed in isothermal conditions at 55°C, for different initial concentrations of plasticizer in the disks (25, 35.5, and 50%). We were not able to measure the DOP concentration on the disk faces. The curves shown in Figure 3 have a symmetrical shape, and they were considered on the whole to obey eq. (3).

The diffusion coefficient values were calculated using eq. (3), with the help of a computer, in spite of the dependence of the diffusion coefficient on plasticizer concentration. This assumption was made by all early workers because of the fact that it was impossible to calculate the D values by eq. (3) in unsteady state when they are dependent on the plasticizer concentration.¹⁹

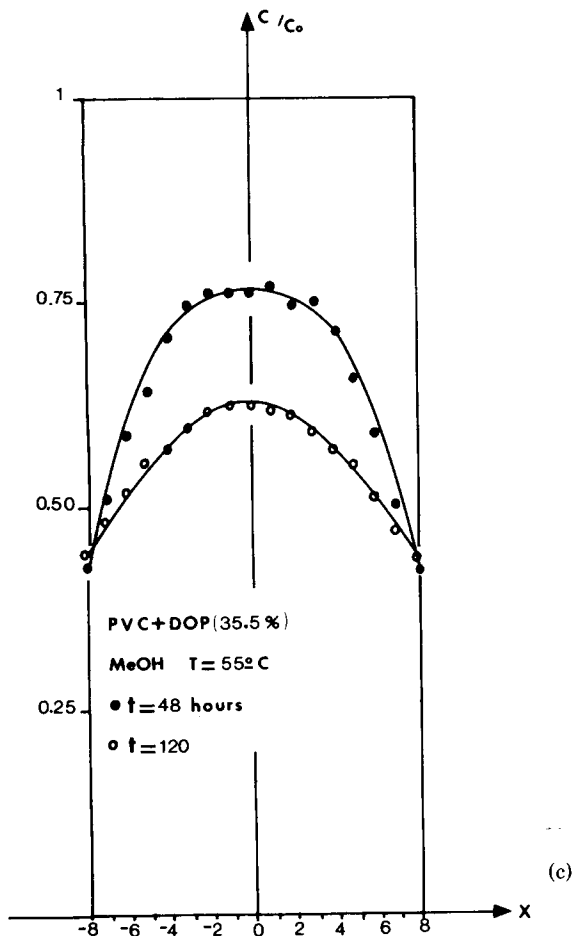


Fig. 4. (Continued from previous page.)

Effect of Temperature on Plasticizer Diffusion Inside the PVC Disks

The DOP concentration values measured in the PVC layers were plotted against the position of the center plane of every layer taken along the PVC disk thickness before cutting, as already shown in Figure 3. Three curves were drawn for different temperatures: 30°C [Fig. 4(a)], 45°C [Fig. 4(b)], and 55°C [Fig. 4(c)] when the initial DOP concentration in the PVC disk was 35.5%. A large decrease in DOP concentration in PVC appeared at both faces of the disk after several hours. This decrease allowed to explain how the second phase of DOP migration took place when this migration was controlled only by diffusion of DOP in PVC itself and when it became insensible to liquid stirring.

The D values calculated by using eq. (3) were shown for these three temperatures (Fig. 5). The diffusion coefficient values of plasticizer in PVC were found to vary largely with the plasticizer concentration. Thus, these values were dependent on time and on the abscissa taken along the thickness of PVC the disk. By comparing the D values shown in Figure 5 at the center plane of the PVC disk and the values quoted in Table II at the same temperature, we found these values to be about of the same order of magnitude. However, the D values in Figure 5 were decreasing too much when DOP inside the PVC was close to the disk faces.

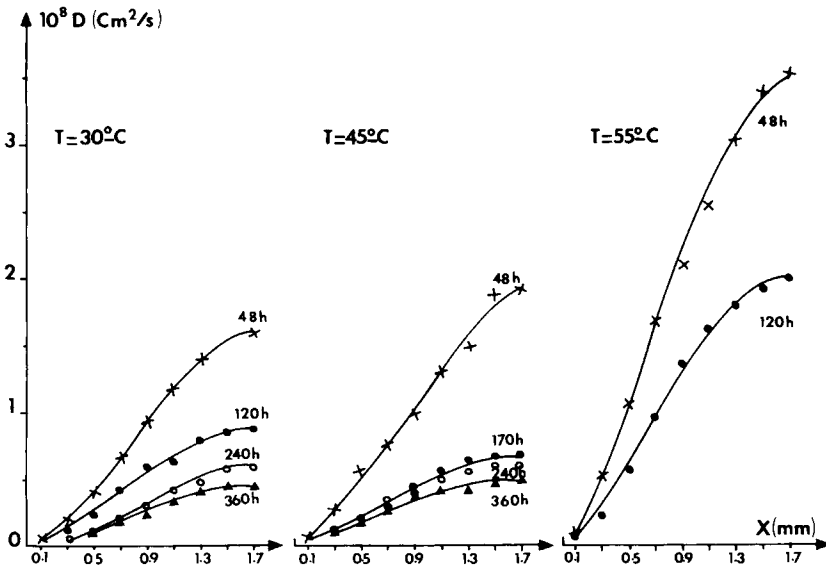


Fig. 5. Variation in diffusion coefficients of DOP inside the PVC along disk thickness, at different times (hr) for different temperatures: abscissa 0: one face of PVC disk; abscissa 1.7: center plane of PVC disk.

CONCLUSIONS

This new study of plasticizer transfer from PVC into a liquid was approached not only by measuring the plasticizer concentration increase in the solution, but also by measuring the plasticizer concentration decrease inside the solid PVC itself.

Diffusion coefficients were calculated for plasticizer transfer by considering a nonsteady-state phenomenon. The transfer of plasticizer into liquid was shown to occur in two distinct phases. In the first phase, for any time lower than 50 hr, the plasticizer transfer was controlled by boundary layer phenomena, and the stirring of liquid appeared to be of importance. The second phase of plasticizer transfer was entirely controlled by internal diffusion in the PVC itself. During this phase, the liquid stirring appeared to be negligible. The division between the two phases was not sharp and the diffusion coefficient of plasticizer transfer was found to decrease regularly with time during the first phase and to reach a constant value at the beginning of the second phase.

The diffusion coefficient value of plasticizer inside the PVC were found to be largely dependent on the plasticizer concentration. That last part of our work calls for further studies for calculating the diffusion coefficient taking that dependence into account.

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