Modelization of Matter Transfers Between Plasticized PVC and Liquids in Case of a Maximum for Liquid-Time Curves

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Synopsis

When plasticized PVC and liquids are contacted with each other, as in liquid and packaging, some matter transfer may occur. The phenomenon is complicated, and no analytic solution can be found. A simultaneous transfer of the liquid into and plasticizer out from the PVC mass takes place with concentration-dependent diffusivities. Very often, liquid concentration-time curves have a maximum, when the rate of transfer is higher for the liquid than for the plasticizer at the beginning of the contact. Another application of short tests has been obtained with success in this hard case. A new model using short test data has been developed. It takes into account not only the diffusion of both liquids through the PVC, but also matter transfers through the liquid—PVC interface with a coefficient of matter transfer, as well as the data corresponding to the equilibrium. Some information of interest is given by way of the materials transferred through PVC faces, and the profile of concentration through the PVC for the liquid and plasticizer.

INTRODUCTION

PVC plays an important role in the plastics industry today, and the greater part of PVC is used as plasticized PVC. In all applications, the plasticized polymer used for product packaging[1] is in contact with some kind of surrounding medium: blood and blood components[2] with extensively plasticized PVC, petroleum oils and aromatic hydrocarbons,[3] alcohols[4-6] (the effect of water percentage in ethanol is very important to plasticizer transfer),[7] drugs and cosmetics or pharmaceutical products,[8,9] or even liquid foods.[10-14] Under these conditions, the plasticizer very often migrates to the surrounding medium with the following results.

1. The surrounding medium is contaminated by the plasticizer and PVC additives.
2. There is a decrease in mechanical properties of the polymer.
   The problem is complicated for several reasons:
1. Many possible factors can affect the migration process.[15] The nature of the polymer and the plasticization process, the surrounding medium, the nature and amount of plasticizer, and the conditions of the migration process, i.e., stirring, time, and temperature.
2. In a variety of contexts, there is a simultaneous diffusion of the liquid

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into, and the previously dispersed plasticizer out of, the PVC slabs,[6,15-18] and liquid diffusion is directly coupled to the plasticizer loss.

3. The experiments are tedious and time consuming.[1]

A highly simplified class of model situations may give a semiquantitative estimate of various effects.[16] Another model, taking into account the simultaneous diffusion of liquid into, and plasticizer out of PVC, and the dependence of diffusivities on liquid and plasticizer concentration, was proposed.[19,20] In this model, short tests were used for determining diffusivities of both liquid and plasticizer,[21] with the following advantages:

1. Very short tests (several minutes instead of months).

2. Concentrations of liquid and plasticizer are known and can be supposed constant during the test. This model[19-21] was able to predict the transfers of both liquid and plasticizer when the amount of liquid transferred into PVC had no maximum.

But very often,[1,6,15,22] the amount of liquid transferred into PVC follows a more complicated phenomenon. This amount increases, rises to a maximum value, and then decreases, the liquid maximum being dependent on the plasticizer concentration in PVC. All previous models[16,19-21] were not able to explain these complex transfers and swelling of the PVC sample. Assumptions were made for boundary value as soon as PVC is soaked into liquid. The concentration is taken as 0 for placticizer and 100 for liquid on PVC faces.[16,23]

The present work deals with the study of model able to take into account the following experimental results:

1. Simultaneous transfers of liquid into and plasticizer out of PVC.

2. The maximum value obtained for the liquid transferred into PVC and a resulting swelling of PVC samples.

3. The concentration of plasticizer on PVC faces is not 0, in agreement with results obtained from a previous study using infrared (IR)-attenuated total reflectance.[18]

This model is built by taking into account the following important points: A coefficient of matter transfer is used for the transfer of liquid and plasticizer through PVC faces. They are determined by short tests at the beginning of the operation.

The transfer of both liquid and plasticizer through PVC mass is obtained by diffusion in unsteady state, and diffusivities are dependent on the concentrations of liquid and plasticizer.

Great attention is given to the values of liquid and plasticizer concentration on PVC faces, where the concentration of the liquid is related to that of the plasticizer by a single equation.

THEORETICAL

Mathematical Treatment

It has been generally assumed that diffusion under transient conditions is described by Fick's equation[23]

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x}\left(D\frac{\delta C}{\delta x}\right) \qquad (1)$$

With the above conditions, especially the concentration-dependent diffusion of both liquids (plasticizer and liquid) and boundary conditions for the PVC sheet, this equation could not find an analytic solution.

However, for very short times, the small amount of substance transferred M_t at time t was very low and could be expressed as a function of M_∞, the quantity after infinite time by a single equation, because the concentration of plasticizer and liquid were about constant during the test.

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{0.5} \tag{2}$$

Numerical Analysis

The problem had to be solved with the help of a numerical method with finite differences. We have chosen an explicit one available for microcomputers.

The PVC sheet was divided into several equal finite slices of thickness Δ_x by concentration-time reference planes (n and i), as shown in Figure 1. The balance of the liquid considered (plasticizer or n-heptane) enabled one to conclude for the plane n within the PVC sheet:

$$C_{n,i+1} = \frac{1}{M_{n,i}}\left[C_{n-1,i} + (M-2)C_{n,i} + C_{n+1,i}\right] \tag{3}$$

with the dimensionless modulus M:

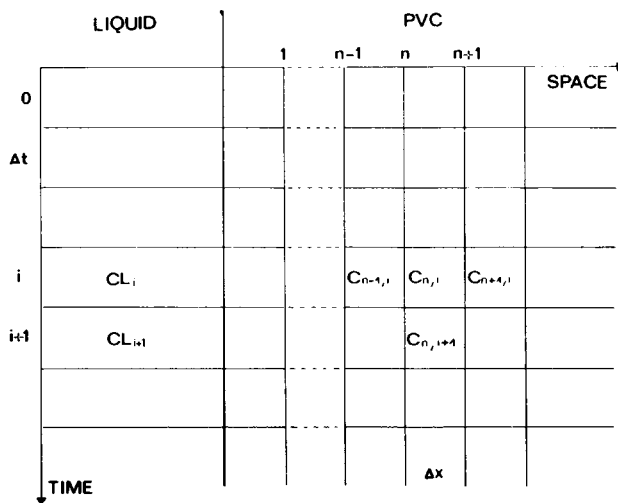$$M_{n,i} = \frac{(\Delta x)^2}{\Delta t}\frac{1}{D_{n,i}} \tag{4}$$

Fig. 1.   Space-time diagram for calculating liquid concentrations through PVC mass.

and the diffusivity:

$$D_{n,i} = \exp\left(- \frac{A}{C_{n,i}^p + \alpha C_{n,i}^l} - B\right) \tag{5}$$

Equations (3) and (4) were available for the plasticizer and liquid located within the plane n by using the corresponding diffusivity.

The diffusivity was found to vary with the total amount of both liquid and plasticizer located in the PVC slice. Coefficient α evaluated the contribution of the liquid according to

$$\alpha_{n,i} = \frac{V_{n,i}^l}{V_{n,i}^l + V_{n,i}^p} \frac{d_p}{d_l} \tag{6}$$

Coefficients A and B were determined by using short test data (Fig. 2) obtained with PVC plasticized with various D E H P percentages (20:25:30:35:50% by weight).

The present model is quite different from the preceding one,[20] because we have considered here the matter transfer through the liquid—PVC interface by a special treatment.

On PVC faces, the variation in the concentration of liquid and plasticizer were calculated by the equation

$$C_{o,i+1} = \frac{1}{M_{o,i}}\left[2mC_{l,i} + \left(M_{o,i} - 2m - 2\right)C_{o,i} + 2C_{1,i}\right] \tag{7}$$

with the modulus M as shown in eq. (4) and the dimensionless number m as
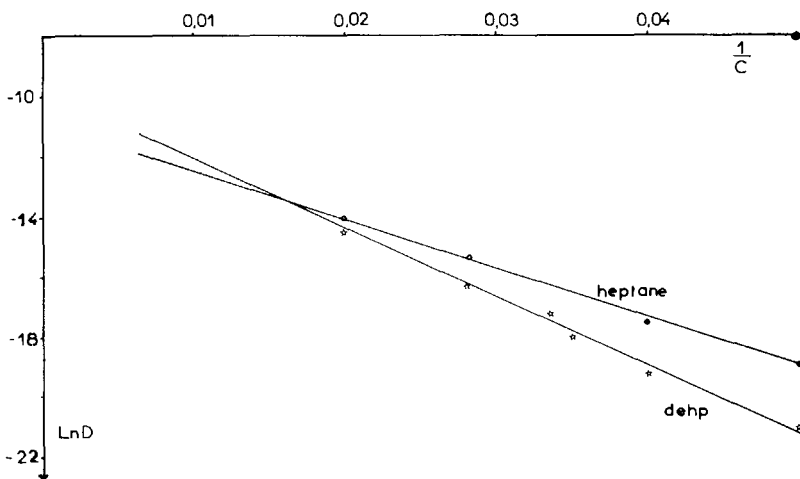
$$m_{o,i} = \frac{h\,\Delta x}{D_{o,i}} \tag{8}$$

Fig. 2. Log D as a function of (plasticizer percentage)$^{-1}$. ($\bullet$), n-Heptane transfer; ($\star$) plasticizer transfer.

where h, the coefficient of matter transfer through the liquid PVC interface, determined with the help of short tests, was expressed by the classic equation

$$h = \frac{\Delta Mt}{S \, \Delta t \, \Delta c} \tag{9}$$

The concentration of the liquid able to enter the PVC, $C_{l,i}$, which appears in eq. (7), did not have the value 100%, because only a part of this liquid can enter the PVC. It was determined as a function of the concentration of plasticizer by eq. (10):

$$X_l = \frac{n^l}{n^p + n^l} \tag{10}$$

where the value of X_l is that obtained at equilibrium, at the end of the transfer process.

The total amount of the liquid and plasticizer transferred through the liquid PVC interface was calculated at different times by integrating the above-mentioned profiles of concentration with respect to time.

EXPERIMENTAL

Materials and Apparatus for Determining Diffusion

PVC compounds were prepared with dioctylphthalate (DOP) as plasticizer at different concentrations: 20:25:30% by weight, and a commercial PVC resin (Lucovyl, Rhone Poulenc) in the form of a white powder. These components were mixed by using a solvent of the plasticizer and drying the mixture. Sheets were prepared by pressing PVC compounds in a steel mold operated by a press at 150°C for 10 min under a pressure of 50 bars. Disks (18 mm in diameter; 3.0 or 1.0 mm thick) were cut from the PVC sheets.

As earlier shown,[19,20] experiments for transfers were carried out with PVC disks soaked in n-heptane in a closed flask by using a controlled rate of stirring determined by the Reynold's number of 3000.[15] Analysis of DOP in the liquid was performed by gas chromatography (IGC 16, Intersmat) after an addition of dioctyladipate as internal standard. The weight of the PVC disk was measured at the same time for determining the amount of liquid (n-heptane) located in the PVC. These experiments were conducted for short tests in order to determine the kinetics of both transfers—the liquid into PVC and the plasticizer out of the PVC—and they were also of help for long real tests.

Calculation for Long Real Tests

Kinetic parameters obtained from short tests and the above-mentioned method with finite differences were used for calculating the profiles of concentration of liquid and plasticizer developed through the PVC sheet. The integration of these concentrations allowed us to obtain the amount of liquid and plasticizer transferred through the liquid PVC interface.

RESULTS AND DISCUSSION

Data Obtained with Short Tests

Experiments were performed under isothermal conditions (30°C) in the well-stirred liquid, by using various PVC disks with a plasticizer percentage ranging from 20 to 50% in weight.

For short tests, the amounts of liquid and plasticizer transferred were very low, so the concentration of plasticizer in PVC could be considered constant during the test. As shown in earlier studies,[19-21] diffusivities of liquids were calculated from the slopes of the straight line obtained by plotting the values of the amount of liquid transferred against the square root at time. As the logarithm of diffusivities of liquids were found to be related to the reciprocal of the initial concentration of plasticizer according to a linear relation (Fig. 2), it was easy to obtain the coefficients appearing in eq. (5). These coefficients are shown in Table I for the plasticizer and n-heptane as liquid for different initial concentration of the plasticizer ranging from 20 to 30%. The values of the coefficient of matter transfer as calculated in eq. (9) are also given, as well as the coefficient X_l shown in eq. (10) and characterizing the equilibrium. This last coefficient X_l was obtained, of course, from long real tests when the equilibrium seemed to be reached.

Amount of Liquids Transferred in Long Real Tests

The amounts of liquid and plasticizer transferred through the liquid PVC interface were plotted against the time, in Figure 3 for 20%, Figure 4 for 25%, and Figure 5 for 30% of the initial concentration of the plasticizer in PVC sheets.

As shown in these figures, the behaviors of the liquid and plasticizer were quite different. The plasticizer was continuously extracted from the PVC and transferred into the liquid until the equilibrium was reached for a long time. A complicated transfer was shown for the liquid, because the amount of liquid located in the PVC passed through a maximum. Of course, when the slope was changed from positive to negative, the sense of the transfer was inverted for the liquid. Another fact of interest to be noted was concerned with the effect of the value given to the initial concentration of plasticizer in PVC. Swelling took place at the beginning of the soaking of PVC sheets in the liquid, because the transfer rate is higher for the liquid than for the plasticizer, and this swelling disappeared when the two curves

TABLE I
Data for Matter Transfers

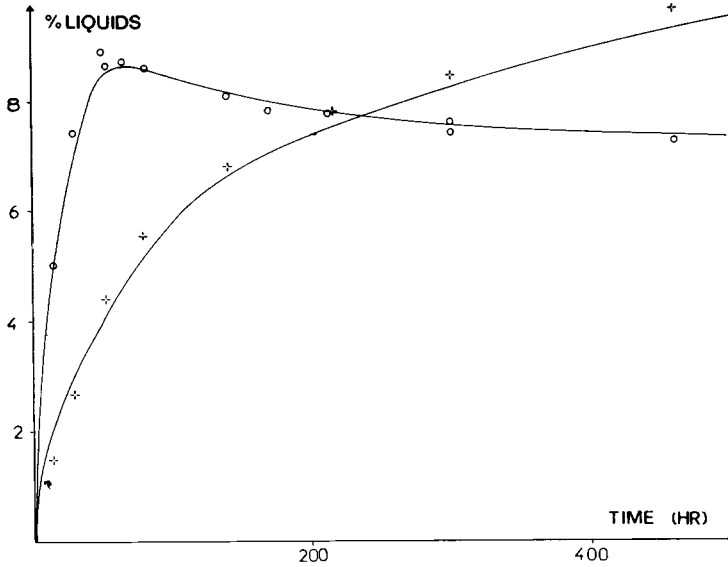|	% DOP	A	B	$h\,10^6$	X_l
DOP	20	234	9.7	8	
	25	234	9.7	18	
	30	234	9.7	30	
Liquid	20	160	10.9	42	0.77
	25	160	10.9	75	0.805
	30	160	10.9	89	0.854

Fig. 3. Long real tests. Kinetics of transfer of *n*-heptane into and plasticizer out of PVC mass; 30° C; initial plasticizer concentration, 20%; (—) theoretical curve; (+) experimental results.

describing these transfers cut each other. After this intersection, a decrease in the weight of PVC could be noticed. Moreover, the effect of the initial plasticizer concentration on the swelling could be appreciated by comparing the curves obtained in these three figures: the lower the initial concentration of plasticizer in PVC, the higher the difference between the rates of transport of liquid and plasticizer.
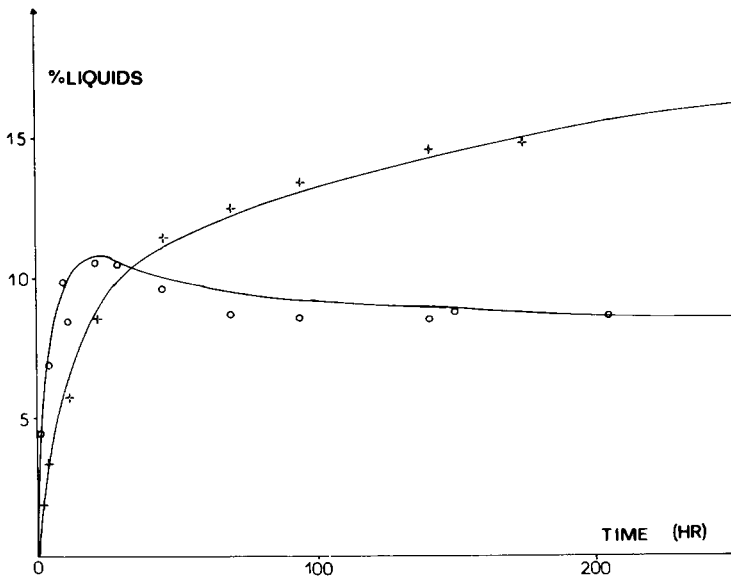

Fig. 4. Long real tests. Kinetics of transfer of *n*-heptane into and plasticizer out of PVC mass; 30°C; initial plasticizer concentration, 25%; (—) theoretical curve; (+) experimental results.
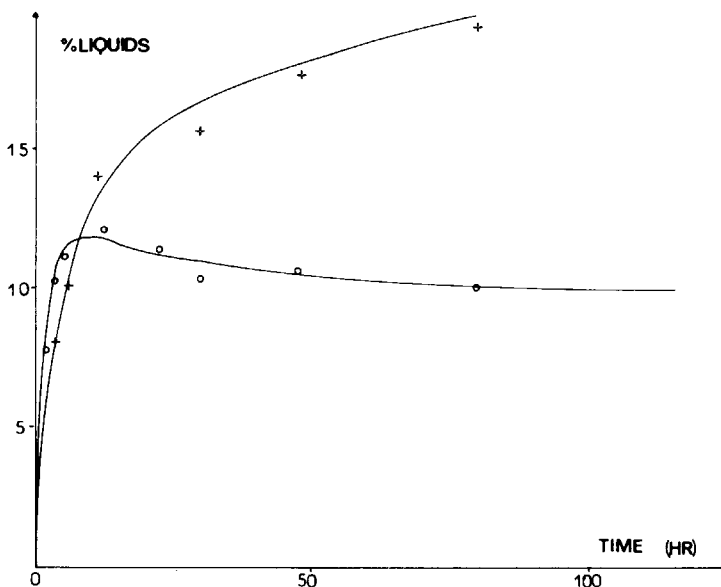
Fig. 5. Long real tests. Kinetics of transfer of n-heptane into and plasticizer out of PVC mass; 30°C; initial plasticizer concentration, 30%; (—) theoretical curve; (+) experimental results.

For both liquids and all these concentrations of plasticizer, experimental values and theoretical ones were in perfect agreement. Although these transfer phenomena were very complicated, our new model was proved to describe them from the beginning to the end.

Profiles of Concentration Developed Through PVC Sheets

Our model was found to be available for determining the profiles of concentration, as the integration of these profiles provided correct values. The calculated profiles of concentration developed against the time at different places within the PVC sheets were shown in Figure 6 for the plasticizer and Figure 7 for the liquid. These curves afforded further insight into the nature of phenomena taking place within the PVC sheets. A continuous decrease in the concentration of the plasticizer could be appreciated with respect to the time and the position in PVC sheets. A complicated transfer was observed for the liquid. At any point within the PVC sheet, the liquid concentration-time curves had a maximum, and the characteristics of this maximum (liquid transferred, time) were depending largely on the position in PVC. The curves shown in Figure 6 were another proof, after the preceding curves, for the complexity of the phenomenon and the heterogeneity of PVC sheets after soaking in the liquid.

These results are expressed in another way in Figures 8 and 9, where the profiles of concentration of liquid and plasticizer developed through PVC sheets are drawn for different times. For the lower initial concentration of plasticizer in PVC, the presence of the maximum of the amount of liquid transferred is indicated by considering the change in the slope of
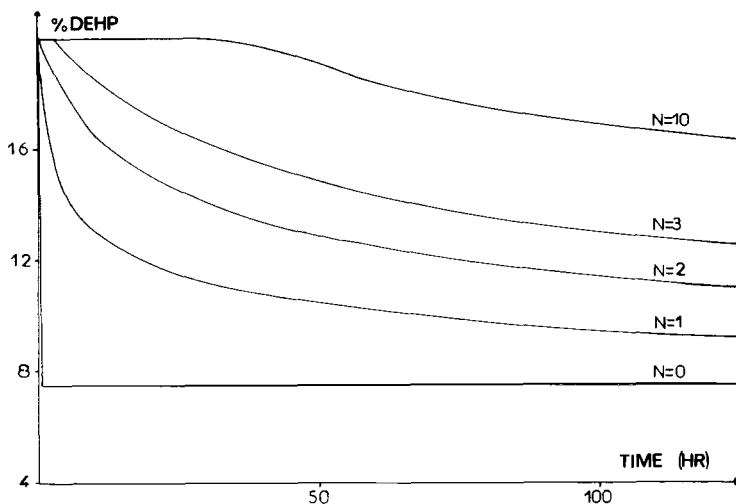
Fig. 6. Plasticizer concentration versus time in different places through PVC mass; 30°C; initial plasticizer concentration, 20%.

these profiles of concentration from negative to positive at about 50 h for 20% and 10 h for 30%. By way of contrast, the slopes are always negative for the plasticizer showing a continuous transfer process.

CONCLUSIONS

This paper has pointed up once again the interest of short tests for studying the matter transfer phenomenon that takes place between a polymer and a liquid, especially a plasticized PVC and *n*-heptane. Not only were they not so time consuming as long real tests, but they were also done with concentrations of liquids in PVC that were about constant, allowing accurate measurements for kinetic studies.
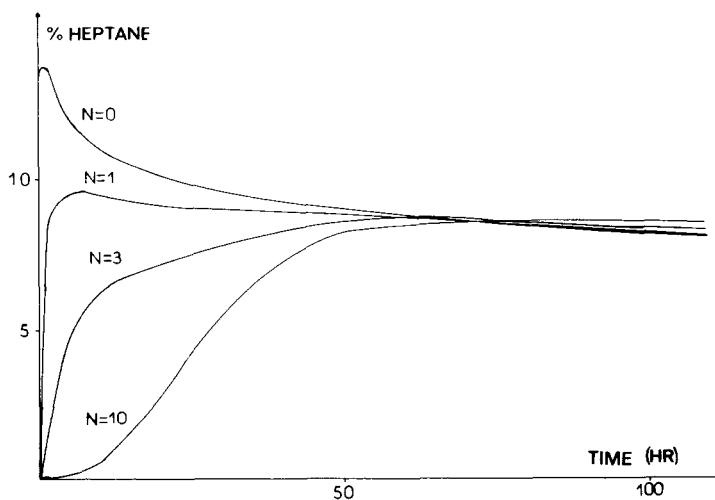

Fig. 7. *n*-Heptane concentration versus time in different places through PVC mass; 30°C; initial plasticizer concentration, 20%.
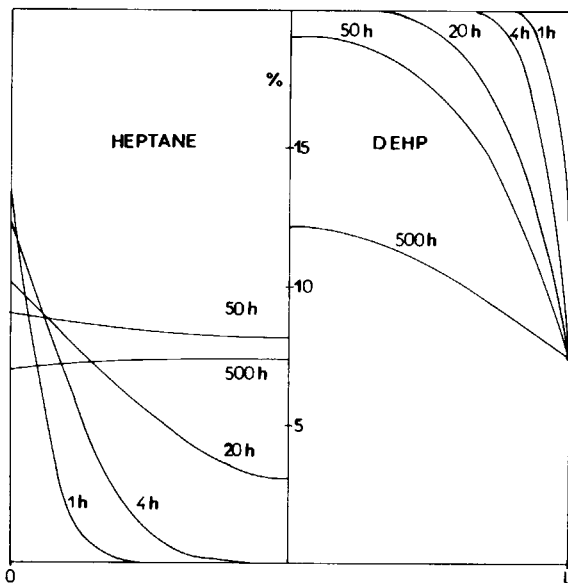
Fig. 8. Profiles of concentration of liquids developed through PVC mass; 30°C; initial plasticizer concentration, 20%.
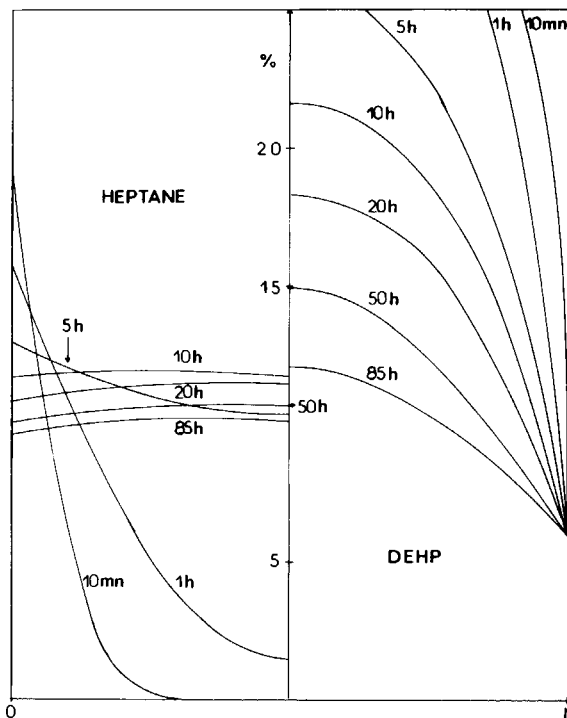

Fig. 9. Profiles of concentration of liquids developed through PVC mass; 30°C; initial plasticizer concentration, 25%.

These results obtained from short tests needed a model able to simulate long real tests. The present model described in this paper took into account three different points: a simultaneous diffusion of the liquid into, and the plasticizer out from the PVC; not only diffusion in transient conditions through the PVC mass with concentration-dependent diffusivities was considered, but also a matter transfer through the liquid PVC interface with a coefficient of matter transfer; and the use of the values of liquid concentrations in PVC obtained at the equilibrium of the transfer.

Using these simulations, it was possible to find results in good agreement with the experimental results determined in the hard case where liquid concentration-time curves passed through a maximum. This case is usual and generally found when the concentration of additives and plasticizer is low and the rate of transfer for the liquid is higher than for the plasticizer at the beginning of the process.

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APPENDIX: NOMENCLATURE

A, B	Constant coefficients in eq. (5) for diffusivity of liquids
$C_{n,i}$	Concentration of liquids in PVC in plane n at time $i \, \Delta t$
$C_{o,i}$	Concentration of liquids on PVC face at time $i \, \Delta t$
$C_{l,i}$	Concentration of the liquid that can be transferred into PVC at time $i \, \Delta t$
$D_{n,i}$	Diffusivity of liquids in plane n at time $i \, \Delta t$
$M_{n,i}$	Modulus for liquids in plane n at time $i \, \Delta t$
$\Delta x,$ $\Delta t, \Delta C$	Increment of space, time, concentration
h	Coefficient of matter transfer per unit area
S	Area of PVC faces
ΔM_t	Amount of liquid transferred through PVC faces during the time Δ_t, eq. (8)
n_i^p, n_i^l	Number of molecules of plasticizer, liquid, at the time $i \, \Delta t$
$V_{n,i}^l$	Volume of liquid in plane n and time $i \, \Delta t$
$V_{n,i}^p$	Volume of plasticizer in plane n and time $i \, \Delta t$
d_p	density of plasticizer
d_l	density of liquid