

Plasticizer Transfer from Plasticized PVC into Ethanol-Water Mixtures

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Synopsis

The transfer of plasticizer from compression-molded sheets of plasticized poly(vinyl chloride) into ethanol-water mixtures was studied over the temperature range of 30–55°C. A simultaneous diffusion occurred for ethanol and water into polymer and for dioctylphthalate plasticizer from polymer into liquid. The concentration of ethanol transferred into the polymer was found to increase, rise to a maximum, and then decrease. Equations of diffusion in unsteady state were found to correlate well with experiments on plasticizer transfer, over the plasticizer concentration range of 25–50 wt %. Stirring, temperature, water concentration in ethanolic solutions, and plasticizer concentration were found to play important roles.

INTRODUCTION

The interaction of liquid food with plastics packaging materials has become of increasing importance because of the legislation or other control procedures being developed for food packaging in the EEC (EEC Commission), United States (Food and Drug Administration), and elsewhere. In order to protect the consumer, it is necessary to know of the transfer of additives of the packaging material into the liquid food and the transfer of components of the food into the plastic.

In most plastics producing countries, PVC is the leading plastic material; in others, for instance, the United States and Japan, it is second to polyethylene. In packaging applications, plasticized PVC is in contact with the liquid food. Under these conditions the plasticizer may stay in place, or it may migrate to the surrounding medium with the following results: (i) the polymer, because of loss of plasticizer, shows considerable change in mechanical properties; (ii) the liquid food is contaminated by the plasticizer.

Possible factors^{1,2} which can affect the migration process can be classified in relation to: the polymer, the plasticizer (nature, amount), the plasticization process, the conditions of the test, i.e., time and temperature, the surrounding medium, and the type of liquid.

The migration of phthalate plasticizers from plasticized PVC to several pure alcohols,³ methanol,⁴ benzyl alcohol,⁵ has been studied quantitatively by different methods. It was proposed to use distilled water and 10% by volume ethanol as simulants for different types of foods.⁶ Both 15% and 96% ethanol were used^{7,8} to simulate alcoholic beverages, while other workers preferred to use 20% and 50% aqueous ethanol.⁹

There were some attempts to construct a model system in order to explain migration in precise terms. Transport processes were divided, rather arbitrarily,

into Fickian and non-Fickian categories.¹⁰ In another work,¹¹ it was suggested that there were three different underlying pathways which could give rise to migration. In the first case, no penetration by the liquid into the plastic takes place. Therefore, the additive migrates spontaneously and continues to do so until an equilibrium is reached.^{5,12,13} The driving force in this case is the distribution factor for the plasticizer between the plastic and the liquid. The second condition arises in the case of a sample in constant motion. An equilibrium of the additive in the food and plastic is reached when its concentration in the plastic is zero.¹¹ The third and most difficult mechanism concerns the case of food and plastic having interactions, i.e., the liquid migrates into the plastic and the plasticizer into the liquid. Although this mechanism has been widely studied,^{11,14-16} it is not yet understood.

As shown in previous papers reporting on the drying of polymer films¹⁷ and on the plasticizer transfer into methanol,⁴ the process occurs in two distinct phases. In the first phase, the transfer is controlled by boundary layer phenomena in the liquid phase. The second phase is controlled entirely by internal diffusion resistance in polymer.

The present work reported the results of the transfer of dioctylphthalate plasticizer from plasticized PVC into several water-ethanol solutions. The influence of the composition of water-ethanol solutions on the DOP transfer was particularly studied. The experiments were carried out within the range 30-55°C, using plasticized PVC with various concentrations of DOP within the range 25-50%. This problem was difficult, as the diffusion of liquid into the PVC, and the diffusion and transfer of DOP from the PVC into the liquid took place simultaneously.

EXPERIMENTAL

Materials

A commercial-grade PVC resin (Lucovyl, Rhône-Poulenc, France) in the form of a white powder was used throughout this work. The plasticizer used was a commercial sample of dioctylphthalate (Rhône-Poulenc). Ethanol of high purity (Rhône-Poulenc) was used for water-ethanol solutions.

Formation of Polymer disks

Plasticized sheets were prepared from PVC and DOP 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.

Disks of the polymer were cut from sheets (18 mm in diameter, 3.4 mm thickness). Homogeneity of the disks was controlled by processing several specimens and titrating plasticizer in them by gas chromatography.

Apparatus for Diffusion

The apparatus and procedure have been described elsewhere.⁴ All experiments were carried out by using 20 PVC disks soaked in 200 mL liquid in a closed flask of 500-mL capacity, using a controlled rate of stirring. Samples were taken

at different times (1 PVC disk and 10 mL solution), so that the weight ratio between the disks and liquid was kept constant.

Analysis 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 and hard with liquid nitrogen. Each layer was weighed, dissolved in acetone and carbon disulfide mixtures, and analyzed by gas chromatography after an addition of an internal standard.

Analysis of DOP

Operational conditions of gas chromatography were as follows: gas chromatograph (IGC 16, Intersmat, France) fitted with a FID detector, working at 270°C. The glass column was 2 m long, and the stationary phase was Chromosorb Q 60/80 mesh and 2.5% OV 17 silicone rubber (Dow Chemical). Dioctyladipate was chosen as internal standard.

Analysis of Water and Ethanol in PVC Disks

The analysis of water and ethanol was performed by gas chromatography after an addition of *n*-propanol as internal standard (F 7, Perkin-Elmer fitted with a thermal conductivity cell). Operation conditions were as follows: Isothermal conditions at 100°C for 2 min, followed by a programming of temperature to 220°C with a heating rate of 10°C/min. The glass column was 1.5 m long and the stationary phase was "Porapak" S 60/80 mesh (Waters). PVC samples were dissolved in an acetone and carbon disulfide mixture, before the injection. The mixture was injected into the GC column without extraction.

Analysis in Liquid

Analysis of DOP in liquid was performed by gas chromatography under the same conditions as stated above for DOP in PVC, by using dioctyladipate as internal standard.

THEORETICAL

Plasticized PVC disks were immersed in the liquid bath. A simultaneous diffusion took place of the liquid into, and the previously dispersed plasticizer out of, the PVC slabs. This simultaneous transfer of liquid and plasticizer was reported in early studies with benzyl alcohol,⁵ and in a mathematical way.¹⁶

The plasticizer transfer from PVC into liquid was shown to occur by considering the following two steps:^{13,17} a diffusion in the liquid controlled by a boundary layer phenomenon; a migration in the PVC itself by internal diffusion.

These transfers in the polymer network were quite dependent on the free volume present, this free volume being a term which refers to the presence of unoccupied spaces, or holes, in plasticized PVC^{10,17} and already shown in other polymers.¹⁸⁻²²

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 into the liquid. The solution was stirred well, and the plasticizer concentration in the liquid depended only on time.

The following assumptions were made:

- (i) The PVC disks were considered as plane sheets.
- (ii) The transport was described by Fick's law expressed in one dimension, when we included a non-concentration-dependent diffusion coefficient.
- (iii) The process was not complicated by the relaxation motion of the polymer in response to swelling stresses that are created as liquid enters the PVC.

The second Fick's law is expressed as follows:

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

where D is the diffusion coefficient taken as non-concentration-dependent, C is the plasticizer concentration at time t , and x is the coordinate dimension in the direction of the transport.

We assumed that an infinite PVC sheet of thickness $2l$ was placed in the liquid; the PVC sheet occupied the space $-l \leq x \leq l$, while the liquid of limited extent occupied the spaces $-l - a \leq x \leq -l$ and $l \leq x \leq l + a$. The initial conditions were

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

The boundary condition expressed that, on the PVC faces, the rate at which plasticizer entered the liquid was always equal to that at which it left the PVC:

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

$2a$ is proportional to the volume of liquid, and $\alpha = a/l$ is the ratio of the volumes of liquid and PVC sheet.

Plasticizer Concentration in PVC Disks. The solution of eq. (1) was given²³ in the form of a trigonometric series

$$\frac{C_{tx}}{C_0} \cdot \frac{\pi}{4} = \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cdot \cos \frac{(2n+1)\pi x}{2l} \cdot \exp \left(-\frac{D(2n+1)^2 \pi^2 \cdot t}{4l^2} \right) \quad (4)$$

where C_{tx} is the plasticizer concentration in PVC disk at time t and at abscissa x , in the case of a bath of infinite volume. In fact, this equation is available when α is more than 10.

Plasticizer Transfer into the Liquid. The solution was obtained²³ in a form expressing the total amount of plasticizer M_t in the liquid at time t as a fraction of the corresponding quantity after infinite time M_∞

$$\frac{M_\infty - M_t}{M_\infty} = \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp \left(-\frac{D \cdot q_n^2 t}{l^2} \right) \quad (5)$$

where the q_n s are the nonzero positive roots of

$$\tan q_n = -\alpha \cdot q_n \quad (6)$$

As was shown in a previous paper,¹³ eq. (5) became more simple when α was more than 10:

TABLE I
Effect of Stirring on DOP Concentration in Liquid (g/L)

Time	2	8	24	48	100
Stationary liquid	1.22	2.56	4.8	7.6	12.8
Liquid in motion	1.93	3.0	5.24	8.0	12.8

$$\frac{M_{\infty} - M_t}{M_{\infty}} \cdot \frac{\pi^2}{8} = \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left(-\frac{D(2n+1)^2\pi^2}{4l^2} t\right) \quad (7)$$

The stirring of the liquid was defined as usual by the Reynold's number.

$$\text{Re} = \frac{L^2 \cdot \rho \cdot n}{\mu} \quad (8)$$

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

RESULTS AND DISCUSSION

The transfer of plasticizer and of liquid were studied separately in this work. The influence on these transfer of parameters, i.e., stirring, plasticizer concentration, temperature, was especially pointed out.

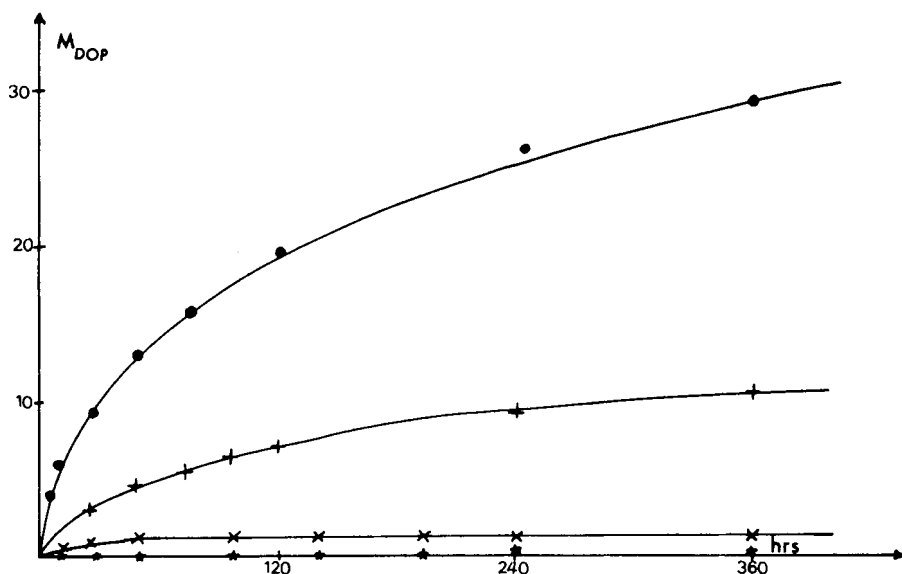


Fig. 1. Plots of DOP concentration in liquid (g/L) vs. time (h), for different water % in liquid. DOP: 38 wt %; temp = 45°C; (●) pure ethanol; (+) ethanol-water, 4/1; (x) ethanol-water, 1/1; (*) ethanol-water, 2/23.

TABLE II
 Effect of Liquid Composition $D \times 10^8$ (cm²/s)

% Water	0.2	20	50	92	100
$D \times 10^8$ (cm ² /s)	2.7	0.21	0.01	No transfer	
DOP amount (g/L)	29	10.4	1	0.0	0.0

Plasticizer Transfer from PVC into Liquid

Effect of Stirring. The significance of stirring on plasticizer transfer into liquid is shown in Table I. Measurements for DOP concentration in pure ethanol were made at 30°C, when the concentration of DOP in PVC disk was 38 wt %. Experiments were performed on the one hand in a stationary liquid and on the other hand in liquid in motion with $Re = 3,000 \pm 500$. For times shorter than 50 h, the DOP transport was found to be controlled by boundary layer phenomena in the liquid near the interface liquid-PVC. All the other experiments were conducted with a liquid in motion.

Effect of Liquid Composition on DOP Transfer. The composition of liquid was expressed by the water percentage in volume. The experiments were performed at 45°C for different compositions within the 0–100% range, while the plasticizer in PVC was 38 wt %. Plots of DOP concentration in different liquids (g/L) against time (h) are shown in Figure 1. The effect of percent water in liquid on DOP transfer is of great importance. There was no transfer into liquids having 8% ethanol or less. A significant transfer took place when the ethanol percentage in liquid was more than 50.

The values of diffusion coefficients calculated by using eqs. (5) and (7) were about the same (Table II).

Effect of Temperature on DOP Transfer. Experiments were carried out in the temperature range of 30–55°C with PVC disks of 38 wt % DOP. The concentration of DOP in liquid (g/L) was plotted against time (h), in Figure 2 for pure ethanol (0.2 wt % water) and in Figure 3 for ethanol–water 4/1 mixture.

Diffusion coefficients were calculated by using eq. (5) and our experimental data shown in Figures 2 and 3 (Table III).

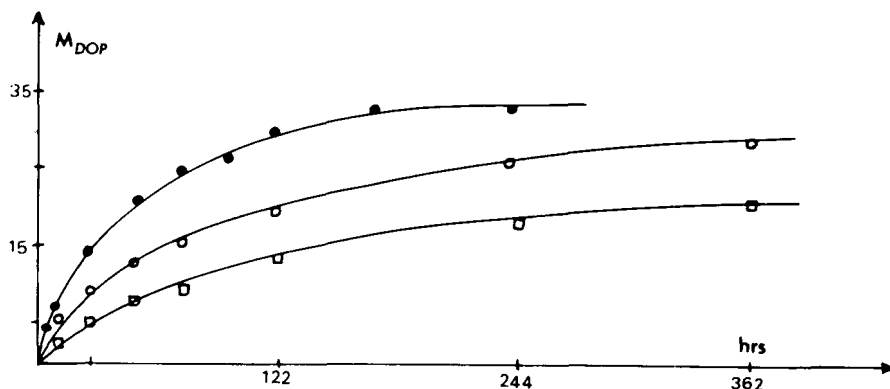


Fig. 2. Plots of DOP concentration in liquid (g/L) vs. time (h), at different temperatures. Pure ethanol; DOP: 38 wt %; temp: (●) 55°C; (○) 45°C; (□) 30°C.

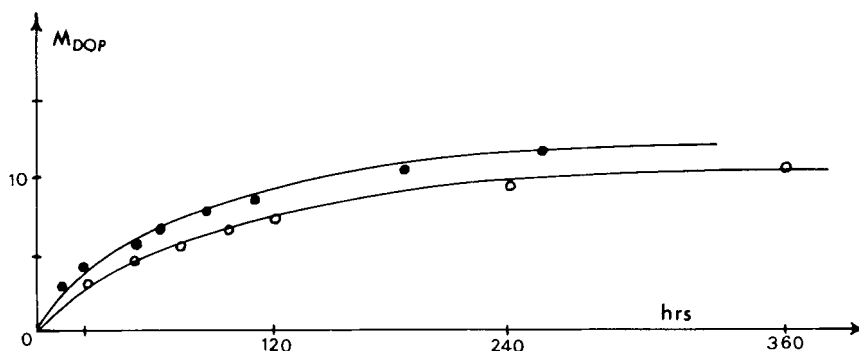


Fig. 3. Plots of DOP concentration in liquid (g/L) vs. time (h) at different temperatures. Ethanol-water: 4/1; DOP: 38 wt %; temp: (●) 55°C; (○) 45°C.

The dependence of temperature on the diffusion coefficient was described by an Arrhenius form, and the activation energy over the whole range of temperature was of about 12.7 kcal/mol for pure ethanol and for an ethanol-water 4/1 mixture.

Effect of the Amount of Plasticizer in PVC. Diffusion coefficients were obtained for plasticizer concentration of 25, 38, and 50 wt %. At each plasticizer concentration, measurements were carried out at 45°C, with pure ethanol as liquid. Typical results are shown in Figure 4 for the migration of plasticizer under these conditions. The amount of plasticizer in PVC affected strongly the migration process as indicated by curves in Figure 4. The greater the amount of plasticizer in PVC, the faster was the plasticizer migration as reported in previous paper.^{1,3} The diffusion coefficients (Table IV) were found to vary largely with the initial plasticizer concentration in PVC, as reported in the literature for other liquids.^{4,5,13,24}

Diffusion of Liquid into PVC Disks

Effect of Temperature on Diffusion of Pure Ethanol into PVC Disks. Diffusion of ethanol into PVC took place, coupled with the transfer of plasticizer from PVC into liquid. Experiments were conducted at the temperature of 45°C and 55°C with pure ethanol as liquid and with PVC disks containing 38 wt % plasticizer.

As shown in Figure 5, for the higher temperature of 55°C, the amount of ethanol transferred into PVC increased at the beginning of the immersion rose to a maximum value, and then decreased. It was a two-step phenomenon with an

TABLE III
Effect of Temperature on Diffusion Coefficients $D \times 10^8$ (cm²/s)^a

Temperature (°C)	30	45	55	<i>E</i> (kcal/mol)	
Pure ethanol,	1.0	2.7	4.75	12.3	0.5
<i>r</i> ²	0.99	0.999	0.99		
Ethanol-water, 4/1,		0.21	0.4	13.3	1
<i>r</i> ²		0.96	0.98		

^a *r*² is the correlation coefficient of the method of least squares; its value near 1 showed a close agreement of experimental data to eq. (5).

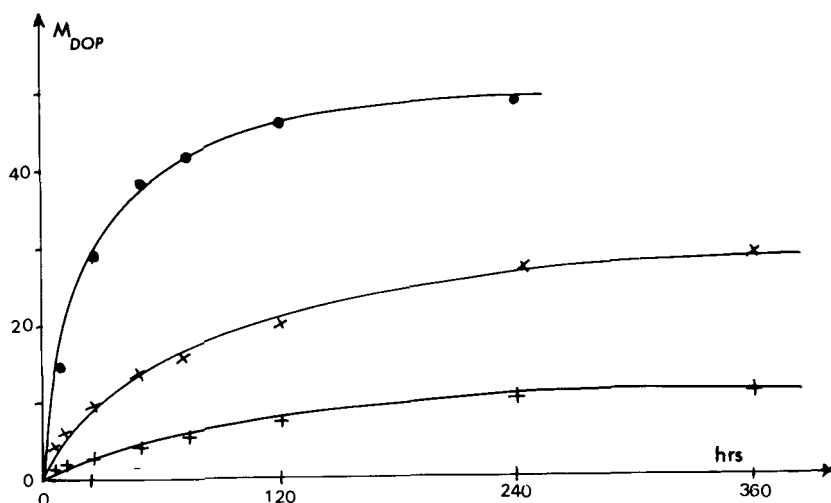


Fig. 4. Plots of DOP concentration in liquid (g/L) vs. time (h), for different DOP wt % in PVC. Pure ethanol; temp = 45°C; (●) 50 wt % DOP; (X) 38 wt % DOP; (+) 25 wt % DOP.

ethanol transfer into, and out of, the PVC slab, successively. The rate of transfer was higher for ethanol when the temperature was increased. A period of induction of about 25 h, without transfer, is shown in Figure 5, at the lower temperature of 45°C.

As a result of the transfer of both DOP and liquid, a part of the plasticizer in PVC was replaced by the liquid. Concentrations of both liquid and plasticizer in PVC were measured at different times and at temperatures of 45°C and 55°C while ethanol was the liquid and at 55°C while the liquid was ethanol-water 4/1 mixture (Table V).

The rate of the exchange between plasticizer and liquid was strongly affected by the temperature when ethanol was the liquid.

Effect of Water Concentration in Ethanol. The migration process of liquid into PVC disks was strongly affected by the % water in liquid, as shown in Table V. After an immersion of 50 h, for instance, a PVC specimen originally plasticized with 35% DOP, became plasticized with 16.5% DOP and 21% ethanol while ethanol was the liquid; the same PVC specimen became plasticized with 33.5% DOP and only 4% water and 4% ethanol, while the liquid was ethanol-water 4/1 mixture.

The total amount of liquid located in PVC disks (DOP and ethanol) decreased regularly with the time, when PVC disks were soaked in pure ethanol. When the liquid was ethanol-water 4/1 mixture, no decrease in the weight of PVC disk occurred.

The amounts of ethanol and water transferred into PVC were about the same,

TABLE IV
Effect of % Plasticizer in PVC on Diffusion Coefficient

DOP wt %	25	38	50
$D \times 10^8$ (cm ² /s),	1.2	2.7	5.3
r^2	0.99	1	0.98

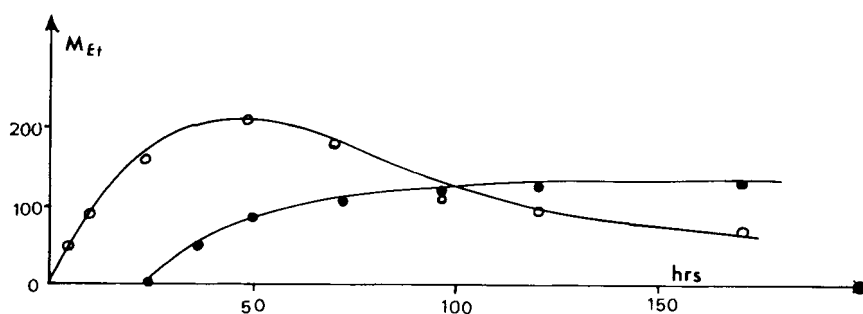


Fig. 5. Ethanol transfer into PVC (g/L) vs. time (h), at different temperatures. Pure ethanol as liquid; 38 wt % DOP; (O) 55°C; (●) 45°C.

while the concentration ratio for ethanol and water was 4/1 in the liquid mixture.

Concentration Profiles of Plasticizer in PVC disks

PVC disks were removed from the liquid at different times and were peeled off in 17 200- μm -thick layers, as described in the Experimental Section. DOP concentration was measured in each layer, and plotted against the position of the center plane of the layer in the PVC disk before cutting. As shown in Figure 6, abscissa $x = 0$ was taken for the center plane of the PVC disk, and abscissa $x = \pm 8.5$ for the faces of PVC disk (or 1.7 mm, 0, and 3.4 mm, respectively, on the other scale).

The concentration profile of DOP was determined in Figure 6, at 30°C, when ethanol was the liquid, and the initial concentration of plasticizer was 38.

CONCLUSIONS

The study of plasticizer transfer from plasticized PVC into water-ethanol mixtures as liquid was conducted by measuring the plasticizer concentration increase in the liquid, but also the concentration of plasticizer and of liquid inside the PVC itself. A simultaneous diffusion of the liquid into, and the previously dispersed plasticizer out of, the PVC disk was proved to take place.

The plasticizer transfer into the liquid was found to obey Fick's law in unsteady state, and the temperature dependence of the diffusion coefficient was described

TABLE V
Concentration of Plasticizer and Liquid in PVC [DOP (38 wt %)]

Conditions		Time (h)			
		25	50	100	150
45°C	DOP (%)	29	25	20	16.7
Ethanol	Ethanol (%)	2	8	12	12
55°C	DOP (%)	24	16.5	10	6
Ethanol	Ethanol (%)	15	21	11	6
55°C	DOP (%)	35	33.5	31.5	30
Ethanol 4	Ethanol (%)	3	4	4	4
Water 1	Water (%)	2.5	4	3.5	3

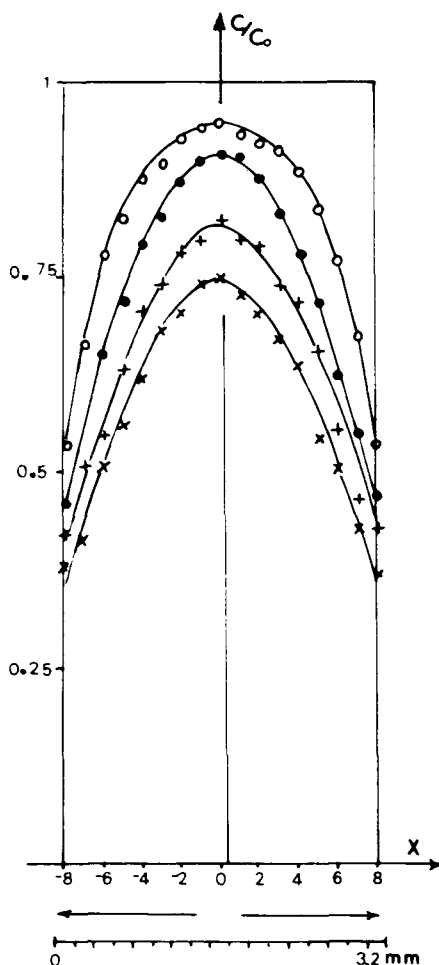


Fig. 6. Concentration profiles of DOP (wt % of PVC disk) along PVC disk thickness, at different times. Pure ethanol; temp = 30°C; 38 wt % DOP; (0 and 3.4 mm) external plane of PVC disk; (O) (as x abscissa) center plane of PVC disk; times: (O) 50 h; (●) 120 h; (+) 240 h; (X) 362 h.

by an Arrhenius form. The activation energy was about the same for pure ethanol and for 4/1 ethanol–water mixture. The value of 12 kcal/mol we found was of the order of magnitude of the activation energy measured with other liquids as methanol,⁴ benzyl alcohol,⁵ and peanut oil,^{25,26} but differed largely from the particular value obtained with *n*-heptane.¹³ The mechanism of plasticizer transfer was proved to occur in two phases, as shown in previous paper with methanol and benzyl alcohol as liquid. In the first phase, for times shorter than 100 h, the plasticizer transfer was controlled by boundary layer phenomena, and the effect of stirring was important. The plasticizer concentration still remained high on PVC disk faces. The second phase of this transfer was controlled by internal diffusion in the PVC itself. The plasticizer concentration then became very low on PVC disk faces. The influence of water concentration in the ethanolic mixtures was proved to be of great importance for the plasticizer transfer. No plasticizer transfer occurred when the water concentration in ethanol was 92% or more.

The amount of the liquid transferred into PVC was found to depend on the temperature, and the water concentration in ethanol. No liquid transfer took place into PVC when the water concentration in the liquid was 92% or more. The rate of the liquid transport into PVC increased with the temperature. At a temperature of 55°C, a maximum value was reached for the amount of the liquid transferred into PVC.

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