Plasticizer Transfer from Plasticized Poly(vinyl Chloride) Sheets to Petroleum Oils

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Synopsis

Plasticizer migration from poly(vinyl chloride) remains a critical problem due to the high consumption of this polymer in a flexible form. The systems poly(vinyl chloride) (PVC)/labeled dioctyl phthalate (DOP)/white spirit, kerosene, white oil, or lubricating oil have been considered in this article. Migration experiments were carried out at three different temperatures (30, 50, and 70°C) for extremely prolonged periods of time. At the initial stages the data collected fit well to short-term Fickian behavior. The respective diffusion coefficients increase with temperature, conforming also to an Arrhenius form, but the eventually obtained migration values seem to pass through a minimum in the case of the lighter oils.

INTRODUCTION

The packaging requirements of a biological system such as foodstuffs and pharmaceuticals are more diverse and complex than those for other products. Protection of the product may be regarded as the rate of change of quality and this includes both physical (mechanical damage during transit or storage, loss of consistency or crispness, loss of appearance, sales appeal), and organoleptic changes (loss of taste, color, odor).[1]

Plastics used for food and pharmaceuticals applications have been produced for many years, but relatively few of them have been studied in detail. Moreover, the plastics themselves are important only as far as their various additives are able to migrate or diffuse through the polymer matrix into its environment. This has a distinct effect also on the properties of the plastic while contamination of the medium in contact is inevitable. A considerable volume of legislation has been developed in the European Economic Community (EEC), United States, and elsewhere, while new findings from migration studies are expected to contribute to new legislation.[2]

It is well documented[3] that additives and monomer residue migration depends on a multiplicity of factors including temperature, the compatibility of the migrant with the polymer, the molecular size of the migrant, the compatibility of the migrant with the phase external to the polymer, and interactions that may occur between the external phase and the polymer.

Plasticizer migration from poly(vinyl chloride) has attracted the interest of numerous investigators[4-18] due to the high consumption figures of this polymer used in great part in the plasticized form. In particular, the case of migration to a liquid medium has been extensively studied, in our laboratory,

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as well,[5a-7,14,15] and it has been suggested that either there is no penetration by the liquid into the plastic or the opposite, that is, plasticizer migrates into the liquid and the latter diffuses into the plastic.[3,5a-8,11-16] On the other hand, the migrating additive is determined either as the amount leaving the polymer or the amount entering the liquid. A wide variety of experimental methods have been used including weight loss,[5a-7] chromatography,[12,13] spectroscopy,[17] and radioactivity.[2,5a-7,11,14,15]

In this report, long-term migration data are presented on the systems PVC/dioctyl phthalate(DOP)/petroleum oils. The typical cases of white spirit, kerosene, white oil, and lubricating oil were selected. Migration experiments were carried out at three different temperatures for extremely prolonged periods of time, until near equilibrium was established. The data collected were compared with previous studies and tested against typical Fickian diffusion behavior.

EXPERIMENTAL

Reagents

PVC: Commercial grade, Esso Co., Greece, with a k value (a molecular weight index for PVC polymers) equal to 70.

Immersion fluids: Technical grade, Fluka AG.

Dioctyl phthalate, stabilizer system, scintillation solution, and all reagents used for the synthesis of labeled dioctyl phthalate: Proanalysis grade, Fluka AG.

Synthesis of Labeled Dioctyl Phthalate (DOP)

Labeled phthalic anhydride (5.2 g; 7-^{14}C; 1 mCi) was transferred to a reaction flask equipped with stirrer, thermometer, N_2 inlet tube, separating funnel, and a side condenser. The reactor was then charged with 2-ethyl hexanol (211 g), phthalic anhydride (80 g), and concentrated sulfuric acid (1.5 mL). The 2-ethyl hexanol was in 50% excess over the theoretical value, while toluene was also added to the reaction mixture (25% v/v based on the amount of 2-ethyl hexanol). The mixture was heated under stirring in an oil bath for 2 h while the temperature was gradually raised to 170°C. During this period, a slow stream of N_2 was passed and toluene was periodically added to compensate for that distilling. After 2 h at 170°C, the mixture was cooled and diluted with 1 L of ether. The ethereal solution was washed with 10% aqueous sodium carbonate solution, then with water, and finally evaporated. The diester obtained was further purified by vacuum distillation. Yield, 89% on phthalic anhydride in labeled DOP. Products with lower radioactivities were obtained by dilution with pure unlabeled DOP.

Plasticization

Suspension PVC was blended, at 80°C, with the calculated amounts of labeled plasticizer and Ba-Cd stabilizer corresponding to levels of 50 and 3 phr, respectively. The dry blend was plasticized for 7 min in a Brabender Plasticorder at 170°C and 30 rpm. The plasticized mass obtained was then hot

pressed to form a sheet of about 2.5 mm thickness. From this sheet, specimens of 20 × 50 mm were cut.

Immersion

Each specimen was immersed in 250 mL liquid contained in a glass-stoppered 300-mL Erlenmeyer flask. All tests were made in duplicate and the flasks were kept in ovens fixed at three different temperature levels: 37, 50, and 70°C (± 1°C).

Radioactivity Measurements

The radioactivity (R_t, counts/mL/min) of the liquid medium represents the concentration of the plasticizer migrated at immersion time t. Divided by the radioactivity of the plasticizer employed (Ro = 3644.4 counts/mg/min) and reduced per liter of the liquid medium, DOP concentration data (Q_t) (mg or g/L) are provided.

The radioactivity of the liquid medium, at a given time after immersion, was measured by transferring 1.0 mL of the contents of the flasks to a glass measuring vial containing 10 mL of the scintillation solution (5 g of PPO and 0.3 g dimethyl-POPOP in 1 L of toluene), shaking to ensure complete dissolution, and measuring the radioactivity by means of a Packard 3003 Liquid Scintillation Spectrophotometer over a period of 10 min. Two samples were taken from each flask, thus, each quoted result represents the average of four measurements. Before sampling, the contents of the flasks were homogenized by swirling.

RESULTS AND DISCUSSION

Migration

In Table I "quasiequilibrium" values of plasticizer migrated are given, expressed as weight percentage of the amount of plasticizer initially contained in the material. It should be mentioned that the levels quoted result after immersion for more than 50 days at 37, 50, or 70°C, respectively. Since for immersion times greater than about 40 days these values negligibly increase, they are considered as equilibrium ones in accordance with previous studies.[5a, 6, 7, 12-15]

TABLE I
Equilibrium Values of Plasticizer Migrated Expressed as Weight Percentage
of the Initial Quantity Contained

	Temperature (°C)		
Liquid environment	37	50	70
White spirit	70	64	75
Kerosene	69	64	70.5
White oil	15	20	33
Lubricating oil	11.5	19	28.5

Based on Table I, the lighter oils can be differentiated from the white oil and the lubricating oil by two points:

1. Independent of immersion temperature, the lighter oils favor considerably higher migration levels.

2. Migration increases with immersion temperature for the white oil and the lubricating oil.

Nevertheless, the second point is not the case for the lighter oils. Indeed, for both white spirit and kerosene, the migration values do drop at 50°C to increase again at 70°C. This behavior is also evident from the series of the primary data Q_t versus immersion time t, for the last stages of the migration process. To our knowledge, the phenomenon has not been realized by previous investigators, but combined with counterdiffusion results proves to be quite interesting.[19]

Elementary Kinetics of the Plasticizer Migration Process

In general, diffusion of low-molecular weight substances in and out of a polymer occurs mainly in the amorphous phase. The mechanism changes character for the polymer in the glassy state below the glass transition region or in the rubbery state above the glass transition region. Certain cases of the diffusion in the glassy state have been described by a so-called Case II behavior, in which diffusion is rapid in comparison with the slow relaxation process of the polymer network in the glassy state.[20] On the contrary, in the rubbery state the diffusion phenomenon generally conforms to Fick's law describing the flux of the diffusing species per unit area as a function of its concentration gradient.

Nevertheless, usual assumptions for the treatment of diffusion behavior may not be applicable in the case of solid/liquid plasticizer migration due to possible state transitions occurring during the diffusion process. This becomes especially important when this diffusional release occurs near the glass transition temperature of the polymer system.[14] In fact, when great rates of plasticizer migration are initially encountered, so that nearly all the plasticizer contained is transferred into the surrounding liquid, the glass transition temperature decreases and deviation from Fickian kinetics is expected. Nevertheless, in many cases, simple migration models have been proposed, based on Fick's law with constant diffusion coefficients, simple boundary conditions, negligible relaxation effects, and constant polymer volume.[21]

It is a known fact that plasticizer migration from the PVC material to the surrounding medium comprises a three-step process: (1) plasticizer transfer in the PVC itself by internal diffusion; (2) plasticizer transfer through the PVC–liquid interface from the solid into the liquid; (3) diffusion of plasticizer in the liquid. Steps 2 and 3 are highly dependent on stirring and plasticizer-liquid compatibility.[3] Returning to our system, and under the experimental conditions examined, the following assumptions were initially made:

1. The process was treated as a nonsteady phenomenon, and the transfer was described by Fick's law.

2. Plasticizer diffusion coefficient was considered to be independent of concentration.

3. The PVC specimens were considered as plane sheets having a thickness $2l$ while dimensional stability was further assumed.[19] The plane sheets were so thin that all the diffusing substance effectively entered through the plane faces and a negligible amount through the edges.

4. The volume of the liquid was supposed infinite. Actually, the latter is quite true as only one specimen was immersed in 250 mL of liquid while standard migration procedures, in the literature, involve up to 20 specimens in 200 mL of liquid.[12, 13] On the other hand, boundary layer phenomena were ignored for two reasons: (a) Compatibility between DOP and petroleum oils is acceptable especially for the low viscosity mediums.[5a] (b) No stirring was applied, however before taking samples, the contents of the flask were swirled thoroughly. This procedure has been applied in all migration studies in our laboratory.[5a-7, 14, 15] Furthermore, it is known that boundary phenomena, when they exist, influence the very initial stages of the migration process.[5b, 12, 13, 22]

Under the above considerations elementary diffusion mathematics can be described as follows[23]: The diffusion equation in one dimension is reduced to

$$\frac{\partial Q}{\partial t} = D\frac{\partial^2 Q}{\partial x^2} \tag{1}$$

where Q is the plasticizer concentration, t is the time, and the abscissa x was taken along the thickness $2l$ of the PVC sheet. The initial conditions are

$$t = 0, \quad -l < x < l, \quad Q = Q_o \text{ sheet space}, \quad Q = 0 \text{ liquid space}$$

and the boundary conditions are

$$t > 0, \quad x = \pm l, \quad Q = 0 \text{ (PVC face)}$$

In other words, on the PVC faces, the rate at which plasticizer enters the liquid is always equal to that at which it leaves the PVC.

The solution to Eq. (1) is given in the form of a trigonometric series for the plasticizer concentration in the PVC space

$$\frac{Q_t}{Q_o} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp\left[-D(2n+1)^2\pi^2 t/4l^2\right]\cos\frac{(2n+1)\pi x}{2l} \tag{2}$$

If Q'_t denotes the total amount of plasticizer desorbed at time t, and Q'_∞ the corresponding quantity after infinite time, then

$$\frac{Q'_t}{Q'_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-D(2n+1)^2\pi^2 t/4l^2\right] \tag{3}$$
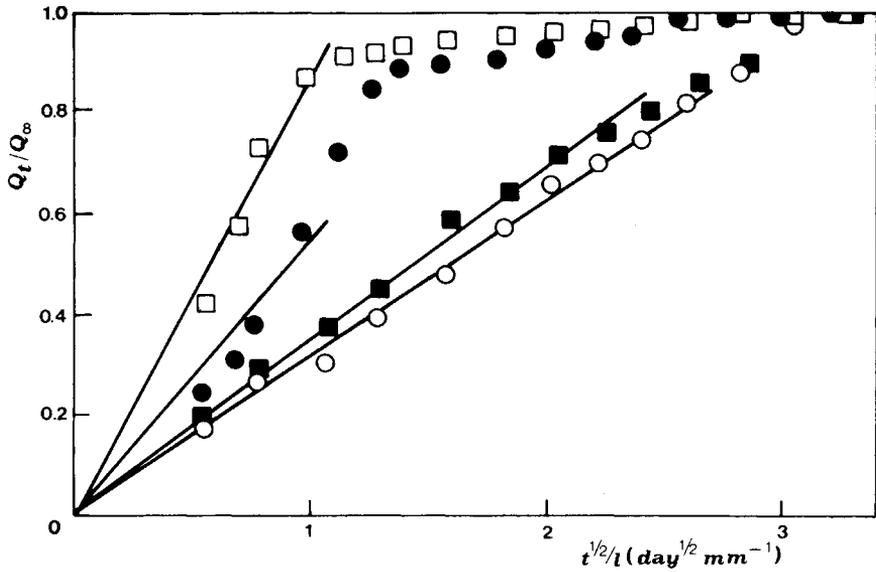
Fig. 1.   Relationship between Q_t/Q_∞ and $t^{1/2}/l$ at 37°C: (●) kerosene; (□) white spirit; (○) white oil; (■) lubricating oil.
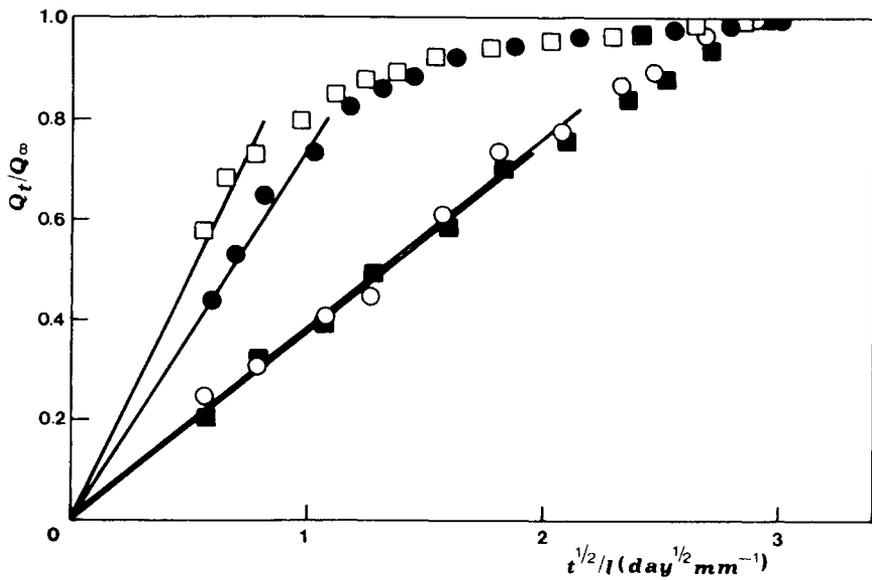
Fig. 2.   Relationship between Q_t/Q_∞ and $t^{1/2}/l$ at 50°C: (●) kerosene; (□) white spirit; (○) white oil; (■) lubricating oil.
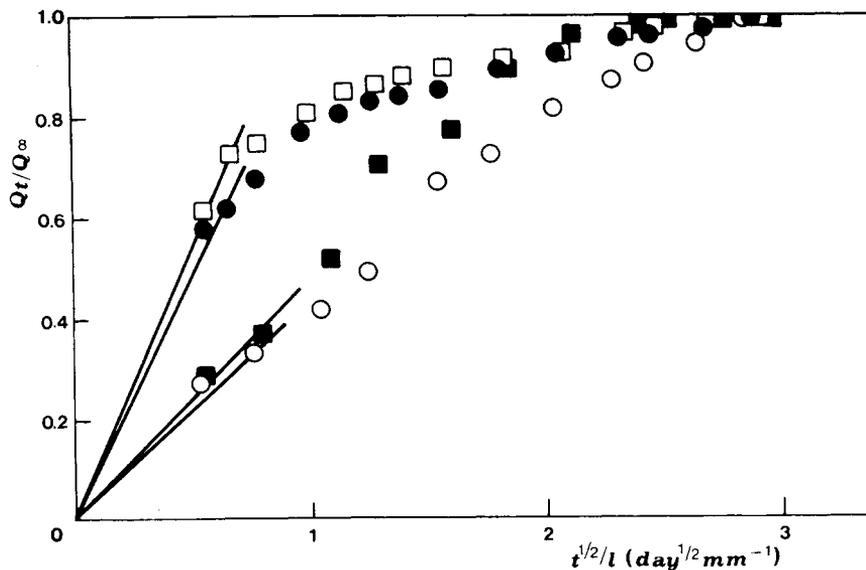
Fig. 3. Relationship between Q_t/Q_∞ and $t^{1/2}/l$ at 70°C: (●) kerosene; (□) white spirit; (○) white oil; (■) lubricating oil.

Equation (3) can be well approximated by the following

$$\frac{Q'_t}{Q'_\infty} = 1 - \frac{8}{\pi^2}\exp\left(-D\pi^2 t/4l^2\right) \tag{4}$$

while the corresponding approximation for small times is

$$\frac{Q'_t}{Q'_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{5}$$

A plot of Q'_t/Q'_∞ against $2(t/\pi l^2)^{1/2}$ is initially linear and provides the diffusion coefficient for the early stages of the desorption process.

In accordance with the above theoretical considerations, plots of $Q'_t/Q'_\infty = Q_t/Q_\infty$ vs. $2(t/\pi l^2)^{1/2}$ were constructed. The results are shown in Figures 1, 2,

TABLE II
Values of Diffusion Coefficient (D) (cm² s⁻¹) Obtained from Figures 1, 2, and 3
(r^2 = Correlation Coefficient)

Liquid environment	Temperature (°)						Activation energy (kcal/mol)	r^2
	37		50		70			
	D	r^2	D	r^2	D	r^2		
White spirit	1.83×10^{-8}	0.99	2.17×10^{-8}	0.99	2.71×10^{-8}	1.00	2.51	1.00
Kerosene	7.07×10^{-9}	0.97	1.26×10^{-8}	0.99	2.15×10^{-8}	0.99	7.05	0.99
White oil	2.24×10^{-9}	1.00	3.24×10^{-9}	0.99	4.42×10^{-9}	0.99	4.30	0.98
Lubricating oil	2.65×10^{-9}	1.00	3.22×10^{-9}	1.00	4.94×10^{-9}	1.00	4.04	0.99

and 3. Independent of temperature and liquid medium, the linearity during the initial stages of the process is evident so that Fickian behavior with constant D indeed can be assumed. Such conformity is not surprising, since during the initial stages the material remains in the rubbery state,[14,20,21] however, for less time as temperature increases. In Table II values of correlation coefficients (r^2) and also D are quoted. The relative magnitude of the latter, of course concerning the initial stages of the migration process, confirms the trends already noticed from the equilibrium plasticizer levels (Table I), with the exception of the continuing increase of the diffusion coefficient with temperature for all the media studied. In particular, the temperature dependence of the diffusion coefficient can be described by an Arrhenius form (Table II). According to the activation energy values determined, the following order is established:

$$\text{kerosene} > \text{white oil} \gg \text{lubricating oil} > \text{white spirit} \qquad (6)$$
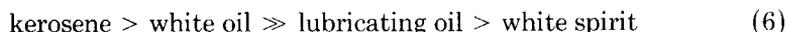
Until now, counterdiffusion processes, namely liquid penetration phenomena into the plastic film, were not taken into consideration. Nevertheless, in order to proceed in a detailed discussion of the results contained herein, it seemed worthwhile to follow this counterdiffusion activity. The findings, indeed very interesting, are presented in the subsequent report and the overall phenomenon is reconsidered.

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