

Some Aspects of Plasticizer Migration from Poly(Vinyl Chloride) Sheets

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Synopsis

Long-term migration data, by radioactivity measurements, are presented for the systems poly(vinyl chloride) (PVC)/labelled dioctyl phthalate (DOP)/methanol, *n*-propanol, or *n*-butanol. At equilibrium, migration levels determined exceed 85% for methanol and reveal complete removal for the higher alcohols. Migration kinetics failed to be described by the long-term Fickian approximation with a diffusion coefficient independent of concentration. Nevertheless, q_t/q_∞ , where q_∞ the amount migrated at infinite time and q_t the amount lost up to time t , increases linearly with $(\text{time})^{1/2}/(\text{thickness})$ during the initial stages of the process and then a linear also relationship appears, but with severely reduced slope. Similar data concerning the systems PVC/DOP/petroleum oils confirm the behavior observed.

INTRODUCTION

Plastics apart from the high polymers also contain oligomers, monomers, and particularly the so-called plastics additives (mainly stabilizers, antioxidants, lubricants, and plasticizers) which may be physiologically objectionable. The addition of these auxiliaries is absolutely necessary for the processing and stability of the plastics and also for establishing certain mechanical strength properties of the final products. Nevertheless, these low-molecular compounds often possess a high mobility, and they can easily migrate from plastics into their environment. This has a distinct effect on the properties of the plastic while contamination of the medium in contact is inevitable. Therefore, the subject becomes extremely important in food packaging and medicine applications comprising usually solid/liquid systems. A considerable volume of legislation has been developed in the EEC, United States, and elsewhere. The need arises to investigate the transfer of additives of the packaging material into the liquid environment (food, blood, etc.), and new findings are expected to contribute to new legislation.

Plasticizer migration from poly(vinyl chloride) has attracted the interest of numerous investigators¹⁻¹⁷ due to the high consumption figures of this polymer used in a great part in the plasticized form. Possible factors which can affect the phenomenon have been extensively studied in our laboratory (such as plasticizer, plasticization process, surrounding medium, and conditions of test,¹⁻³ even if in some cases, as in alcoholic environments,² short-term behavior was examined. On the other hand, other studies aim to give a mathematical or physical explanation of the observed behavior.^{8-11, 13, 14}

Transport processes fall into "Fickian" and "non-Fickian" categories. Solvent diffusion in rubbery polymers can generally be described by Fick's law

of diffusion. Glassy polymers, on the other hand, because of their time-dependent responses exhibit non-Fickian or "anomalous" diffusion kinetics.^{18,19} Depending on the relative rates of penetrant mobility and polymer segment relaxations, case I (Fickian) and case II are viewed as the two limiting types of transport process. Migration can be faced as a typical desorption process, and any attempt to construct a model has to be considered under these elementary principles.

In the case of plasticizer migration to a liquid medium, it has been suggested either no penetration by the liquid into the plastic or the opposite, i.e., plasticizer migrates into the liquid and the latter diffuses into the plastic.^{1-9,11-14} Such an interaction may result to an ever-thickening inhomogeneous layer of mixed polymer and liquid medium, and then the problem belongs in the general class of diffusion processes with moving boundaries.^{20,21} Nevertheless, it has been observed that the plasticizer-liquid medium mixture, which plasticizes the polymer, becomes gradually a nonsolvent and separates as a second phase in the mass.² Clearly, these effects complicate considerably the mathematical treatment of the overall phenomenon.¹²

The migrating plasticizer can be 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,^{1-3,6} chromatography,^{14,15} spectroscopy,^{16,17} and radioactivity.^{1-3,5,6,9-11,13} In this paper long-term results, obtained by radioactivity measurements, are presented concerning the transfer of labeled DOP from plasticized PVC into alcohols, namely methanol, *n*-propanol, or *n*-butanol. Migration tests, exceeding 3 months, were carried out at 35°C starting from a DOP concentration equal to 50 phr. Furthermore, an attempt to test the data obtained, as well as similar provided from the literature,¹ against typical Fickian models is also included.

EXPERIMENTAL

Synthesis of ¹⁴C-Labeled Dioctyl Phthalate

As previously described (1).

Plasticization

Suspension PVC of *K* value 65 was blended, at 80°C, with the calculated amounts of labeled plasticizer and Ba-Cd stabilizer. The latter was kept at the level of 3.0 phr. 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 of the specimens was immersed in 250 mL liquid contained in a glass-stoppered Erlenmeyer flask of 300 mL. All tests were made in duplicate, and the flasks were kept in an oven fixed to 35 ± 1°C. To monitor weight and dimensional changes, the specimens were removed from the liquid environment, wiped with a tissue, and immediately weighed, and dimensions were measured.

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 R_0 (c/mg min) of the plasticizer employed and reduced per liter of the liquid medium, DOP concentration data (q_t) (mg or g/L) are provided. The detailed procedure for measuring radioactivity has been described elsewhere.¹⁻³

RESULTS AND DISCUSSION

Plasticizer Migration

In Figure 1 migration curves are presented for the alcohols considered. q_t data have been further reduced per mm of the specimen thickness¹ so that slightly different specimens can be readily compared.²² Obviously, equilibrium is early attained with the higher alcohols in contrast with methanol, for which more than 4 months time is required. Furthermore, q_t/l values follow the quoted series: n -butanol \geq n -propanol $>$ methanol in agreement with the literature,² where the effect of molecular weight is referred.

It is worthwhile to emphasize that under our experimental conditions the equilibrium values of plasticizer loss, compared with the initial quantity

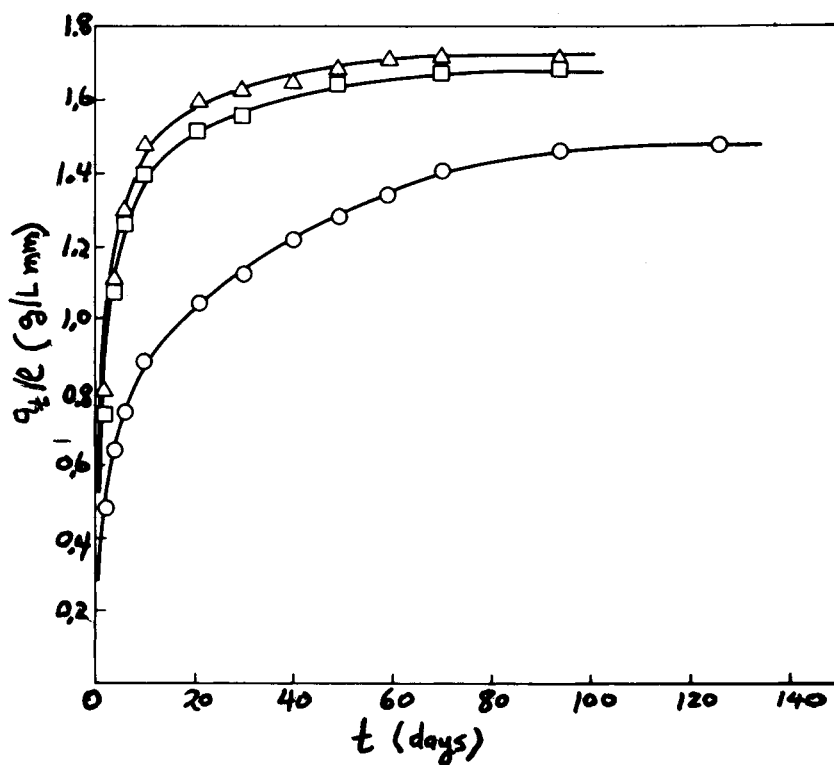


Fig. 1. Plots of q_t/l vs immersion time t : (○) methanol; (□) n -propanol; (Δ) n -butanol.

contained, reveal complete removal of the plasticizer for propanol and butanol while for methanol the percentage loss reaches the level of 86%. Furthermore, independently of the alcohol nature, the specimens tested started losing their flexibility, and after about 6 days immersion became quite brittle. No considerable shrinkage was detected.

Alcohol Diffusion into Poly(vinyl Chloride)

The equilibrium amount of the alcohol counterdiffused into the immersed plastic, when considered in terms of moles, seems to depend on molecular weight. In fact, relevant data were found, expressed in mmol of liquid medium penetrated per mm of the specimen thickness, equal to 3.38, 2.15, and 1.72 for methanol, propanol, and butanol, respectively. On the other hand, in agreement with Kampouris, et al.,² the phenomenon resulted in opacity accompanied also by separation of a second phase within the plastic mass.

Plasticizer Migration Kinetics

In an attempt to examine plasticizer migration kinetics, Fickian behavior was considered described, for plane sheet, by the well-known equation¹⁸

$$\frac{q_t}{q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-[(2n+1)\pi/l]^2 Dt\}}{(2n+1)^2} \quad (1)$$

where q_∞ represents the plasticizer concentration at equilibrium and D the diffusion coefficient.

For long times and when D is supposed to be independent of concentration eq. (1) may be approximated by

$$q_t/q_\infty = 1 - (8/\pi^2)\exp(-\pi^2 Dt/l^2) \quad (2)$$

By plotting a curve of $\ln[1 - (q_t/q_\infty)]$ against t , fitting and diffusion coefficients, can be evaluated. Nevertheless, the approximation for short times

$$q_t/q_\infty = (4/l)(Dt/\pi)^{1/2} \quad (3)$$

is also useful. A plot of q_t/q_∞ against $4(t/\pi l^2)^{1/2}$ is initially linear and has a slope of $D^{1/2}$

In accordance with the above analysis, plots of $\ln[1 - (q_t/q_\infty)]$ vs. t were first constructed to test the conformity of our long-term migration data, before equilibrium, to the approximated eq. (2). Considerable deviation from linearity was evident, independently of alcohol nature, in agreement with the least squares test: Correlation coefficients r^2 were found equal to 0.95, 0.89, and 0.86 for methanol, propanol, and butanol, respectively. Consequently, when accepting Fickian behavior, severe variation of D during migration should be expected.

In Figure 2 curves q_t/q_∞ against $t^{1/2}/l$ are presented, and indeed—during the initial stages—linearity is evident, as eq. (3) for Fickian behavior predicts. Accordingly, in Table I values of r^2 and also D are quoted. The latter,

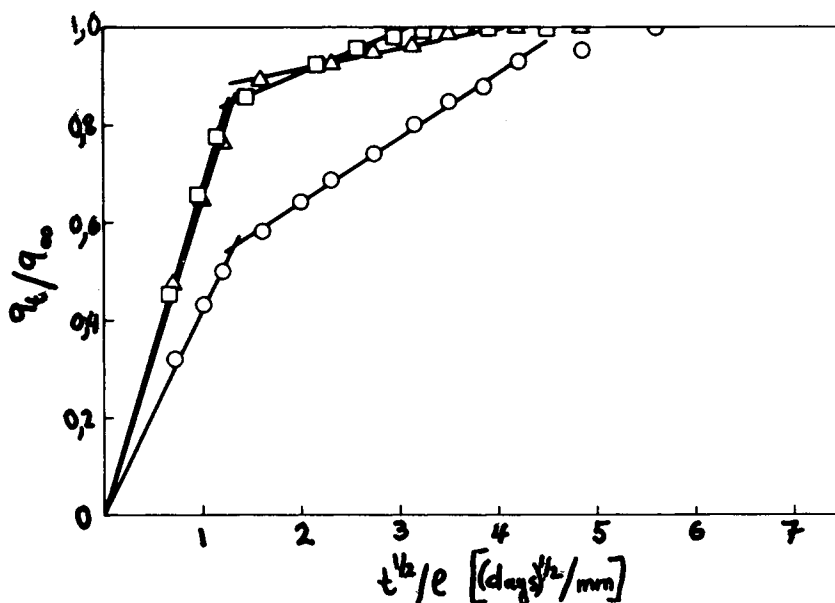


Fig. 2. Relationship between q_t/q_∞ vs. $t^{1/2}/l$: (○) methanol; (□) *n*-propanol; (△) *n*-butanol.

TABLE I
 q_t/q_∞ vs. $t^{1/2}/l$ Linear Correlation of Migration Data

Liquid medium	Initial stages		Afterwards stages r^2
	r^2	D (cm^2/s)	
Methanol	1.00	4.0×10^{-9}	1.00
<i>n</i> -Propanol	1.00	1.0×10^{-8}	0.98
<i>n</i> -Butanol	1.00	9.5×10^{-9}	0.98

concerning initial stages, are quite similar for the greater molecular weight alcohols while higher for that for methanol. Nevertheless, for all alcohols, after about 6 days immersion, a transition does occur so that linearity is further extended but with considerably reduced slope. It is worthwhile to notice that this phenomenon corresponds to a remaining plasticizer level of about 20 phr for methanol and 12 phr for propanol and butanol. According to the literature,²³ at the immersion temperature studied (35°C) and within the above stated concentration range, the system PVC/DOP exhibits nonrubbery or nearly nonrubbery behavior, in agreement with the macroscopic observations. Furthermore, no considerable plasticization effect should be expected from the alcoholic medium sorbed due to its well-marked separation in a second phase. On the other hand and in conformity with these results, data q_t/q_∞ against t definitely fail to provide a linear relationship corresponding to segmental relaxation control ($0.88 < r^2 < 0.94$ either for initial or afterwards stages).

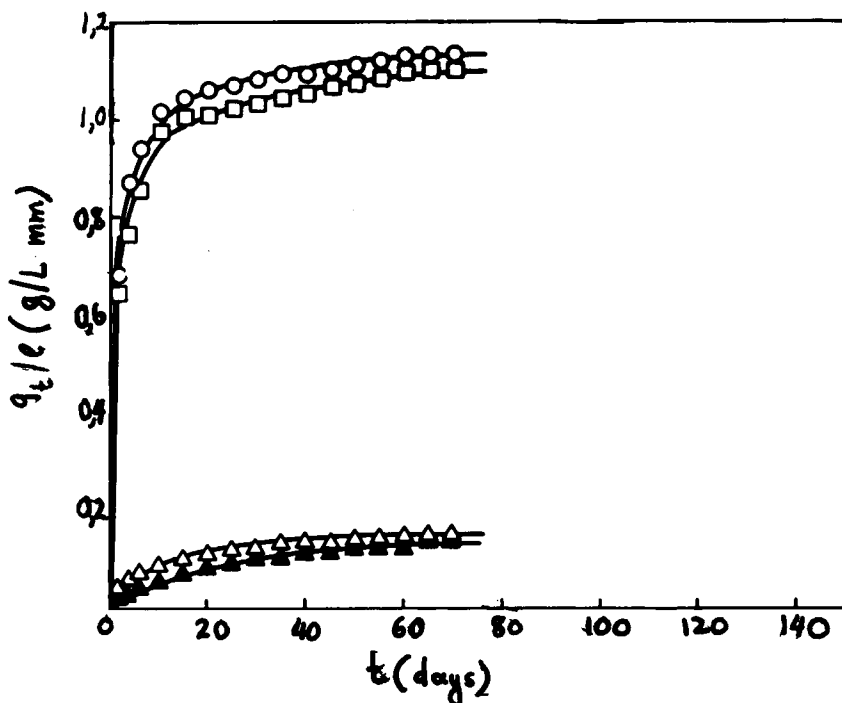


Fig. 3. Plots of q_t/l vs t : (○) white spirit; (□) kerosene; (△) paraffin oil; (▲) lubricating oil.

The consideration above stated undoubtedly is quite simplified, ignoring, for instance, boundary layer phenomena—even if the latter fail for long times to affect the overall process¹⁴—but it may be successfully extended to other migration studies. Accordingly, primary data presented by Kampouris were studied concerning the systems PVC/DOP/petroleum oils.¹ The typical cases of white spirit (low in aromatics), kerosene, paraffin oil, and lubricating oil (A) were selected. As stated, white spirit and kerosene result in considerable migration, nearly up to complete removal of the plasticizer, while for paraffin oil and lubricating oil the phenomenon is continuously maintained at negligible levels (Fig. 3). On the other hand, liquid counterdiffusion is referred to be of minor extent, especially for paraffin oil and lubricating oil.

The conformity of these migration data was first tested against eq. (2). Clearly, when plasticizer removal is not favored, typical Fickian behavior with nearly unvaried D was encountered ($r^2 = 0.99$ and 1.00 for paraffin oil and lubricating oil, respectively). On the contrary, the fitting was distinctly poor with white spirit ($r^2 = 0.79$) and kerosene ($r^2 = 0.82$) for which transition from the rubbery to the hard state and also separation effects have been detected.^{1,24} In this respect a behavior similar with that presented by the alcohols is observed: Plots of q_t/q_∞ versus $t^{1/2}/l$ (Fig. 4) reveal negligible deviation from linearity, either on initial or afterwards stages basis. Nevertheless, during the overall process and in agreement with the tests against eq. (2), paraffin and lubricating oil are accompanied by a slight variation of the slope,

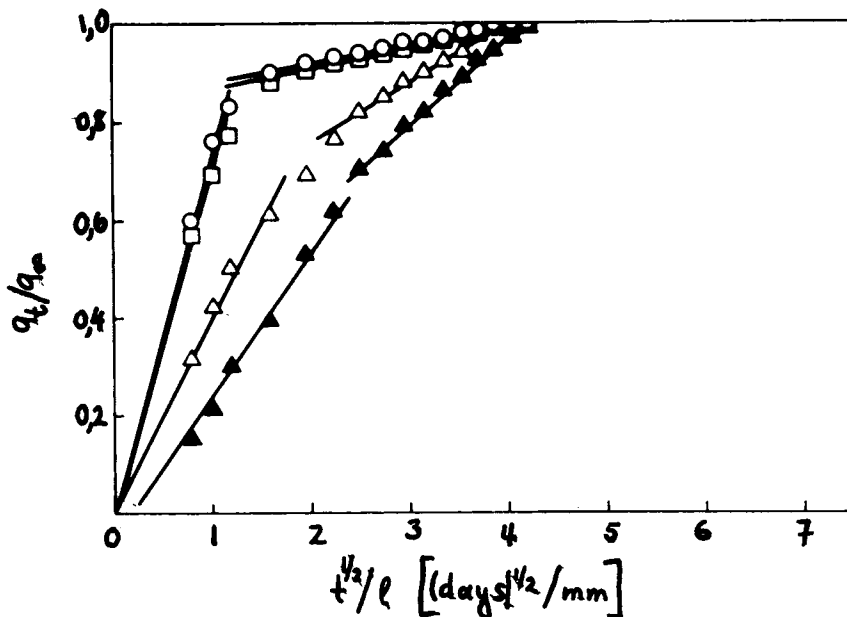


Fig. 4. Relationship between q_t/q_∞ vs. $t^{1/2}/l$: (○) white spirit; (□) kerosene; (△) paraffin oil; (▲) lubricating oil.

i.e., of the diffusion resistance, in contrast with white spirit and kerosene for which a distinct transition clearly appears.

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Received March 11, 1986

Accepted March 17, 1986