

Diffusion of additives and plasticizers in poly(vinyl chloride): 4. A programmed temperature technique for the determination of the diffusion parameters of three dialkylphthalates

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A programmed temperature technique has been developed for the measurement of the self-diffusion coefficients of additives in polymers. This has been applied to the diffusion of three dialkylphthalate plasticizers in poly(vinyl chloride). Values of the self-diffusion coefficients and the calculated activation energies obtained in this way have been compared with values previously obtained from measurements at constant temperature. It has been shown that the programmed temperature technique gives a very rapid method for the estimation of the activation energy of self-diffusion.

Keywords Programmed temperature change; di-n-butylphthalate; di-n-decylphthalate; di-n-hexylphthalate; poly(vinyl chloride); self-diffusion coefficient; activation energy

INTRODUCTION

The measurement of the temperature dependence of a diffusion coefficient customarily involves a series of experiments on the system under investigation, each of which is made at a constant temperature, and can be very time consuming.

In many areas of scientific investigation, the application of the principle of programmed temperature changes to the system under study has greatly facilitated the acquisition of data. It was thought that application of this principle to the measurement of diffusion coefficients would provide a method by means of which a rapid survey of the effect of temperature on diffusion could be made and the value of the activation energy for the diffusion process obtained from a single experiment in which there is a slow programmed temperature increase. In a previous paper¹ the self-diffusion coefficients of di-n-butylphthalate, di-n-hexylphthalate and di-n-decylphthalate in poly(vinyl chloride) (PVC), obtained from constant temperature measurements, were reported. The application of a programmed temperature technique to these systems enables comparisons to be made between the values of diffusion coefficients obtained by the two methods.

THEORETICAL

When a uniform disc of polymer of thickness h containing β -emitting radioactive diffusant is attached face to face with another disc of thickness m containing non-radioactive diffusant at the same concentration, the β -emission of the initially non-radioactive surface increases with time and that of the initially radioactive surface decreases. It can be shown^{2,3} that, for such a system at constant temperature when time t is large, the relationship

between the β -activity A_t from the initially non-radioactive face at time t , the β -activity A_∞ at infinite time and the self-diffusion coefficient D , is

$$\ln(A_\infty - A_t) = P - \pi^2 Dt/l^2 \quad (1)$$

where P is a dimensionless time-invariant parameter and $l = h + m$.

When t is not large and $h = m$, the percentage error in the diffusion coefficient measured from the slope of $\ln(A_\infty - A_t)$ vs t is as indicated below¹:

A_t/A_∞	0.155	0.273	0.367
Error (%)	10	3	1

It follows that for the constant temperature conditions and when $A_t/A_\infty > 0.2$, the diffusion coefficient can be evaluated from

$$D = -\frac{l^2}{\pi^2} \frac{d \ln(A_\infty - A_t)}{dt} \quad (2)$$

with an error of less than 5%. When the temperature of the system is changed to a higher value, it is clear that the value of D at this new temperature can still be calculated using equation (2).

The temperature intervals can be reduced until in the limit the continuous change in temperature results in a curved plot of $\ln(A_\infty - A_t)$ against time. Under these conditions it is easy to show from a simple mathematical transformation⁴ that the slope of this plot at a given time, and hence at a given temperature within the temperature range studied, enables the instantaneous value of D to be calculated from equation (2).

EXPERIMENTAL

^{14}C -labelled dialkylphthalates were prepared by reaction of ^{14}C -carbonyl-labelled phthalic anhydride and the required alcohol with toluene sulphonic acid present as catalyst to the extent of 0.1% of the weight of the anhydride.

Toluene, to the extent of 20% of total reactant weight, was added to form an azeotropic mixture with the water produced in the reaction. This mixture was collected in a Dean and Stark trap as the mixture was refluxed in a stream of nitrogen at 100°–140°C. When the reaction was ended, as indicated by the volume of water formed, the product was purified by several redistillations at reduced pressure ($\approx 10^{-3}$ Torr). The purity of the product was determined by elemental analysis, measurement of refractive index and i.r. and n.m.r. spectroscopy. The unlabelled phthalates were prepared using the same experimental technique.

BP Chemicals Ltd kindly provided a single batch of mass polymerized PVC ($M_n=46000$; $M_w=154000$). This was purified by solution in tetrahydrofuran and precipitation into a large excess of methanol followed by prolonged drying at 30°C *in vacuo*. Plasticized PVC film (≈ 0.25 mm thick) was prepared from a solution of the appropriate quantities of PVC and dialkylphthalate in peroxide-free tetrahydrofuran by casting in a glass ring resting on a flat glass plate. The final traces of solvent were removed by vacuum storage over silica gel. Discs of 20 mm diameter were cut from the film for the diffusion experiments described in this paper. These measurements were commenced by joining, face to face, a radioactive disc to a non-radioactive disc of similar composition and the same thickness. The composite disc, thus produced, was mounted in a holder which could be firmly and reproducibly mounted a few millimetres below the window of an end-window Geiger-Müller tube in an ERD lead castle.

The whole assembly was contained in a thermostat, the temperature of which was regulated with a control thermometer. A slow change in the temperature of the thermostat was effected by using a synchronous motor to drive the spindle of the control thermometer to give a constant rate of temperature increase.

The temperature was recorded continuously using a Cu/Cu-Ni thermocouple in the lead castle, and the activity of the originally inactive face of the composite disc was measured continuously from the ratemeter output of a Nuclear Enterprises SR5 scaler-ratemeter which was fed to a Servoscribe chart recorder.

The experiment was allowed to run until an equilibrium activity was reached.

RESULTS AND DISCUSSION

A typical plot of $\ln(A_\infty - A_t)$ vs. t is shown in Figure 1. The diffusion coefficients were calculated from the slopes at a number of points along the curve (beyond $A_t/A_\infty=0.20$).

Table 1 gives the values of the self-diffusion coefficients for each of the three dialkylphthalate plasticizers at 100 phr (parts (by weight) of plasticizer per hundred parts of resin) in PVC, determined from the slopes of the $\ln(A_\infty - A_t)$ vs. t plot for each plasticizer.

Figure 2 shows the good agreement between the values of the self-diffusion coefficient for di-n-butylphthalate, determined by the temperature programmed technique,

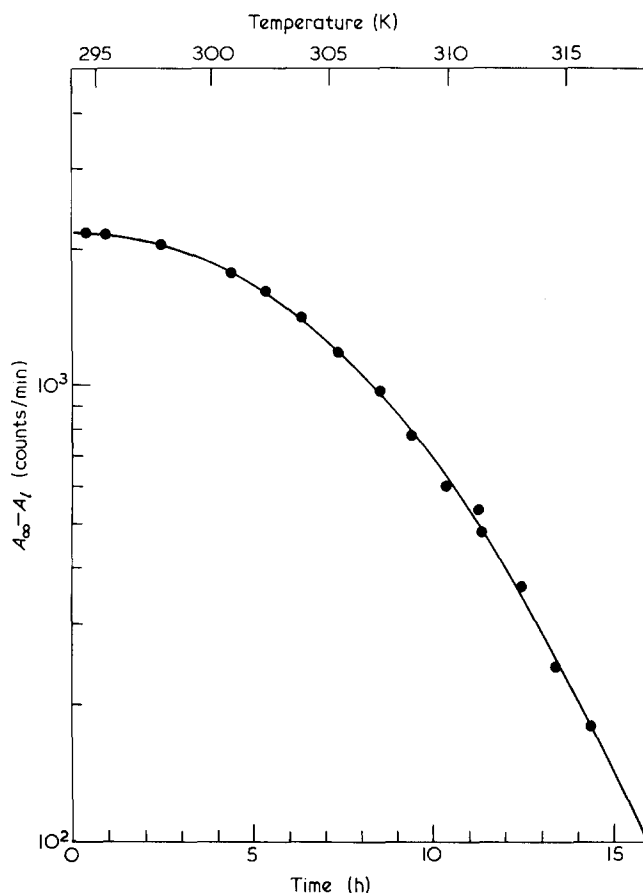


Figure 1 Variation of $\ln(A_\infty - A_t)$ with time t for a programmed temperature experiment (di-n-decylphthalate at 100 phr in PVC)

and those determined by single constant temperature experiments using the more accurate 1:2 double disc method³.

The change in diffusion coefficient with size of phthalate molecule is small and has been discussed elsewhere¹.

Figure 3 shows the temperature dependence of the self-diffusion coefficients of the three dialkylphthalates at 100

Table 1 Diffusion coefficients for dialkylphthalate plasticizers at 100 phr in PVC obtained from programmed temperature measurements

Plasticizer	T (K)	$10^{14} D$ ($\text{m}^2 \text{s}^{-1}$)
Di-n-butylphthalate	303.2	122
	305.6	146
	308.2	171
	311.4	207
	313.2	260
	315.8	283
Di-n-hexylphthalate	298.2	82
	303.0	96
	308.2	190
	313.2	262
	315.8	292
	317.0	323
Di-n-decylphthalate	303.2	121
	304.0	127
	308.2	191
	311.2	201
	315.8	310
	317.0	340

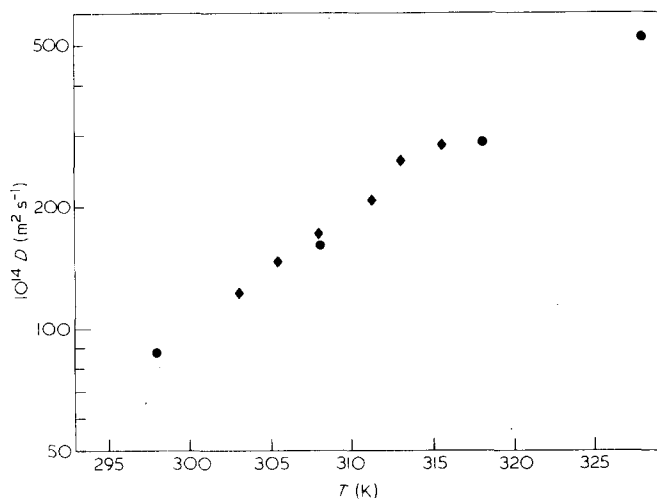


Figure 2 Self-diffusion coefficients for di-n-butylphthalate (100 phr in PVC): ●, constant temperature determination; ◆, programmed temperature determination

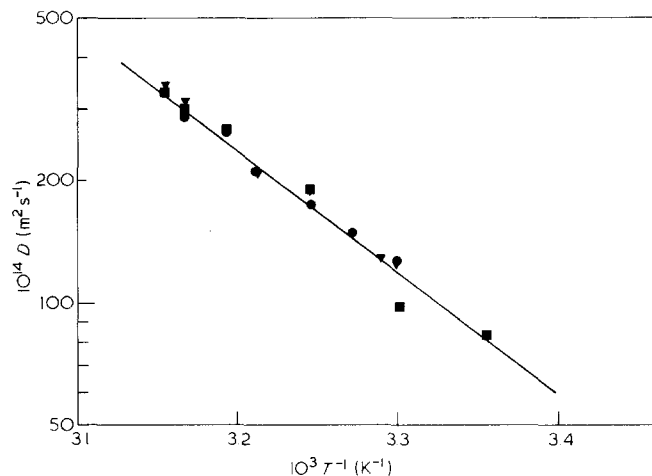


Figure 3 Arrhenius relationship for the self-diffusion coefficients D of dialkylphthalates at 100 phr in PVC, from programmed temperature experiments: ●, di-n-butylphthalate; ■, di-n-hexylphthalate; ▼, di-n-decylphthalate

phr in PVC, as determined from temperature programmed runs. From this plot an activation energy of 57 kJ mol^{-1} is obtained compared with the value of 50 kJ mol^{-1} obtained from constant temperature measurements of the self-diffusion coefficients of the three plasticizers at 100 phr in PVC at a series of temperatures in the same range as those of the programmed measurements. The data were obtained from just three experiments as opposed to the 18 which would have been required for constant temperature conditions.

Thus, by using temperature programming, a rapid study may be made of the temperature dependence of diffusion coefficients of additives in solid polymeric systems.

REFERENCES

- 1 Griffiths, P. J. F., Krikor, K. G. and Park, G. S. *ACS Organic Coatings and Plastics Chemistry Preprint* 1982, **32** (No.1); Diffusion of additives and plasticizers in poly(vinyl chloride) III, in 'Polymer Additives', (Ed. J. E. Kresta), Polymer Science and Technology Series, Plenum Press, New York and London, 1983
- 2 Griffiths, P. J. F. and Park, G. S. in 'Radiotracer Techniques and Applications' Vol.I (Eds. A. Evans and M. Muramsatsu), Marcel Dekker, New York and Basel, 1977, p.546
- 3 Park, G. S. and Tran Van Hoang, *Eur. Polym. J.* 1979, **15**, 817
- 4 Crank, J. 'The Mathematics of Diffusion', 2nd Edn., Clarendon Press, Oxford, 1975, p.104