The sorption of iso-propyl nitrate and acetone into nitrocellulose/nitroglycerine films

J. D. Cosgrove, T. G. Hurdley and T. J. Lewis
Ministry of Defence, PERME, Waltham Abbey, Essex, UK
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Rates of sorption of iso-propyl nitrate and acetone vapour into nitrocellulose films plasticized with nitroglycerine have been measured. In all cases, although fractional uptakes were approximately proportional to the square root of time, they were also independent of film thickness. Such behaviour indicates a 'Case III' mechanism in which the film expands uniformly with no appreciable concentration gradients. A kinetic equation, which describes uptakes of up to 90% is suggested.

Keywords Sorption; nitrocellulose; films; iso-propyl nitrate; acetone Case III; kinetics

INTRODUCTION

The term 'Case III' was first used to describe the sorption behaviour of iso-propyl nitrate (IPN) into a film of nitrocellulose (NC) which was already partially plasticized by the diffusant[1]. This note presents data to show that similar sorption kinetics are experienced with nitrocellulose films plasticized with material other than the diffusant. It is also not limited solely to the sorption of nitric esters.

Glassy polymers generally absorb organic vapours in a non-Fickian manner. If the weight increase of a thin film is plotted against the square root of time, sigmoid curves are usually observed. In some cases it is possible to interpret these curves still retaining Fickian concepts, but postulating that either *D*, the diffusant coefficient, or the equilibrium surface concentration changes with time[2]. However, it is more usual to abandon the diffusion theory and consider that the ability of a material to absorb is controlled by its ability to swell and accommodate the diffusant. Two limiting cases have been described. In Case II, a sharp boundary between swollen and unswollen material moves with constant velocity into the sheet[3]. In these circumstances it is clear that percentage uptake is proportional to t/l, i.e. directly proportional to time and inversely proportional to film thickness. In Case III, percentage uptake at any given time is independent of film thickness. To achieve such a situation it is necessary to postulate that the film is expanding uniformly and that there are no appreciable concentration gradients within the film. In both cases the amount of sorption is controlled by the extent of lattice relaxation. The difference between the two cases is essentially in the rate of Fickian diffusion through the unexpanded lattice compared with the rate of lattice expansion. In Case II the Fickian diffusion through the unexpanded lattice is effectively zero. In Case III the Fickian diffusion is very rapid. This maintains a uniform concentration and a state of quasi-equilibrium is rapidly reached. The position of this quasi-equilibrium level then slowly increases due to the comparatively slow process of molecular disentanglement and lattice expansion.

The dependence of the fractional weight increase (m_t/m_∞) on time, and of the time taken to reach one half equilibrium sorption, $t_{1/2}$, is summarized in *Table 1*.

The relationship between m_t/m_∞ and t in Case III is uncertain. In some circumstances it is approximately linear[1]. In the work reported in this report it follows more closely the square root of time. However, it will be shown that a power law in t is not the best description, and a more acceptable equation, derived on the basis of certain assumptions on the rate of lattice expansion, is proposed.

EXPERIMENTAL

The sorption apparatus has been described previously[1]. The method was the familiar one of suspending the film sample on a quartz spring in an evacuated chamber, and introducing the organic vapour (iso-propyl nitrate or acetone) at a vapour pressure controlled by the temperature of the reservoir. For iso-propyl nitrate the sample was kept at 30°C and the reservoir at 25°C; for acetone the sample was at 25°C and the reservoir at 0°C.

Films of nitrocellulose/nitroglycerine (NC/NG) were cast on glass from a solvent containing 40% acetone, 40% ethanol and 20% acetate. The solvent was removed by first drying in air at atmospheric pressure, then immersing the films in water for 24 h, and finally drying under vacuum. The films contained from 10 to 45% of NG and were between 0.03 and 0.15 mm thick.

RESULTS AND DISCUSSION

Figures 1 and *2* show the uptake of IPN into NC/NG films

Table 1 Dependence of fractional weight increase on time and time taken to reach one half equilibrium sorption

		Fickian	Case II	Case III
m_t/m_∞	$\propto$	$t^{1/2}$	t	?
$t_{1/2}$	$\propto$	l^2	l	l^0

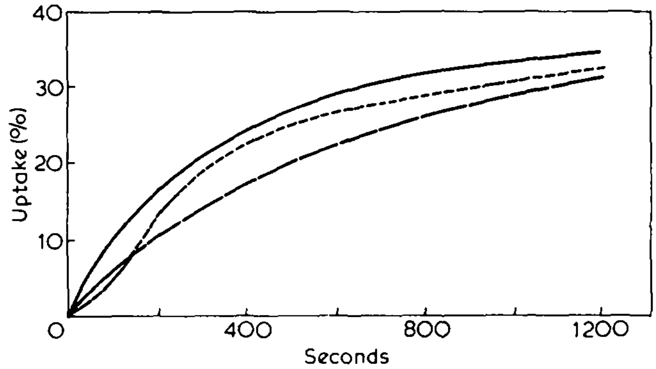

Figure 1 Sorption of IPN into NC (55%)/NG (45%) film: uptake *versus* time. Film thickness: (- - - -), 0.03 mm; (———), 0.075 mm; (— — —), 0.14 mm

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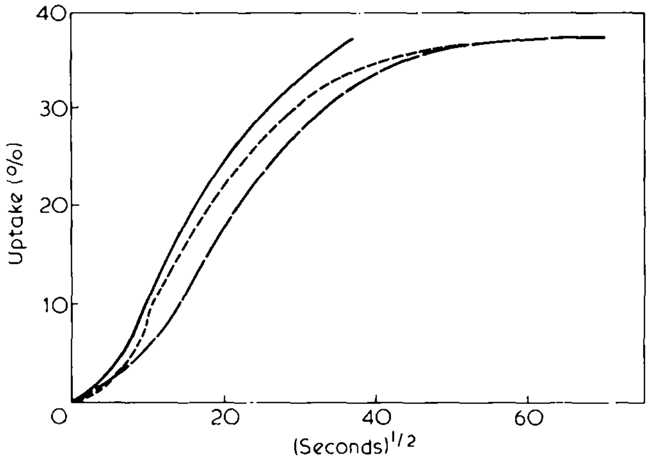

Figure 2 Sorption of IPN into NC (55%)/NG (45%) film: uptake *versus* (time)$^{1/2}$. Film thicknesses:– (- - - - -), 0.03 mm; (———), 0.075 mm; (— — — —), 0.14 mm

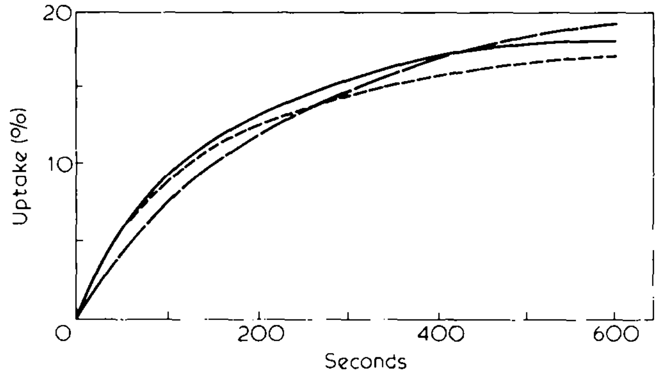

Figure 3 Sorption of acetone into NC (55%)/NG (45%) film: uptake *versus* time. Film thicknesses:– (- - - - -), 0.03 mm; (———), 0.075 mm; (— — — —), 0.145 mm

containing 45% of NG. In each case three different film thicknesses are shown. *Figures 3* and *4* show similar plots for the sorption of acetone.

It can be seen that sorption is not proportional to t (*Figures 1* and *3*), and any possibility of a Case II mechanism operating may be immediately rejected. However the plots against $t^{1/2}$ (*Figures 2* and *4*) show distinct sigmoid characteristics. This sigmoid characteristic becomes much less noticeable as the concentration of NG in the film decreases. At 10% NG a fairly good linear plot with $t^{1/2}$ is obtained. Since the $t^{1/2}$ plot is so much better than the t plot, Fickian diffusion, perhaps with some modification, might be suspected. However, by far the most striking feature in both the IPN and the acetone cases is the independence of the degree of sorption on film thickness. Since, in Fickian sorption, the percentage uptake should be proportional to $t^{1/2}/l$, one would expect the curve for the 0.03 mm film to rise nearly five times more steeply than the 0.14 mm film. In fact, it was rarely the thinnest film which showed the most steep rise, and any differences in the behaviour of the films shown in *Figures 1–4* (or similar plots for other NG concentration) seem to be more or less random. Such behaviour is characteristic of Case III sorption, as previously defined.

If rate of sorption is controlled by the rate of lattice expansion there is no reason why it should follow either a time or (time)$^{1/2}$ dependancy. A more reasonable suggestion is that sorption rate will be proportional to the difference in osmotic pressure inside and outside the film. As a first approximation one can relate this to simple vapour pressure, and if, up to the equilibrium point, the vapour pressure of IPN in the film is proportional to its concentration, the following first order equation is obtained:

$$dc/dt = k(c_\infty - c) \tag{1}$$

where c is the concentration at time t, c_∞ the equilibrium concentration at infinite time, and k is a constant. On integration this gives

$$\ln(c_\infty - c)/c_\infty = -kt \tag{2}$$

Figures 5 and *6* show the data of *Figures 1–4* plotted in this way. Reasonable linearity is obtained for IPN up to 80% of the equilibrium sorption, and for acetone up to

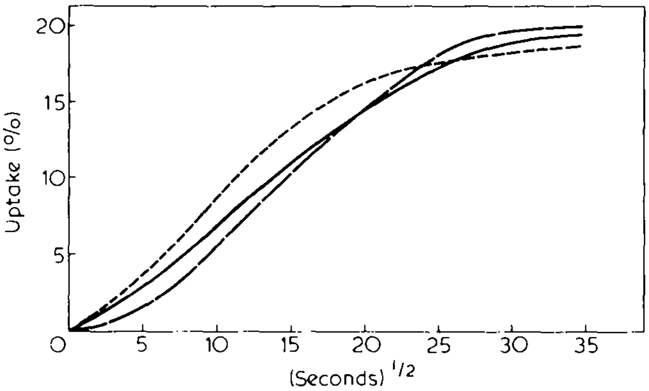

Figure 4 Sorption of acetone into NC (55%)/NG (45%) film: uptake *versus* (time)$^{1/2}$. Film thicknesses:– (- - - - -), 0.03 mm; (———), 0.075 mm; (— — — —), 0.125 mm

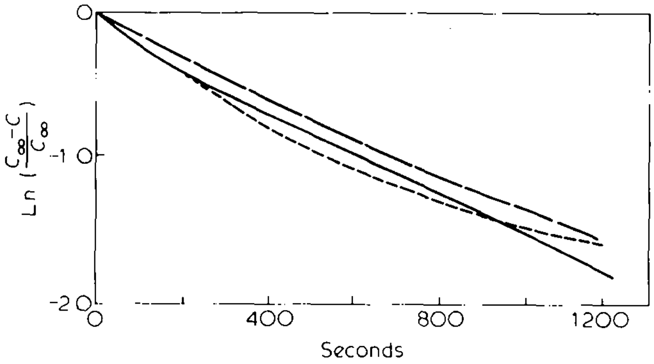

Figure 5 Sorption of IPN into NC (55%)/NG (45%) film: ln$(c_\infty - c)/c_\infty$ *versus* time. Film thicknesses:– (- - - - -), 0.03 mm; (———), 0.11 mm; (— — — —), 0.14 mm

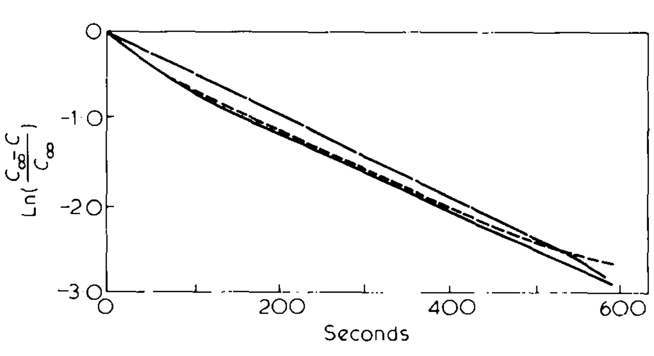

Figure 6 Sorption of acetone into NC (55%)/NG (45%) film: ln$(c_\infty - c)/c_\infty$ *versus* time. Film thicknesses:– (- - - - -), 0.03 mm; (———), 0.075 mm; (— — — —), 0.145 mm

Table 2 Equilibrium uptake (w/w %) and k (s^{-1}) for various NC/NG films

	10% NG		35% NG		45% NG	
Film composition	c_∞	k	c_∞	k	c_∞	k
IPN	32.3	0.0018	34.9	0.0016	41.6	0.0014
Acetone	17.9	0.0054	17.7	0.0050	19.0	0.0046

about 90%. In such treatment it is necessary to know c_∞ accurately, and this figure is more difficult to obtain with IPN than with acetone, probably because conditions are closer to saturation.

Table 2 gives the equilibrium uptake (as a percentage of the initial film weight) and k, calculated in the above manner, for a series of NC/NG films. It can be seen that whilst there is a tendency for the equilibrium uptake to increase with increasing NG content (particularly noticeable for IPN sorption), there is a corresponding fall in the value of k.

In comparing these values with those for pure NC films it must be remembered that the latter absorb by a Case II mechanism and any attempt to analyse by equation (2) will give a value of k which depends on film thickness[1]. However, for films of comparable thickness, $t_{1/2}$, the time taken for uptake to half the equilibrium value, is about 30 times greater for NC than for NC/NG films in the case of IPN and about 3 times greater than in the case of acetone. Thus plasticization by NC increases the rate of sorption, but once sufficient plasticizer is present to change the rate controlling mechanism from Case II to Case III further addition has a comparatively small effect.

A warning is frequently given that 'a moving boundary does not necessarily imply a Case II mechanism', and for Case II to be proved it is necessary to show that the boundary moves linearly with time. We would add a second warning—that a $t^{1/2}$ sorption law, particularly if approximate, does not necessarily imply Fickian diffusion. Film thickness should always be an examined parameter, and Fickian sorption is only proved if uptake is proportional to $t^{1/2}/l$.

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Reactivity ratios of styrene–*N*-iso-butylmaleimide and methyl methacrylate–*N*-iso-butylmaleimide

Mieczysław Kucharski and Bozena Sanecka
Institute of Chemical Technology, I. Lukasiewicz Technical University, 35-959 *Rzeszów, Poland*

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The copolymerization of styrene and methyl methacrylate with *N*-isobutylmaleimide (*N*-iso-BMI) has been investigated. The reactivity ratios of these pairs of comonomers were determined by following the Fineman–Ross method. *N*-iso-BMI was found to be of limited use in modifying methylmethacrylate but was better suited to mass polymerization of styrene.

Keywords Polymerization; reactivity ratio; styrene; methyl methacrylate; *N*-isobutylmaleimide; modification

INTRODUCTION

Within the scope of our investigations concerning the chemical modification of vinyl polymers with heterocyclic monomers we have investigated the copolymerization of styrene and methyl methacrylate with *N*-iso-butylmaleimide. Because the constitution of the copolymer is a function of the reactivity ratios we have found it useful to determine these values for the copolymerization of *N*-iso-butylmaleimide with styrene and methyl methacrylate. As far as we know the reactivity ratios for the above mentioned pairs of comonomers have not yet been presented.

In determining the reactivity ratios we followed the Fineman–Ross method[1] making use of the equation

$$\frac{P-1}{R}=r_1-\frac{P}{R^2}r_2$$

where: P is the molar ratio of the comonomers in the copolymer; R is the initial ratio of molar concentrations of the comonomers; r_1 is the reactivity ratio of styrene or methyl methacrylate and r_2 is the reactivity ratio of *N*-iso-butylmaleimide.

EXPERIMENTAL

Monomers

(i) *N*-iso-butylmaleimide (N-iso-BMI) was obtained by a two stage method[2,3]. In the first stage of the reaction, from a maleic anhydride and isobutylamine in toluene at 363K we obtained *N*-iso-butylmaleamic acid which was then submitted to cyclodehydration in methylene chloride at 273K; acetic anhydride and triethylamine were used as catalysts. The product was purified by distillation under reduced pressure (30 mm Hg) at 343–348K. *N*-iso-

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