

Diffusion of isopropyl nitrate, acetone and water into nitrocellulose

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(Received 19 September 1977; revised 13 October 1977)

The sorption kinetics of isopropyl nitrate, acetone and water into nitrocellulose films show marked differences from each other. The movement of water is essentially Fickian. That of acetone on all cycles and of isopropyl nitrate on the first cycle are characterized by a boundary between swollen and unswollen material moving at constant velocity into the film (Case II swelling). Sorption of isopropyl nitrate on all but the first cycle is characterized by a uniform concentration at all times throughout the expanding film (Case III swelling). Variations in the equilibrium sorption of isopropyl nitrate have been interpreted as indicating that the degree of crystallinity of the nitrocellulose fibres and films.

INTRODUCTION

Over the past fifty years, commercial and military interest has stimulated a number of researches into the nature of the interaction between nitrocellulose and plasticizers. Many investigators have studied equilibrium sorption isotherms over a range of plasticizer activity, and generally relate to nitrocellulose in the form of fibres. Kinetic diffusion studies at selected activities of diffusant have been fewer in number, and have been restricted to solvent-cast films. The present study developed partly from a need for quality control data covering properties of nitrocellulose not included in the present specification, and partly from a need for information concerning the processes occurring during propellant manufacture. Isopropyl nitrate was chosen as a model alkyl nitrate of convenient vapour pressure which might be expected to show similarities to the important energetic plasticizer, nitroglycerine.

The diffusion of water in nitrocellulose films has been shown to be basically Fickian¹, whereas sorption of acetone vapour shows marked departures from Fickian behaviour². Such behaviour is characteristic of the glassy state. (T_G for nitrocellulose $\sim 56^\circ\text{C}$)³. A review of non-Fickian sorption has been given by Park⁴ and by Alfrey *et al.*⁵. Although data may often be interpreted in different ways there is general agreement that the further a system departs from Fickian conditions the more important becomes lattice relaxation (swelling) in determining rates of sorption. Alfrey⁵ defines a limiting case, 'Case II swelling', in which m_t/m_∞ is proportional to t/l (in Fickian sorption m_t/m_∞ is proportional to $t^{1/2}/l$), where m_t is the mass sorbed at time t , m_∞ the mass sorbed at time ∞ and l is the film thickness. Case II swelling is characterized by a sharp boundary between swollen and unswollen material moving with constant velocity through the polymer. We should like to define a third limiting case, Case III swelling, in which m_t/m_∞ is independent of l . Such a case is implicit in the mechanism suggested by Bagley and Long⁶ for the sorption of acetone by cellulose acetate. In this mechanism, rapid Fickian diffusion keeps the concentration of diffusant at a uniform quasi-equilibrium level throughout the

film, but this equilibrium level is itself determined by the degree of lattice relaxation, i.e. swelling, which has already taken place.

In the present investigation all three limiting laws have been observed. The sorption of water is essentially Fickian, Case II swelling occurs with both acetone and isopropyl nitrate, and Case III swelling occurs when isopropyl nitrate is sorbed into material which has already undergone at least one sorption-desorption cycle. Whether Case II or Case III swelling equations are followed will depend on the magnitude of the diffusion coefficient describing the small amount of Fickian sorption which takes place. Evidently the loosening of the lattice and the retention of a small proportion of the isopropyl nitrate during the sorption-desorption cycle results in a much increased diffusion coefficient on successive cycles.

Interpretation of data relating to sorption into fibres is more difficult, owing to the fact that the observed weight increase curves are the sum of many such curves on individual fibres. Each fibre is of different thickness, and hence presents a different diffusion path to the plasticizer. However, information has been gathered on the accessibility of various regions of the fibre to various solvents and plasticizers, and some of the diffusion behaviour shown by plasticizers in films of nitrocellulose may be expected to apply also in the case of fibres.

EXPERIMENTAL

The sorption apparatus was similar to that used by many previous workers, and consisted of suspending the nitrocellulose on a quartz spring (sensitivity 2.5 mg/mm) within an evacuated, thermostatically controlled chamber. Films were attached directly to the spring. Fibres were enclosed in a nylon bag which sorbed a negligible quantity of isopropyl nitrate and acetone vapour, but appreciable quantities of water vapour. Appropriate corrections were made in this case. After evacuation, diffusant vapour was introduced from a side arm in which a liquid reservoir was kept at the same temperature as the sorption chamber in the case

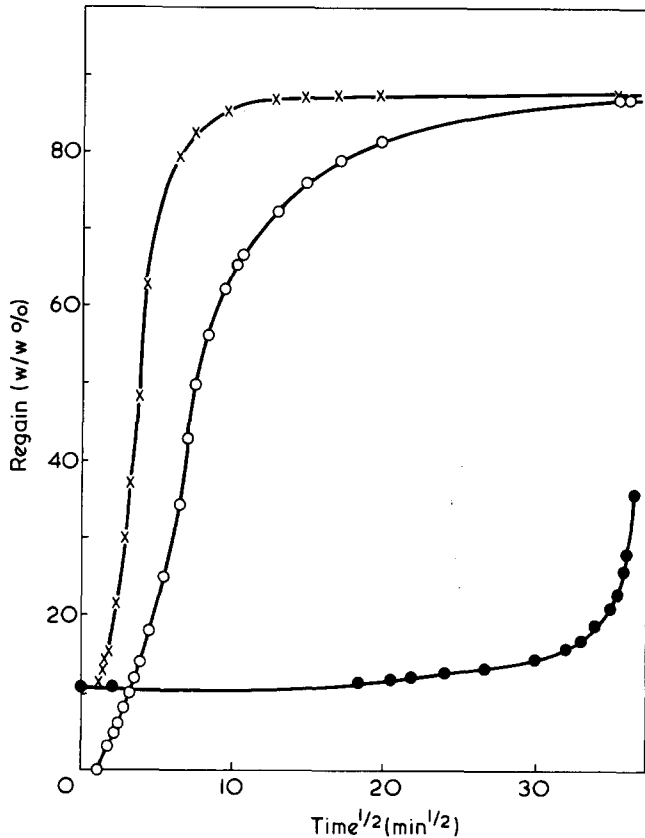


Figure 1 Sorption and desorption of isopropyl nitrate. O, 1st sorption; ●, 1st desorption; X, 2nd sorption. Film thickness = 0.030 mm, $T = 25^{\circ}\text{C}$

of isopropyl nitrate and water and at a lower temperature (0°C) in the case of acetone. Thus all measurements on isopropyl nitrate and water were made under saturation conditions. Observations of weight changes were often made over a period of several days by means of a collimated telescope.

Most measurements were made on nitrocellulose containing 12.6% nitrogen (Pyro/mechanical, cotton linter precursor) supplied by NEC Ltd, Stevenston, Ayrshire. A few results were obtained on 13.4% nitrogen material ('High nitrogen', mechanical, cotton linter precursor) also obtained from NEC Ltd, and on 12.2% nitrogen (displacement, wood fibre precursor) obtained from ROF Bishopton. Films were cast from acetone on glass. On storage for several weeks in damp air the acetone content fell to about 0.5%. This is lower than could be achieved by vacuum drying owing to the phenomenon of permanent sorption described below (see Figure 4).

RESULTS AND DISCUSSION

Isopropyl nitrate into NC films and fibres

Figure 1 shows successive sorption-desorption cycles for isopropyl nitrate at saturation pressure with a typical nitrocellulose (12.6% nitrogen) film. Some characteristics which are common to all such curves are:

- (1) The sigmoid shape of the sorption curves.
- (2) The very fast rates of desorption. The slopes of the desorption curves are generally at least 50 times greater than those of the corresponding sorption curves (see Table 1).
- (3) The existence of 'permanent sorption'. An appreciable

Table 1 Values of $t_{1/2}$ for sorption and desorption of plasticizers by NC. (All values in minutes)

(i) Isopropyl nitrate: $T = 25^{\circ}\text{C}$; $p = 34\text{ mm}$ ($p/p_0 = 1$)

Nitrogen in NC (%)	Cycle	Film thickness (mm)						Fibres	
		0.013		0.030		0.085		Sorption	Desorption
		Sorption	Desorption	Sorption	Desorption	Sorption	Desorption		
12.2	1							114	1.7
	2							42.2	0.8
12.6	1	32	0.5	52.0	0.5	190	0.8	70	0.5
	2	14.3	0.5	14.6	0.5	21.0	0.8	22	0.5
13.4	1							86	0.5
	2							22	0.5

(ii) Acetone: $T = 25^{\circ}\text{C}$; $p = 69\text{ mm}$ ($p/p_0 = 0.315$)

Nitrogen in NC (%)	Cycle	Film thickness (mm)				Fibres	
		0.022		0.055		Sorption	Desorption
		Sorption	Desorption	Sorption	Desorption		
12.6	1	3.2	0.5	6.8	4.4	4.3	3.1
	2	3.0	0.5	5.2	4.4	3.3	2.5

(iii) Water: $T = 25^{\circ}\text{C}$; $p = 24\text{ mm}$ ($p/p_0 = 1$)

Nitrogen in NC (%)	Cycle	Film thickness (mm)						Fibres	
		0.013		0.020		0.05		Sorption	Desorption
		Sorption	Desorption	Sorption	Desorption	Sorption	Desorption		
12.6	1	0.75	0.4	1.0	1.3	7.8	2.9	16	1.7
	2							11	1.7

Table 2 Equilibrium uptake of plasticizer by NC (w/w %)

 (i) Isopropyl nitrate: $T = 25^\circ\text{C}$; $p = 34$ mm ($p/p_0 = 1$)

Nitrogen in NC (%)	Film thickness (mm)			Fibres
	0.013	0.030	0.085	
12.2				62.8
12.6	121.2	87.4	72.5	62
13.4				61.4

 (ii) Acetone: $T = 25^\circ\text{C}$; $p = 69$ mm ($p/p_0 = 0.315$)

Nitrogen in NC (%)	Film thickness		Fibres
	0.022	0.055	
12.6	19.0	19.0	19.0

 (iii) Water: $T = 25^\circ\text{C}$; $p = 24$ mm ($p/p_0 = 0.315$)

Nitrogen in NC (%)	Film thickness (mm)			Fibres
	0.013	0.020	0.05	
12.6	5.4	4.4	4.0	5.6

proportion of the isopropyl nitrate cannot be removed despite continuous pumping for several days at 25°C .

(4) Sorption is slower on the first cycle than in all successive cycles (see *Table 1*).

All of these characteristics except (4) have been observed before for the sorption of acetone into nitrocellulose². They are typical of 'non-Fickian' sorption into glassy polymers.

Table 2 shows the final equilibrium uptake of isopropyl nitrate at 25°C for various samples of films and fibres.

Although these observations alone do not show whether there are distinct accessible and inaccessible regions within the fibres and films, there is strong independent evidence that this is so. It has been shown⁷ that sorption of isopropyl nitrate, like that of all alkyl nitrates, does not change the unit cell dimensions of nitrocellulose. Clearly, it does not enter the crystalline regions of fibres and films, but enters and swells only the amorphous regions. On this interpretation it may be said that thin films have less crystalline character than thick films, but that all films have less crystalline character than fibres. The degree of crystallinity of fibres is probably more a function of the crystallinity of the cellulose precursor than of the nitrogen content, or of any other property with which it is endowed during manufacture. A similar interpretation has been made for the difference in uptake of water by natural and regenerated cellulose fibres⁸. It is, however, difficult to interpret the data of Moore⁹, who found that nitrocellulose (13.2% nitrogen) fibres sorbed *more* of certain esters than did films made from the same material. He, like us, found that the sorption of acetone and other ketones by fibres and films was identical (see below).

Figures 2a and *2b* shows the first sorption curves for sheets of various thicknesses. It can be seen that uptake approximates to a linear function of t/l , where l is the film thickness. This is the equation followed by 'Case II swelling', in which a sharp boundary between swollen and unswollen material moves at a constant velocity into the film.

Figure 3 shows that for the second and subsequent sorption, not only is m_t/m_∞ a linear function of t , but it is also independent of the film thickness, l . This is 'Case III swelling' as defined in the Introduction. On undergoing a

sorption-desorption cycle the film is left with some permanent sorption and swelling. The Fickian diffusion coefficient for isopropyl nitrate, which was effectively zero on the first sorption cycle, is now increased to such an extent that diffusion throughout the film precedes swelling. A state of quasi-equilibrium is rapidly attained, the position of which slowly changes as the lattice further relaxes and further swelling occurs. A uniform concentration is maintained at all times across the film, and thus the proportional uptake will be independent of film thickness.

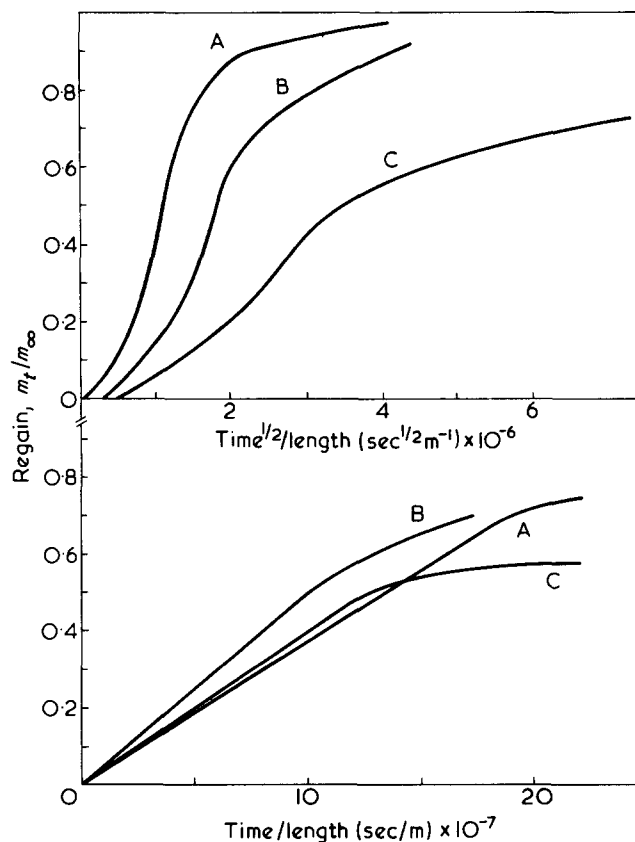


Figure 2 1st sorption of isopropyl nitrate into films of various thicknesses. A, thick film (0.085 mm); B, Medium film (0.030 mm); C, thin film (0.013 mm). $T = 25^\circ\text{C}$

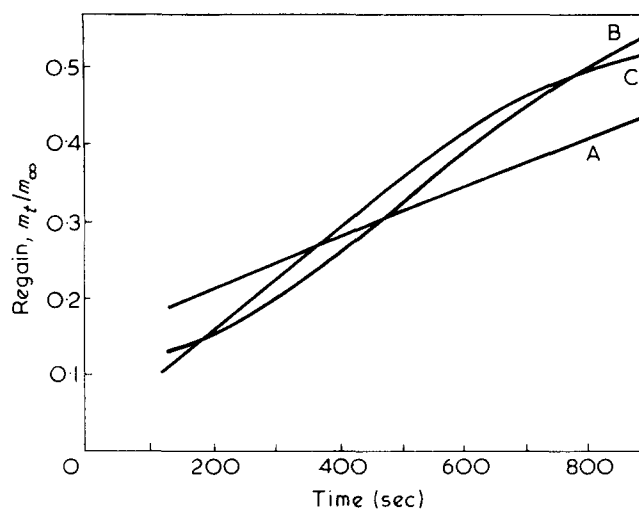


Figure 3 2nd sorption cycle of isopropyl nitrate. A, thick film (0.085 mm); B, medium film (0.030 mm); C, thin film (0.013 mm). $T = 25^\circ\text{C}$

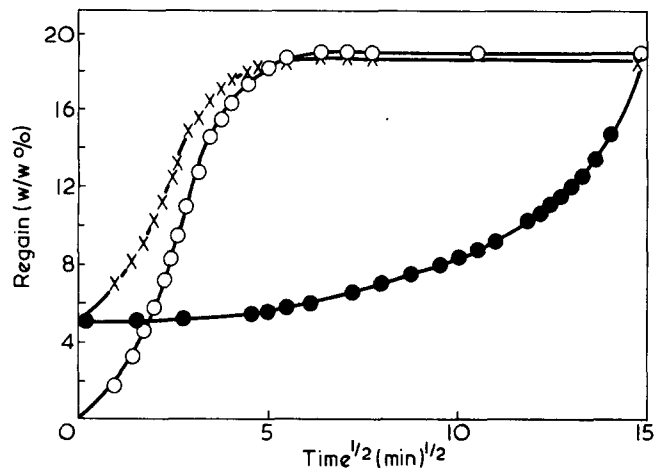


Figure 4 Sorption and desorption of acetone. \circ , 1st sorption; \bullet , 1st desorption; \times , 2nd sorption. Film thickness = 0.055 mm. $T = 25^\circ\text{C}$

For this change from Case II swelling to Case III swelling to occur there must be a very sharp increase in the Fickian diffusion coefficient with isopropyl nitrate concentration. There are a number of features which corroborate this conclusion. The rate of desorption is extremely rapid. It may be supposed that here, unlike the sorption mechanism, there is no constraint placed on the movement of isopropyl nitrate by any need for lattice relaxation. The high desorption rate must be limited only be diffusion through the film or by evaporation at the surface. At all events, the diffusion of isopropyl nitrate through a film already expanded with this same material is necessarily rapid. In previously published data it is not generally possible to identify and isolate the Fickian component in glassy polymers, but in the 'interval sorption' of acetone into cellulose acetate the diffusion coefficient has clearly been shown to increase with acetone concentration⁶. Of course, in systems which are entirely Fickian there are numerous instances of diffusion coefficient increasing with concentration of diffusant.

Some attention should now be paid to the phenomenon which we have termed 'permanent sorption', the amount of plasticizer left in the nitrocellulose after extended pumping. A typical curve for isopropyl nitrate (Figure 1) would show about 80% desorption after 10 min, then a slow removal of a further 10% of sorbant over the next 400 min, and thereafter no measurable weight loss. Once again, such a phenomenon is typical of diffusion in glassy polymers⁴. Previous examples have been interpreted as the trapping of plasticizers as the time- and concentration-dependent diffusion coefficient falls to zero at the surface of the desorbing film. However, the present study suggests that the trapping of diffusant takes place in many parts of the contracting lattice, and is not due merely to an impervious surface layer. Film thickness has only a slight effect on the degree of permanent sorption, and there is little difference between films and fibres. Furthermore, desorption rate from a sample in which sorption is stopped at, say, half the equilibrium level is the same as that of a sample at the midpoint of desorption from the full equilibrium level. This would indicate that there were no great concentration gradients during desorption, and that the concentration is changing uniformly throughout the film. This is the reverse of Case III swelling, and under these

circumstances it would seem probable that diffusant is retained uniformly throughout the lattice. Bonding to certain groups on the nitrocellulose molecule is probable, and was postulated many years ago by Hess and his coworkers¹⁰.

Acetone into NC films and fibres

Figure 4 illustrates the sorption-desorption behaviour of acetone vapour with nitrocellulose films. Qualitative similarities with Figure 1 are immediately apparent. The curves are again sigmoid, desorption is again faster than sorption, sorption is again slower on the first cycle than on subsequent ones, and permanent sorption is again a noticeable feature. However, a number of important quantitative differences from the previous case exist.

(a) Total sorption at equilibrium is independent of film thickness. It is also the same for films and fibres (see Table 2).

(b) On the first cycle, sorption rate is about 15 times faster for acetone than for isopropyl nitrate (see Table 1).

(c) With acetone, the increase in sorption rate on the second and subsequent cycles is less marked than with isopropyl nitrate. (About 30% increase, compared with 100–200% increase with IPN, see Table 1).

(d) With acetone the rate of desorption is only a factor of 2 or 3 greater than the rate of sorption. With isopropyl nitrate the factor is over 50. Desorption is therefore slower with acetone than with isopropyl nitrate (see Table 1).

Figures 5a and 5b show that when regains are plotted against $t^{1/2}/l$ and against t/l for two different values of l , it is once more the t/l graph which is both linear and coincident for the two film thicknesses. Case II swelling is occurring. However, unlike the case of isopropyl nitrate, Figure 6 shows a similar law is obeyed for the second and subsequent sorption cycles. It would seem that Case III swelling does not

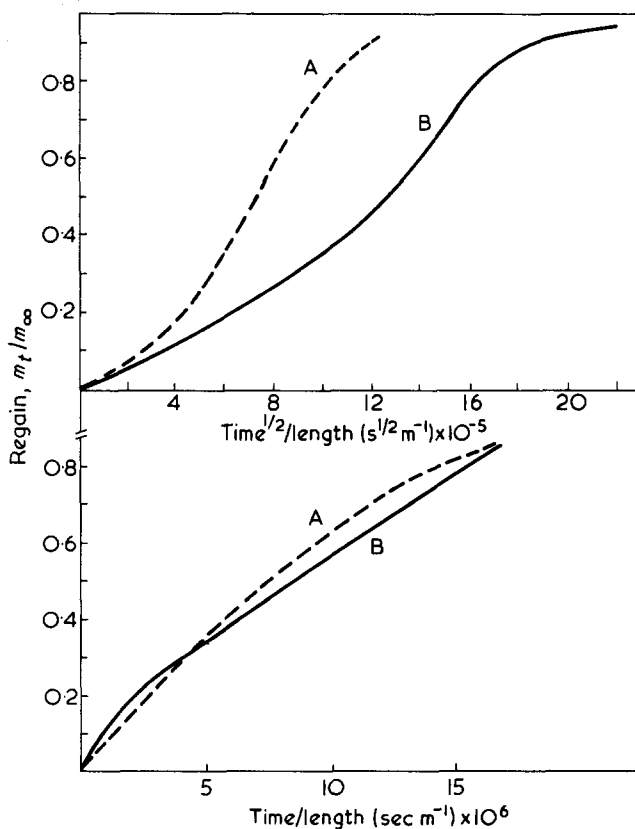


Figure 5 1st sorption of acetone into films of different thicknesses. A, thick film (0.055 mm); B, thin film (0.022 mm). $T = 25^\circ\text{C}$

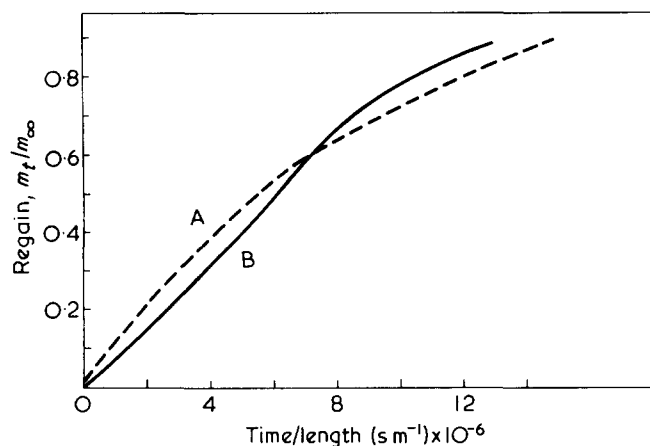


Figure 6 2nd sorption cycle of acetone. A, thick film (0.055 mm); B, thin film (0.022 mm). $T = 25^\circ\text{C}$

occur in the case of acetone sorption, probably because the rate of progression of the boundary between swollen and unswollen material is greater, and overtakes any Fickian diffusion before quasi-equilibrium can be reached.

Desorption is slower than for isopropyl nitrate and follows a roughly Fickian law, i.e. $m_t/m_\infty \propto t^{1/2}/l$. This is in contrast to desorption of isopropyl nitrate, which is almost independent of l .

The overall picture for acetone sorption is that of a Fickian diffusion coefficient of the same order of magnitude as that for isopropyl nitrate. However, the more rapid swelling and boundary movement in the case of acetone prevents the establishment of uniformity of concentration ahead of the boundary. In this it differs from the second and subsequent sorption cycles of isopropyl nitrate. Case II rather than Case III swelling laws are always obeyed.

Water into NC films and fibres

The few results available for the diffusion of water into nitrocellulose show a marked contrast to those for acetone and isopropyl nitrate diffusion. Tables 2 and 3 show that the level of equilibrium sorption is low, but that it is rapidly attained. There is, however, a further small increase in the sorption equilibrium as the lattice relaxes over a matter of days. Figure 7 shows that in nitrocellulose films the sorption of water is almost Fickian. In all respects we are in agreement with Long and Thompson¹, who also found that the diffusion of water into NC films was essentially Fickian, in sharp contrast to acetone, which had been studied earlier by the same group². Our value for the diffusion coefficient ($1.8\text{--}3.2 \times 10^{-13} \text{ m}^2\text{s}^{-1}$) at 25°C is rather lower than the value of $1.8\text{--}3.8 \times 10^{-12} \text{ m}^2\text{s}^{-1}$ at 39.8°C found by Long and Thompson, but it is interesting to note that they found that diffusion coefficient increased with film thickness. Their lower figure was for a film of 0.086 mm and their higher figure was for a film of 0.197 mm. If this trend were continued our lower figures might be expected.

Thus with water it is possible to see a rapid Fickian sorption, similar to that which was postulated for isopropyl nitrate and acetone, but which could not be easily seen in those cases due to the much greater sorption accompanying the swelling reaction. Any swelling which occurs in the case of water is too slow to mask the Fickian sorption. It should not be thought that in other glassy polymers water behaves in the same manner. In cellulose itself, for instance¹¹, diffusion kinetics more closely resemble those of acetone in nitrocellulose.

CONCLUSIONS

The sorption kinetics of isopropyl nitrate, acetone and water into nitrocellulose show marked differences from each other. The movement of water is essentially Fickian. That of acetone on all cycles and isopropyl nitrate on the first cycle is characterized by a boundary between swollen and unswollen material moving at constant velocity into the film (Case II swelling). Sorption of isopropyl nitrate on all but the first cycle is characterized by uniform concentration at all times throughout the film (Case III swelling). The mechanism operating will depend on the relative values of the Fickian diffusion coefficient and the velocity of boundary movement, which is itself controlled by the rate of relaxation of the polymer matrix. With acetone, the rate of swelling is rapid, and there is no appreciable Fickian diffusion in front of the boundary. With isopropyl nitrate, although the rate of swelling is much lower, Fickian diffusion is effectively zero on the first cycle. However, residual material left behind after desorption greatly increases the diffusion coefficient, and on the second and subsequent cycles diffusion is rapid and ensures uniformity of concentration throughout the slowly swelling film. Swelling is, however, sufficiently rapid for the Fickian diffusion to be masked under most conditions. Water is really an extreme example of a Case III swelling mechanism. Here the swelling is so slow that the purely Fickian sorption may be easily observed.

In all cases studied, desorption is more rapid than sorption and does not always follow the same rate law. It is particularly fast in the case of isopropyl nitrate, and is independent of film thickness. Desorption of acetone and water follow basically Fickian laws. In the case of water the diffusion coefficient for desorption is only marginally greater than that for sorption.

Differences between the equilibrium concentrations of these three plasticizers in nitrocellulose fibres and films are related to the degree of crystallinity of the nitrocellulose lattice, and whether the plasticizer does or does not pene-

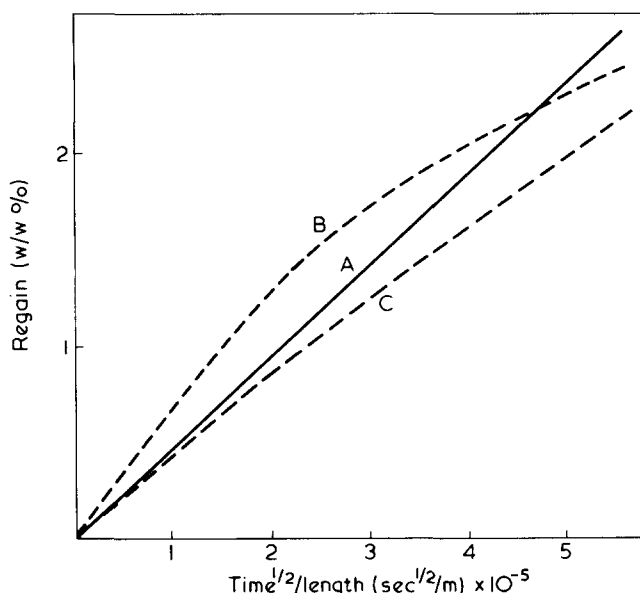


Figure 7 Sorption of water into films of different thicknesses. A, thick film (0.050 mm); B, medium film (0.020 mm); C, thin film (0.013 mm). $T = 25^\circ\text{C}$

trate into the crystalline regions. Acetone, which reaches all parts of the polymer, both crystalline and amorphous, has the same equilibrium sorption in both fibres and films. Isopropyl nitrate, on the other hand, does not penetrate into the more crystalline parts of the nitrocellulose lattice. Consequently, equilibrium sorption is less in fibres than in films, and less in thicker, more crystalline films than in thin amorphous ones.

Desorption of isopropyl nitrate and acetone is never complete, and leads to the concept of 'permanent sorption'. Evidence is presented to show that this is not due to the trapping of plasticizer by an impervious surface skin of depleted material but to a more general entrapment of material throughout the contracting lattice.

ACKNOWLEDGEMENTS

Thanks are due to Mr J. D. Cosgrove for valuable discussion and to Mr R. Spencer for carrying out the experimental work.

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