Modelling of nitroglycerine and water migration behaviour through unsaturated chloropolyesters

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The kinetics of migration of nitroglycerine (NG) and water through unsaturated chloropolyesters and their blends has been reported. The matter sorbed at infinite time (M_∞) is found to be related to the flexibility of the material, and if flexibility increases, M_∞ also increases in the case of NG as well as water. Similarly, diffusivity (D) also increases with flexibility in the case of water. In contrast, D has no specific trend in the case of NG. A comparison of concentration profiles shows that equilibrium is achieved faster in NG compared to water.

(Keywords: modelling; nitroglycerine; migration; unsaturated chloropolyesters; kinetics)

INTRODUCTION

The kinetics of nitroglycerine (NG) and water (H_2O) migration through semi-rigid unsaturated polyesters (SRUPs) has recently been reported by us[1], and it is observed that the matter transferred at equilibrium (M_∞) is achieved after 8–10 days in the case of water. In contrast, it is difficult to achieve M_∞ in the case of NG, which is a highly corrosive and polar liquid[2]. It has been reported by Agrawal *et al.*[3–5] that chloropolyesters possess low NG absorption, which is one of the most favourable factors to make them potential candidates for bulk production of inhibited double-base propellants. The low NG absorption of chloropolyesters may be illustrated on the basis of structures of a model unsaturated polyester, chloropolyester and nitroglycerine. The structures are given in *Figure 1*.

It is clear from *Figure 1* that an unsaturated polyester has a number of electron donor sites whereas NG has a number of electron acceptor sites. An electrostatic force of attraction operates between the two, leading to migration of NG from propellant to unsaturated polyester which is used as inhibitor. If electron acceptor groups such as chloro/bromo are introduced into the aromatic acid, the structure of chloro/bromopolyester will become as shown in *Figure 1* and the electrostatic force of attraction between NG present in propellant and chloro/bromopolyester is reduced, resulting in a considerable reduction of migration/absorption of NG from propellant to chloro/bromopolyester (inhibitor). Also, it improves the chemical resistance of the resulting chloro/bromopolyesters. It is in this context that the chloropolyesters based on tetrachlorophthalic anhydride (TCPAn), maleic anhydride (MAn) and one of two glycols, and blends of these two chloropolyesters, have been selected for this study. The object of the present paper is to report the kinetics of NG and water migration through these materials and propose a model for the prediction of concentration profiles developed through the sheet, which will enable us to gain further insight into NG and water migration.

THEORETICAL

The following assumptions have been made in order to

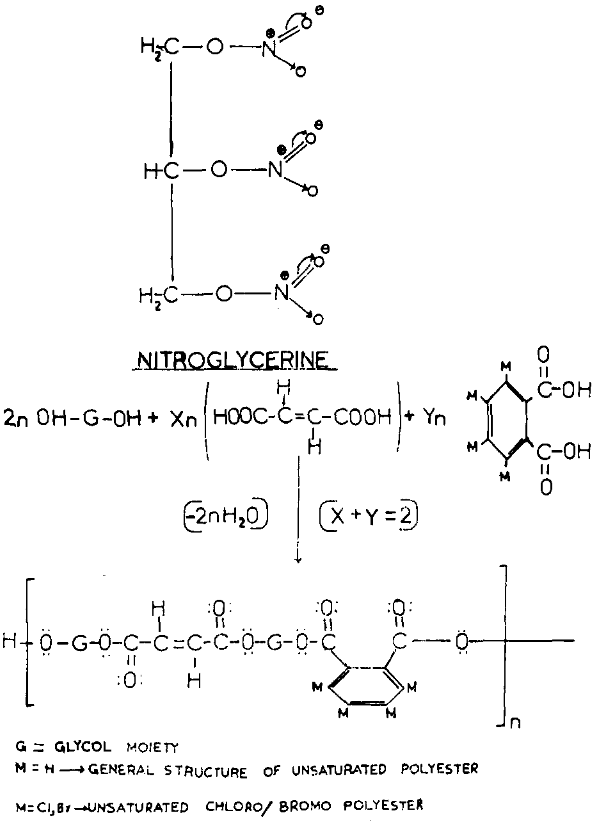

Figure 1 Structures of nitroglycerine, unsaturated polyester and chloro/bromopolyester

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treat mathematically the diffusion process of migration of NG and H_2O through a thin sheet.

(i) Diffusion through a thin sheet of chloropolyester is considered unidirectional.

(ii) NG and H_2O migration takes place under transient conditions with a constant diffusivity (D).

(iii) The concentration of NG/H_2O on the face of a plane thin sheet reaches equilibrium as soon as it is immersed in NG/H_2O.

MATHEMATICAL TREATMENT

The equation for unidirectional diffusion as advanced by Fick through his second law[6,7] is:

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

With initial and boundary conditions such as

$$t=0, \qquad 0<x<L, \qquad C=0 \tag{2}$$

$$t>0, \qquad x=0, x=L, \qquad C=C_\infty \tag{3}$$

the analytical solution of equation (1) for concentration of liquid developed through the sheet of chloropolyester at time t and distance x is given by:

$$\frac{C_{(t,x)}}{C_\infty} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)} \times \exp\left(-\frac{D(2n+1)^2\pi^2}{L^2}t\right)\sin\left(\frac{(2n+1)\pi x}{L}\right) \tag{4}$$

where $C_{(t,x)}$ and C_∞ are the concentrations of matter sorbed at time t and distance x and at equilibrium respectively, D is the diffusivity and L is the thickness of the sheet.

From equation (4) the amount of matter sorbed by the sheet is given by:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{D(2n+1)^2\pi^2}{L^2}t\right) \tag{5}$$

where M_t is mass sorbed at time t and M_∞ is mass sorbed at infinite time.

The equation used for calculation of D is:

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{0.5} \tag{6}$$

and this is of special interest for mass taken up at short times.

EXPERIMENTAL

Materials

The materials required for the work, tetrachlorophthalic anhydride (m.p. 255–258°C and chlorine content 48.5%), propylene glycol (BDH, L.R.), poly(ethylene glycol) (mol. wt 200, BDH, L.R.), maleic anhydride (technical, m.p. 51±2°C and purity 98.5% min.) and styrene monomer (b.p. 145±2°C and specific gravity 0.9055 at 25°C), were procured from trade sources and used as such without further purification.

Nitroglycerine solution, composition as given in our earlier communication[1], and double-distilled water were used for NG and water absorption studies.

Preparation of chloropolyesters and their blends

Polyesterification was carried out in an electrically heated four-necked flask fitted with stirrer, thermometer and inert-gas inlet leading to the bottom of the reaction mixture, and an upright water-cooled condenser. Propylene glycol (1.5 mol) and TCPAn (0.5 mol) were charged into the flask and the temperature was raised to 160°C. After 4 h condensation, the condenser was replaced by a Dean and Starks' tube and the water produced was removed till the acid value (defined as milligrams of KOH required for neutralization of 1 g resin) came to 50. The reaction mixture was cooled and 0.5 mol of maleic anhydride was added and it was refluxed for 2 h. The temperature was then raised and water produced by the reaction was distilled off till an acid value of 50 was achieved. The chloropolyester was cooled, a vacuum applied and then 0.02% of hydroquinone (based on the weight of resin) was added. The finished chloropolyester was partially cooled, mixed with 25% styrene and cooled to room temperature. This chloropolyester was designated as CP-1.

CP-2 based on poly(ethylene glycol) of mol. wt 200 (PEG-200, 1.2 mol), TCPAn (0.5 mol) and MAn (0.5 mol) was also made by a similar two-step process. The acid values before and after adding MAn were 50 and 50 respectively.

Blends of CP-1 and CP-2 in different proportions were prepared by mixing CP-1 and CP-2 and designated as CPB-2 (CP-1:CP-2::20:80), CPB-4, CPB-6 and CPB-8. They were allowed to achieve equilibrium before determining their characteristics. The details are given in *Table 1*.

Preparation of specimens and determination of NG and water absorption and mechanical properties

The specimens for water and NG absorption migration studies were prepared as reported in our earlier

Table 1 Composition of chloropolyesters and their blends (CPBs)

	Molar ratios of ingredients				Acid values		Composition of blends	
Designation	Poly(ethylene glycol) mol. wt 200 (PEG-200)	Propylene glycol (PG)	Tetrachloro-phthalic anhydride (TCPAn)	Maleic anhydride (MAn)	Before addition of MAn	After addition of MAn	CP-2	CP-1
CP-2	1.2	0.0	0.5	0.5	50	50	–	–
CPB-2	–	–	–	–	–	–	80	20
CPB-4	–	–	–	–	–	–	60	40
CPB-6	–	–	–	–	–	–	40	60
CPB-8	–	–	–	–	–	–	20	80
CP-1	0.0	1.5	0.5	0.5	50	50	–	–

communication[1]. The mechanical properties (tensile strength and elongation) were measured by following the ASTM method[8].

Derivation of kinetics and concentration profiles of NG/H_2O developed through chloropolyester sheet

Straight lines are obtained (*Figures 2* and *3*) when NG/H_2O absorption at different time intervals was plotted against the square root of time. The diffusivities were calculated by using the slopes of these straight lines and the amount of NG/H_2O sorbed at infinite time (M_∞) with the help of equation (6). Further, the mass sorbed at different time intervals was calculated theoretically with the help of equation (5) using D and M_∞, whereas the profiles of concentration of NG/H_2O developed at different times and distances in the sheet was calculated with the help of equation (4).

RESULTS AND DISCUSSION

The mechanical properties are given in *Table 2*. It is seen that tensile strength and elongation are inversely related to each other and that tensile strength decreases from CP-1 to CP-2 through their blends CPB-8, CPB-6, CPB-4 and CPB-2, i.e.

CP-1 > CPB-8 > CPB-6 > CPB-4 > CPB-2 > CP-2

This is a shared general characteristic of polyesters[9,10], chloropolyesters[3] and most other crosslinked polymers[11,12]. CP-1 is based on propylene glycol (PG), which

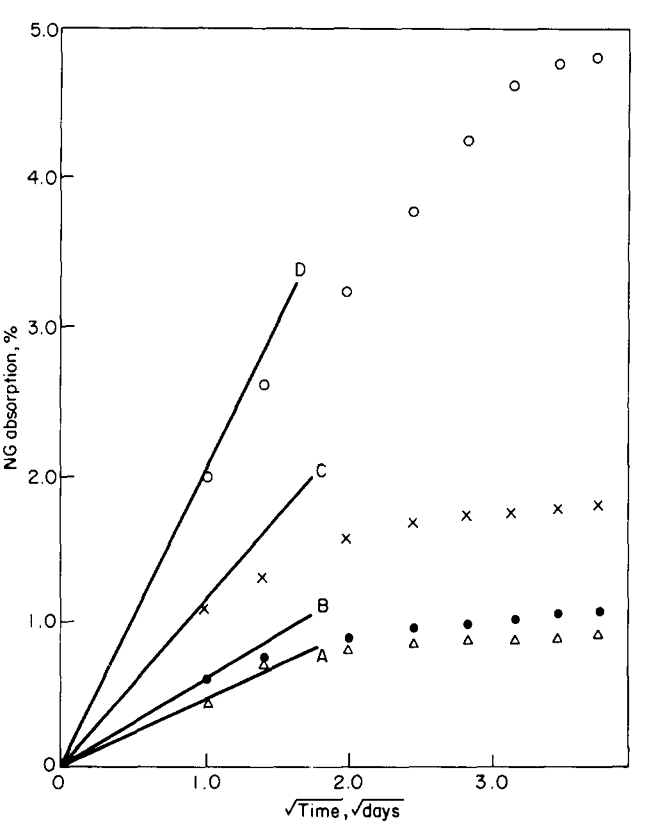

Figure 2 Nitroglycerine (NG) transfer as a function of $(\text{time})^{0.5}$: A, CP-1; B, CPB-8; C, CPB-6; D, CPB-4

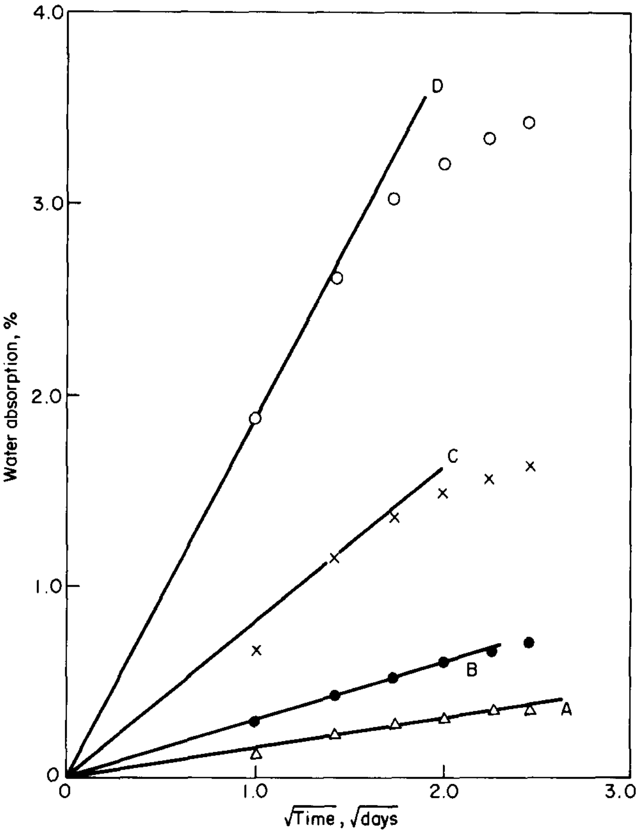

Figure 3 Water (H_2O) transfer as a function of $(\text{time})^{0.5}$: A, CP-1; B, CPB-8; C, CPB-6; D, CPB-4

Table 2 Mechanical properties, mass transferred at equilibrium (M_∞) and diffusivity data for chloropolyesters and their blends (for both nitroglycerine and water absorption)

Designation of chloropolyesters and their blends	Tensile strength (kg cm^{-2})	Elongation (%)	Mass sorbed at equilibrium, M_∞ (%)		Diffusivity, D (10^{-8} cm^2 s^{-1})	
			NG	H_2O	NG	H_2O
CP-1	340.0	1.66	0.88	0.40	6.0	3.0
CPB-8	298.0	3.0	1.08	0.80	3.8	3.5
CPB-6	155.0	11.0	1.78	1.8	5.3	4.0
CPB-4	58.20	19.0	4.85	3.6	3.0	5.7
CPB-2	13.75	23.0	*a*	*b*	*a*	*b*
CP-2	5.40	–	*a*	*b*	*a*	*b*

[a] M_∞ could not be determined experimentally even after 14 days immersion in NG solution. Specimens shattered into small pieces because of poor mechanical strength and excessive NG absorption

[b] M_∞ could not be determined experimentally even after 6 days immersion in water. Specimens shattered into small pieces because of poor mechanical strength and excessive water absorption

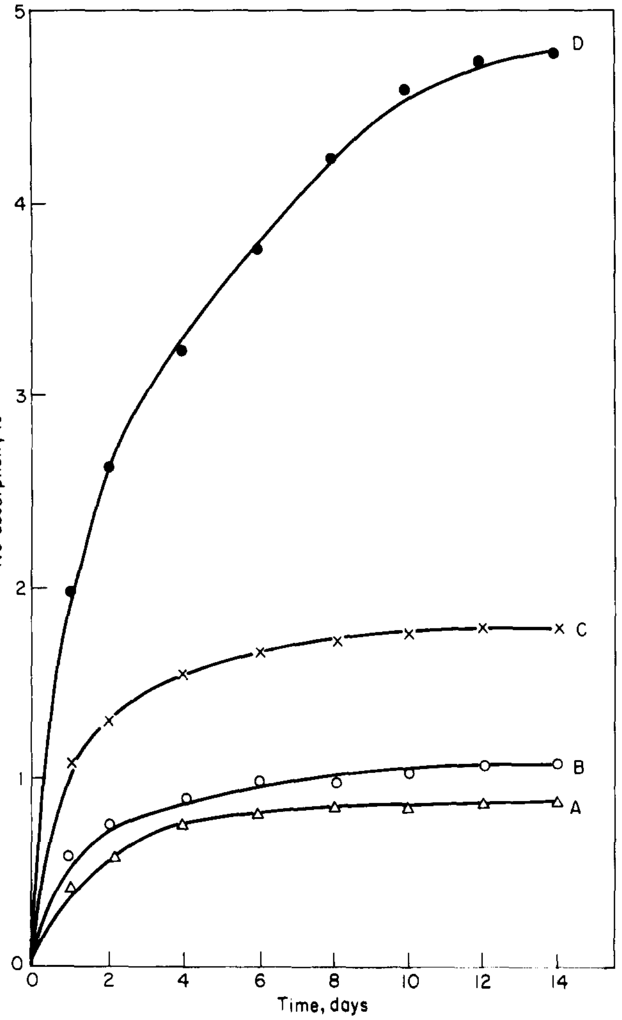

Figure 4 Kinetics of NG transfer: A, CP-1; B, CPB-8; C, CPB-6; D, CPB-4. Experimental results (△, ○, ×, ●) and calculated values (——)

is a short-chain glycol, whereas CP-2 is based on poly(ethylene glycol) of mol. wt 200 (PEG-200), a long-chain glycol. This means that CP-1 consists of short chloropolyester chains and CP-2 of long chloropolyester chains and, therefore, a specified weight of CP-1 contains more chloropolyester chains than CP-2 in order to maintain the same molecular weight[9] (the number-average mol. wt $\bar{M}_n$ is of the same order in the case of CP-1 as well as CP-2 as the acid value is practically the same). Also the number of chloropolyester chains depends on the proportions of CP-1 and CP-2 in their blends. As the proportion of CP-1 decreases from CPB-8 to CPB-2, it is expected that the number of chloropolyester chains also decreases. As various chloropolyester chains are linked to one another through the conversion of –C=C– to –C–C– bonds with the help of styrene monomer, resulting in a three-dimensional network, the tensile strength decreases, which is observed experimentally. In other words, crosslinking density decreases in this order. Once crosslinking density decreases from CP-1 to CPB-2, the mass sorbed at equilibrium (M_∞) will increase in this series. In the case of CPB-2 and CP-2, it is difficult to achieve M_∞ as they are very flexible and, owing to excess absorption of liquid, shattering of specimens into small pieces is observed. However, there is no specific trend in diffusivity, as seen from *Table 2*. The pattern of M_∞ data in the case of water absorption is similar to NG but diffusivity also increases regularly from CP-1 to CPB-4 (*Table 2*), contrary to the diffusivity pattern in NG absorption. The diffusivity data of CP-1 also show that the rate of matter transfer is double in the case of NG.

The experimental and theoretical variation of NG and H_2O using D and M_∞ are plotted in *Figures 4* and *5* respectively. The calculated values are about the same as the experimental ones at different time intervals and both curves show a close agreement between them.

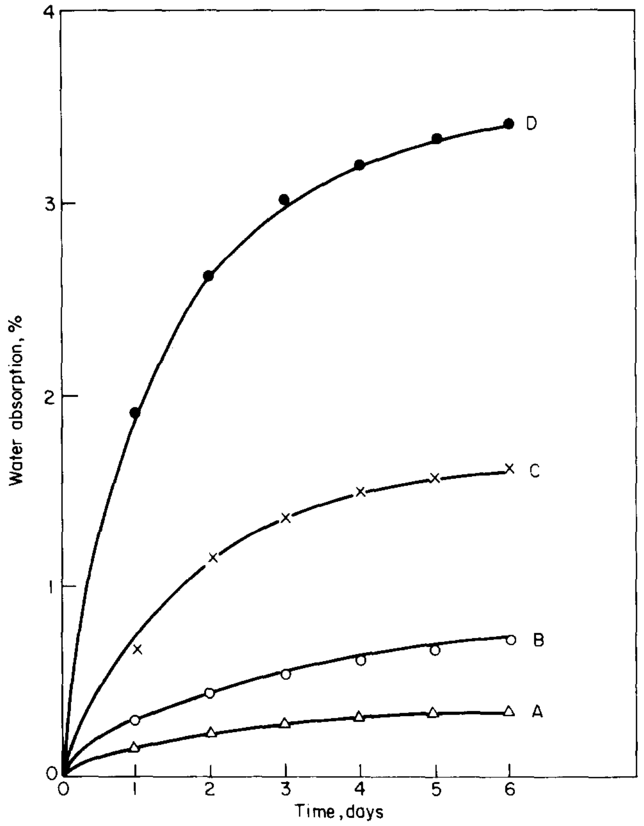

Figure 5 Kinetics of H_2O transfer: A, CP-1; B, CPB-8; C, CPB-6; D, CPB-4. Experimental results (△, ○, ×, ●) and calculated values (——)

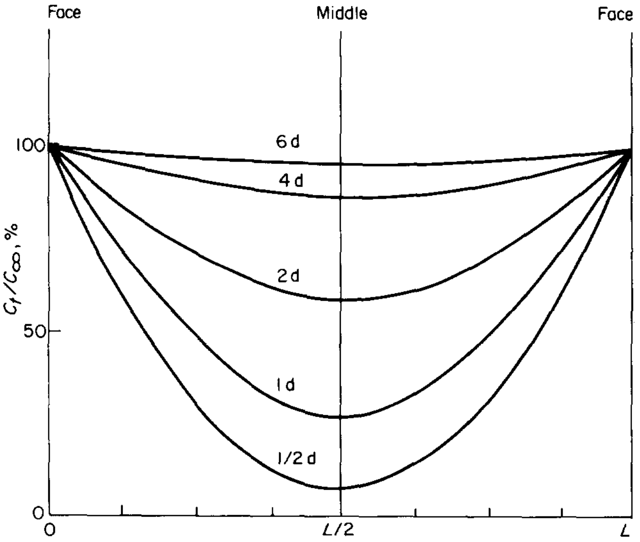

Figure 6 Profiles of NG concentration developed through a sheet of rigid chloropolyester (CP-1) as a function of time (days, d)

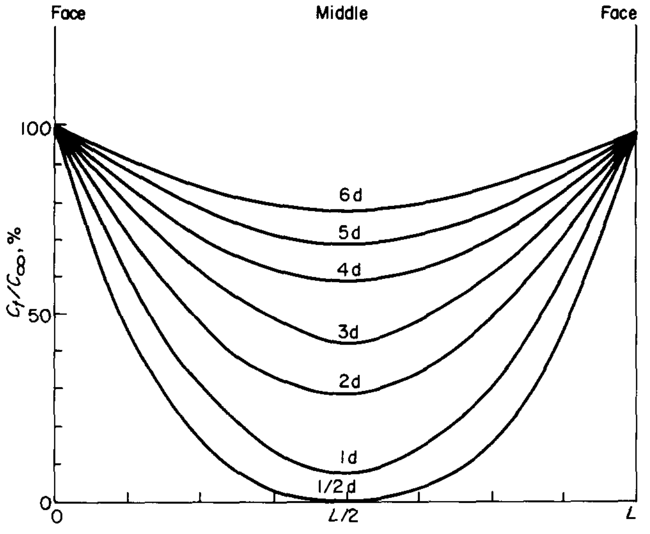

Figure 7 Profiles of H_2O concentration developed through a sheet of rigid chloropolyester (CP-1) as a function of time (days, d)

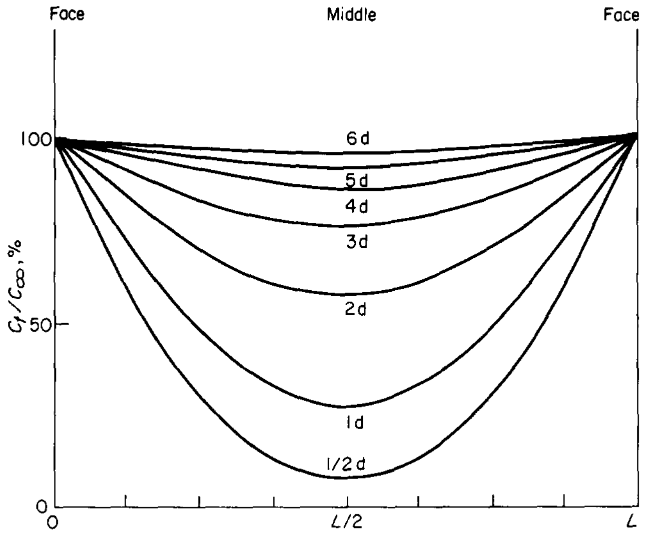

Figure 8 Profiles of H_2O concentration developed through a sheet of flexible chloropolyester blend (CPB-4) as a function of time (days, d)

Profiles of concentration of NG and water

The calculated profiles of concentration of NG and H_2O in the sheets at different times and distances from the centre are shown in *Figures 6–8*. The profiles show that there is a regular increase in concentration as the time increases and also as the distance from the centre to the face increases, i.e. the concentration at the faces of the sheet is 100% and decreases steadily from the face to the centre of the sheet in NG and water absorption as well. Further, a comparison of NG and H_2O profiles brings to light a new fact that the equilibrium for NG in the sheet is achieved much faster compared to that of water (*Figures 6* and *7*). The concentration of NG at the centre of the sheet, i.e. $L/2$ (L = thickness of the sheet), in the case of CP-1 is 96% whereas it is only 77% for water after immersion for 6 days. A comparison of water concentration profiles of CP-1 (rigid chloropolyester, *Figure 7*) and CPB-4 (flexible chloropolyester blend, *Figure 8*) shows that the concentration of water in the former is only 77% as against 95% in the latter. This indicates the vital role played by the molecular rigidity of material on the development of concentration profiles in the sheet.

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