



**A Model for non-linear creep and physical ageing in PVC**

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## ABSTRACT

The creep behaviour of polymers depends on the physical age of the material at the time of stress application. Creep curves shift to longer times for more highly aged material and, in PVC, this can be modelled by an empirical equation in which the magnitude of an effective mean retardation time parameter is dependent upon, and increases with, the age of the polymer. Creep compliances for PVC also depend on the magnitude of the applied stress when this exceeds about 4 MPa. This non-linear behaviour is caused, at short creep times, by a reduction in the value for the retardation time parameter on application of the creep stress. Specimens appear therefore to be initially de-aged by elevated stresses. Subsequently, this parameter increases with creep time implying that physical ageing has been reactivated, but the rate of increase also depends on the stress level. These influences of elevated stresses can be described by an extension of the creep model, and parametric expressions have been derived which relate creep compliance values to time, stress and the age of the polymer. It is shown how the parameters can be determined from a short series of creep experiments and thus how creep deformations can be calculated over wide ranges of time, stress and age.

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## 1 INTRODUCTION

The creep behaviour of polymers is dependent upon a number of factors which include the temperature and the magnitude of the applied stress. The creep behaviour is also strongly influenced by the physical age of the material<sup>1-3</sup>. Physical ageing takes place when the polymer is cooled from an elevated temperature where the molecular mobility is high to a lower temperature where relaxation times for molecular motions are long in comparison with the storage time at that temperature. Under these circumstances, changes in the structure will take place over a long period of time involving rearrangements in the shape and packing of molecules as the polymer approaches the equilibrium structural state for the lower temperature. Associated with this ageing process, there is a progressive decrease in the molecular mobility of the polymer even if the temperature remains constant. As a direct consequence of this, the creep deformation produced by an applied stress will depend upon the age of the polymer, creep rates being lower in the more highly aged material.

At low values of stress, the time-varying creep strain  $\epsilon(t)$  is linearly related to the stress  $\sigma$ . The creep compliance function  $D(t)$ , defined by

$$D(t) = \frac{\epsilon(t)}{\sigma} \quad (1)$$

is then independent of the magnitude of  $\sigma$ . At higher values of stress, the linearity implied by equation (1) is no longer valid and  $D(t)$  becomes stress-dependent. There is evidence<sup>1,4-7</sup> that this onset of non-linear behaviour is caused by an increase in molecular mobility, analogous to a reduction in the state of physical ageing, brought about by the application of the elevated stress. Subsequently, a progressive reduction in mobility occurs, analogous to a reactivation of physical ageing, at a rate that is dependent upon the stress level. The mechanisms whereby elevated stresses induce non-linearity in the creep behaviour are apparent in both the short-term and long-term regions of a creep experiment.

The short-term region is defined as the period after load application during which changes in molecular mobility brought about by further physical ageing are negligible. This implies therefore that the age of the specimen does not change significantly in this period and its duration thus depends on the age of the polymer on load application. In this period, the creep compliance for amorphous polymers can be modelled by the empirical relationship

$$D(t) = D_0 \exp \left( \frac{t}{t_0} \right)^\gamma \quad (2)$$

$D_0$  is the compliance in the limit of short creep times and  $t_0$  is effectively the mean retardation time for the creep mechanism whose distribution of retardation times is characterised by the parameter  $\gamma$ .

An analysis of the short-term region of creep tests on specimens of PVC of different physical age (see figure 1) reveal that  $t_0$  is the main parameter that is influenced by physical ageing and is larger the older the specimen. When specimens of the same age are loaded to different stress levels,  $t_0$  is observed to decrease rapidly on application of stresses above the limit for linear behaviour, the decrease being greater the higher the stress. It is this decrease in  $t_0$ , occurring on application of elevated stresses, that is responsible for the early dependence of  $D(t)$  upon stress (see figure 2) and the onset of non-linear creep behaviour.

Equation (2) is only valid for creep times that are sufficiently short that changes in  $t_0$  are negligible (the short-term region). As the specimen continues to age during the creep loading,  $t_0$  will progressively increase, and, in this long-term region of creep time, the creep curve will depart from equation (2). An analysis of long-term creep experiments indicates that the rate at which the polymer ages, and hence the rate of increase of  $t_0$  with creep time, also depends on the magnitude of the stress. This introduces an additional dependence of  $D(t)$  upon stress.

In this paper, an expression for the creep compliance function is derived for an amorphous polymer PVC in terms of parameters which depend upon the applied stress and the age of the polymer. Relationships for the stress and age dependence of these parameters are investigated with the aim of establishing procedures whereby creep compliances can be derived by calculation over wide ranges of time, stress and age. In section 3, the analysis of selected short-term creep tests is described to determine the stress- and age-dependencies of the parameters in equation (2). In section 4, expressions are explored for describing the increase of  $t_0$  with creep time (apparent reactivation of physical ageing) subsequent to the short-term response. Calculated creep compliances are compared in section 5 with experimental data obtained in tension and compression. Differences in creep behaviour under tensile and compressive stresses are traced to different magnitudes of two of the parameters in the model. In section 6, the scope for using the model to calculate creep compliances from an analysis of a limited quantity of experimental creep data is discussed.

## 2 EXPERIMENTAL

Creep test specimens were cut from an extruded sheet of PVC manufactured by ICI plc under the trade name of Darvic. The sheet thickness was 10 mm. Specimens for tensile creep measurements were approximately 200 mm x 10 mm x 4 mm and for compressive creep measurements were approximately 90 mm x 10 mm x 8 mm.

Prior to each creep test, specimens were heated to 85 °C for 30 minutes and quenched in water at 23 °C to erase previous physical ageing. They were then stored at 23 °C for periods of elapsed time  $t_e$  prior to the start of a creep experiment. The elapsed time then serves to characterise the state of physical ageing of the specimen.

## 3 THE INFLUENCE OF STRESS AND AGEING ON SHORT-TERM CREEP

Figure 1 shows the short-term regions of a series of creep curves obtained at a stress level at which the behaviour is just outside the linear range on specimens having different states of physical ageing defined by the elapsed time  $t_e$  between quenching and load application (see section 2). The duration of each test is significantly less than the age  $t_e$  of the specimen so its age is effectively constant during this period of the test. As indicated in section 1, this part of a creep curve for amorphous polymers can be described by equation (2). The shift in the curves to longer creep times with increasing age can be modelled predominantly by assigning values of  $t_0$  that increase with age  $t_e$ , although this is accompanied by a small decrease in  $D_0$  with increasing age. No dependence of  $\gamma$  upon the state of physical ageing is evident from the data in figure 1.

At higher stresses, short-term creep curves generated on specimens of the same age shift to shorter times as shown in figure 2. The non-linear response appears to be associated with a reduction in the magnitude of the parameter  $t_0$  (a physical de-ageing) brought about by the application of elevated stresses. In previous work on a different grade of PVC, it was shown that equation (2) is also capable of describing short-term creep at these elevated stresses but, in addition to  $t_0$ , the parameters  $D_0$  and  $\gamma$  also appeared to depend on the stress<sup>6,7</sup>. In this earlier work, values for  $D_0$  for each stress were obtained from an extrapolation of compliance data obtained between 10 s and 100 s of creep time to zero time. Whilst these values are appropriate for describing creep up to 100 s, an alternative analysis used in this paper gives values for  $D_0$  and  $\gamma$  that are more valid for modelling the short-term creep at longer times.

In this alternative analysis, the following relationship is used, derived from equation (2).

$$\frac{d \ln D(t)}{d \ln t} = \gamma \ln D(t) - \gamma \ln D_0 \quad (3)$$

A plot of the gradient of a short-term creep curve on double logarithmic axes against  $\ln D(t)$  should therefore be linear with gradient  $\gamma$ . The creep curve gradients were determined as a function of  $D(t)$  by fitting a polynomial to experimental data for  $\ln D(t)$  against  $\ln t$  and generating the derivatives from a knowledge of the coefficients of the polynomial. Values for  $\gamma$  cannot be obtained this way with high confidence but they showed no systematic variation with either age state or stress and fell in the range 0.30 to 0.34. A constant value for  $\gamma$  of 0.32 has therefore been assumed. The plots given by equation (3) were reanalysed using a constant gradient of 0.32, and values for  $D_0$  were obtained from the intercepts at  $\ln D(t) = 0$ .

Once  $D_0$  and  $\gamma$  are known, a value for  $t_0$  for each test can be derived using equation (4) which follows from equation (2).

$$\left( \ln \frac{D(t)}{D_0} \right)^{\frac{1}{\gamma}} = \frac{t}{t_0} \quad (4)$$

A plot of  $\left( \ln \frac{D(t)}{D_0} \right)^{\frac{1}{\gamma}}$  against  $t$  is therefore linear in the short-term region of a creep test

(where  $t_0$  is effectively constant) and has a gradient of  $1/t_0$ . Examples of these plots are shown in figure 3 for a number of elapsed times at a single stress of 24 MPa. The times at which data depart from the initial linear region are indicated by arrows and mark the onset of long-term creep where  $t_0$  increases with time through a continuation of physical ageing whilst under stress.

Values for  $t_0$  and  $D_0$  are listed in table 1 over ranges of stress and age state for a constant value of  $\gamma = 0.32$ . It is apparent that  $D_0$  decreases slightly with increasing age of the polymer and possibly increases marginally with increasing stress. Changes in  $t_0$  are however more substantial. Values increase with increasing age but are decreased by the application of elevated stresses.



**Table 1** Values for the parameters  $D_0$  and  $t_0$  in equation (2) and  $\delta$  in equation (12) at different stresses and ages defined by the elapsed times  $t_e$  after quenching.  $\gamma$  is constant and equal to 0.32.

Stress (MPa)	$t_e$ (h)	$D_0(\text{GPa})^{-1}$	$t_0$ ( $10^5\text{s}$ )	$\delta$ ( $10^5\text{s}$ )
6	3	0.323	3.2	
	7	0.323	7.0	2.4
	24	0.321	20	
	72	0.319	55	
	240	0.316	135	
12	7	0.323	2.9	1.6
	24	0.321	9.6	
	240	0.318	60	
18	7	0.326	1.5	1.0
	24	0.323	3.9	2.5
	240	0.320	18	
	620	0.318	40	
24	7	0.330	0.48	0.3
	24	0.326	1.1	0.6
	240	0.320	6.5	
	620	0.320	14	

In previous work<sup>6</sup>, it has been shown that the variation of  $t_0$  with elapsed time  $t_e$  at low stresses, where the short-term creep behaviour is linear, can be represented by the relationship

$$t_0 = A t_e^\mu \quad (5)$$

Figure 4 shows plots of  $\log t_0$  against  $\log t_e$  at four stress levels. It is apparent that equation (5) is satisfactory at the lowest stress of 6 MPa where the gradient  $\mu = 0.86$ . At the higher stresses, the use of equation (5) with a constant value for  $\mu$  appears adequate although there is some indication that possibly  $\mu$  depends on stress (as observed by previous investigators<sup>1,8,9</sup>) or the relationship between  $\log t_0$  and  $\log t_e$  is curved in the region below  $\log t_0 \sim 5.5$ . Further short-term creep tests at elevated stresses are needed to resolve these possibilities but, for the remainder of this paper, equation (5) is assumed to hold for a

constant value of  $\mu = 0.86$  with A being stress-dependent. Values for A derived from figure 4 are recorded in table 2.

Table 2 Values for the parameters A in equation (5) and C in equation (8) for tensile and compressive creep in PVC.

Stress (MPa)	Tension		Compression	
	A ( $s^{1-\mu}$ )	C ( $s^{1-\mu}$ )	A ( $s^{1-\mu}$ )	C ( $s^{1-\mu}$ )
6	105	80	110	70
12	50	51	96	65
18	17	35	55	57
24	5.5	22	28	46

#### 4 INFLUENCE OF STRESS AND AGEING ON LONG-TERM CREEP

The analysis of creep data described in the previous section shows that in the early stages of creep, creep compliances can be described by equation (2) using a value for the retardation time parameter  $t_0$  which depends on the applied stress and the age of the material on load application. This parameter increases with the physical age of the specimen implying that, as the polymer ages during long-term creep loading, the compliance function must depart from equation (2) in order to take account of the increase in  $t_0$  with creep time. If the time-dependence of the retardation time is  $t_0(t)$ , then the long-term creep function  $D(t)$  is given from equation (2) by

$$D(t) = D_0 \exp \left( \int_0^t \frac{du}{t_0(u)} \right)^\gamma \quad (6)$$

From this equation, it follows that the instantaneous value for  $t_0(t)$  at any creep time  $t$  is given by

$$\frac{1}{t_0(t)} = \frac{d}{dt} \left( \ln \frac{D(t)}{D_0} \right)^{\frac{1}{\gamma}} \quad (7)$$

The variation of  $t_0(t)$  with time can thus be derived from experimental creep data by determining the gradients of a plot of  $\left(\ln \frac{D(t)}{D_0}\right)^{\frac{1}{\gamma}}$  against  $t$  as a function of time. Such plots are shown in figure 3 and are used, as described in section 3, to obtain values for  $t_0$  from the gradient of the initial linear region of each plot. The onset of curvature marks the creep time for each plot at which the retardation time parameter begins to increase significantly with creep time and hence the onset of long-term creep.

Values for  $t_0(t)$  were derived in this way from creep tests carried out at different stresses and elapsed times. Figure 5 shows values obtained at a stress of 24 MPa. The initial horizontal regions represent the short-term period in each test where  $t_0(t)$  is effectively constant. Subsequently,  $t_0(t)$  increases through physical ageing, but, with increasing creep time,  $t_0(t)$  values converge as differences in the initial ages of the specimens become progressively less significant.

The data in figure 5 resemble a family of hyperbolae approaching a common asymptote which is curved and concave to the time axis. The general equation for this family takes the form

$$t_0^2(t) = t_0^2 + C^2(t^\lambda)^2 \quad (8)$$

where  $C$  is a constant and the parameter  $\lambda$  accounts for the curvature in the asymptote. Values for  $C$  and  $\lambda$  for each set of data in figure 5 were obtained from plots of  $\log(t_0^2(t) - t_0^2)$  against  $\log t$  and were found to be independent of  $t_0$ . Similar plots for creep data obtained at different stresses support the applicability of equation (8) and indicate that  $C$  is dependent upon stress (see table 2). Values for  $\lambda$  over the stress range from 6 MPa to 24 MPa fell in the range 0.8 to 0.9 but no trend with stress was apparent.

A combination of equations (6) and (8) shows that the dependence of  $C$  upon stress gives rise to another contribution to non-linear behaviour, in this case during long-term creep. It is also apparent that if the retardation time parameter  $t_0(t)$  for creep deformation is considered a measure of the effective age of the polymer, then physical ageing rates under creep loading depend on the stress level.

Substitution of equation (5) into equation (8) gives

$$t_o^2(t) = A^2 t_e^{2\mu} + C^2 t^{2\lambda} \quad (9)$$

Equation (5) implies that, under zero stress,  $t_o(t)$  increases with time (physical ageing) according to the relationship

$$t_o(t) = A (t_e + t)^\mu \quad (10)$$

Comparison with equation (9) implies that as  $\sigma \rightarrow 0$ ,  $C \rightarrow A$  and, since  $\lambda$  is observed to be independent of stress,  $\lambda$  must equal  $\mu = 0.86$ . In the limit of small stresses, equation (9) therefore becomes

$$t_o(t) = A (t_e^{2\mu} + t^{2\mu})^{1/2} \quad (11)$$

This equation is consistent with equation (10) at long creep times but departs significantly at short times. To resolve this, a modification of the hyperbolic relationship of equation (8) is proposed as follows

$$(t_o(t) - \delta)^2 = (t_e - \delta)^2 + C^2 t^{2\mu} \quad (12)$$

This is still a family of hyperbolae but the asymptote intersects the  $t_o(t)$  axis at  $\delta$ , and, if  $\delta$  depends upon  $t_e$ , then each hyperbola in a family will have its own asymptote. When  $\sigma = 0$ , it is proposed that  $\delta = t_e$  and equation (12) is then much closer to equation (10). The magnitudes of  $\delta$  at other stress levels and any dependence upon  $t_e$  has been investigated through comparisons of calculated long-term creep compliances with experimental data described in the next section.

## 5 COMPARISON OF CALCULATED AND MEASURED CREEP CURVES

The compliance function for long-term creep is obtained by substituting equation (9) or equation (12) into equation (6). Considering initially the more simple expression for  $t_o(t)$  represented by equation (9), this gives

$$D(t) = D_o \exp \left( \int_0^t \frac{du}{(A^2 t_e^{2\mu} + C^2 u^{2\mu})^{1/2}} \right) \quad (13)$$

## 5.1 Tensile Creep Behaviour

Compliance curves were calculated by the numerical integration of equation (13) using the values for A and C given in table 2 and constant values for  $D_0 = 0.32 \text{ (GPa)}^{-1}$ ,  $\gamma = 0.32$  and  $\mu = 0.86$ . Curves derived for a stress of 24 MPa are compared with experimental data at different elapsed times in figure 6. The agreement is satisfactory for the longer aged material but there are significant departures of the model from measured compliances at the shorter elapsed times of 7h and 24h. At lower stresses, there are similar, but smaller, departures of calculated and experimental creep curves which are apparent only at the shorter elapsed times. At longer elapsed times, equation (13) is valid for all stress levels.

The applicability of the modified relationship for  $t_0(t)$  given by equation (12) has been explored in an attempt to resolve these discrepancies. Values for the parameter  $\delta$  were obtained from plots of  $t_0(t)$  against  $t^\mu$ . For these plots the asymptote is a straight line of gradient C. In tests carried out at high stress and short elapsed time, the short-term region is complete early in the test and therefore, for much of the test,  $t_0(t)$  values lie close to the asymptote (see for example figure 5). It is therefore possible to obtain estimates for  $\delta$  by a short linear extrapolation of  $t_0(t)$  data back to  $t = 0$ . Values for  $\delta$  are shown in table 1 for those tests where some departure of the model from experimental data was evident. Combining equation (12) with equation (6), new compliance curves were calculated for the 7h and 24h elapsed time tests in figure 6. These are indicated by the broken curves in figure 6 and show satisfactory agreement with experimental data.

The values for  $\delta$  in table 1 appear to increase with decreasing stress and increasing elapsed time. The variation with stress is consistent with the proposal made at the end of section 4 that  $\delta = t_0$  at  $\sigma = 0$ . Despite these trends in the value of  $\delta$ , it appears that the relationship for  $t_0(t)$  given by equation (8) (which neglects  $\delta$ ) is adequate for all tests except for those where  $t_0$  is very small ( $\leq 5 \cdot 10^5 \text{ s}$  in the case of PVC).

## 5.2 Compressive Creep Behaviour

The creep behaviour of PVC under a compressive stress has been investigated over the stress range between 6 MPa and 24 MPa and at two ages of 24h and 240h. The influences of elapsed time and elevated stress on creep rates follow the same trends as those observed with tensile tests. Curves shift to longer times with increasing age of the specimen and to shorter times with increasing applied stress. The shift with stress is however significantly smaller in compression than in tension. Values for the parameter  $\gamma$  could not be determined with an uncertainty of less than  $\pm 0.01$ . No dependence upon stress or age was evident, and

a mean value of  $\gamma = 0.32$  was obtained comparable with the tensile value. Values for the parameters  $D_0$  and  $t_0$  and for the time-dependence of  $t_0(t)$  for each test were derived using the same procedures as those described in sections 3 and 4 for tensile data.

The magnitudes of  $D_0$  were found to decrease slightly with specimen age but were independent of stress and so were essentially the same as the values obtained in tension. The variation of  $t_0$  with specimen age  $t_e$  was assumed to follow equation (5). The limited range of elapsed time covered by the compressive creep measurements has prevented an accurate determination of the magnitude of  $\mu$  so a value of  $\mu = 0.86$  has been assumed, independent of stress and equal to the value in tension. This gave from equation (5) the values for A at each stress shown in table 2. Values for the parameter C are also recorded in table 2 obtained using equation (9) and an analysis of long-term data which assumes that  $\lambda = \mu = 0.86$ .

Experimental compressive creep curves obtained at different stresses on specimens having an age of 24h are compared in figure 7 with calculated compliances derived using equation (13) and the parameters in table 2. A fixed value for  $D_0 = 0.32 \text{ (GPa)}^{-1}$  was used.

## 6 DISCUSSION

In this section, the scope is considered for using the model to calculate the creep behaviour of a polymer over wide ranges of time, stress and age state from an analysis of a limited quantity of creep measurements. The results reported in section 4 show that creep compliances for PVC can be calculated using equation (13) and a knowledge of the magnitude of certain parameters. The parameters  $D_0$ ,  $\gamma$ ,  $\mu$  and A can be obtained from a series of short-term creep tests over a range of elapsed times and at a number of stresses producing both linear and non-linear behaviour. Long-term tests are then required at the same stresses and selected elapsed times to determine C and  $\lambda$  as a function of stress. In the case of PVC,  $D_0$ ,  $\gamma$  and  $\mu = \lambda$  appear to be essentially constant but this may not be true for other polymer types and further analysis may be necessary to reveal any stress dependence of  $\gamma$ ,  $\mu$  or  $\lambda$ .

The number of tests required to achieve adequate accuracy and confidence in derived values for the parameters cannot be specified from the results of the work reported here. Experience has shown that factors such as material variability, the stability and the accuracy in the measurement of temperature and consistency in heat treatments can each influence the reproducibility of measurements.

In order that creep compliances can be calculated at arbitrary values of stress, relationships are needed which express the dependencies of A and C on stress. From table 2 and section 3, it is apparent that A changes very little at low stress levels where the short-term creep behaviour is linear. At higher values of stress, A falls rapidly and is responsible for the observed non-linearity in creep behaviour at short times. The variation of A with stress is shown in figure 8 to be approximately linear when  $\ln A$  is plotted against  $\sigma^2$ . This implies a relationship for A of the form

$$A = A_0 \exp -\alpha \sigma^2 \quad (14)$$

where  $A_0$  is the value for A at zero stress and  $\alpha$  is a constant given by the slope of the line in figure 8. The value for  $\alpha$  is different in tension and compression reflecting differences in non-linear behaviour generated by the two types of loading.

Bearing in mind that  $C \rightarrow A$  as  $\sigma \rightarrow 0$  and  $C = A$  at  $\sigma = 0$ , the values in table 2 indicate that C starts to decrease with stress at lower values of stress than does A. At higher stresses however the decrease is less rapid. The relationship

$$C = A_0 \exp -\beta |\sigma| \quad (15)$$

appears to adequately describe the stress-dependence of C although, as shown in figure 9, the relatively high experimental uncertainty in the determination of C leaves some doubts regarding its validity.  $\beta$  is a constant which takes different values in tension and compression and  $|\sigma|$  signifies the positive value of the magnitude of the stress. Since equation (15) is not continuous at  $\sigma = 0$ , it cannot be valid at very low stresses but associated errors in predicted creep compliances are likely to be small.

Values for  $A_0 = 120 \text{ s}^{(1-\mu)}$ ,  $\alpha = 5.6 \cdot 10^{-3} \text{ (GPa}^{-2}\text{)}$  and  $\beta = 7.0 \cdot 10^{-2} \text{ (GPa}^{-1}\text{)}$  were obtained from linear least-squares fits to the tensile creep data in figures 8 and 9. These can be used in equation (13) with values for the parameters  $D_0 = 0.32 \text{ (GPa}^{-1}\text{)}$ ,  $\gamma = 0.32$  and  $\mu = 0.86$  to calculate creep compliances for PVC at arbitrary values of time, stress and age state. In figure 10, calculated creep curves are compared with experimental data for different stress levels and an elapsed time of 240h. The agreement is generally satisfactory, and the correction which includes the parameter  $\delta$  using equation (12) is evidently unnecessary at this value of elapsed time.

## 7 CONCLUSIONS

The creep behaviour of plastics depends on the physical age of the material through an increase in the creep retardation time with increasing age state. Linear creep behaviour in PVC is confined to stress levels below 4 MPa. At higher stresses, non-linear behaviour is caused at short creep times by a rapid reduction in the retardation time which depends on the magnitude of the stress and is analogous to a stress induced de-ageing. At longer creep times, the retardation time increases again (analogous to a reactivation of physical ageing) at a rate which also depends on the stress magnitude. This gives rise to another contribution to non-linearity in creep behaviour.

Equation (13) is an expression for the creep compliance function of PVC which includes the influences of stress and physical ageing on creep behaviour. The parameters  $D_0$ ,  $\gamma$ , and  $\mu$  in this function are essentially independent of stress and age. The parameter  $A$  can be related to stress through the parameters  $A_0$  and  $\alpha$  in equation (14). These parameters can be determined experimentally from an analysis of short-term creep tests carried out over ranges of stress and elapsed time.

The parameter  $C$  is then obtained from long-term tests at selected stresses and elapsed times. The parameter  $C$  can be related to stress through the parameters  $A_0$  and  $\beta$  in equation (15). Very short elapsed times should be avoided for this purpose. From a knowledge of these parameters, creep curves can be calculated at arbitrary times, stresses and age states. The agreement between calculated and measured compliances for PVC are very good except at short elapsed times under high stress. Under this narrow range of conditions, an additional term must be included in equation (13) to obtain a satisfactory prediction.

It remains to be established whether this model is valid for other polymers such as semicrystalline and fibre reinforced materials.

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## FIGURE CAPTIONS

- Figure 1 Short-term creep curves for PVC at a stress of 6 MPa and at different ages  $t_e$ . The solid lines are given by equation (2) using values for the parameters  $t_0$  and  $D_0$  listed in Table 1 and a constant value for  $\gamma = 0.32$ .
- Figure 2 Short-term creep curves for PVC at a fixed age of 24h and at different stresses  $\sigma$ . The solid lines are given by equation (2) with values for the parameter  $t_0$  and  $D_0$  given in Table 1 using a constant value for  $\gamma = 0.32$ .
- Figure 3 Plots of  $\left( \ln \frac{D(t)}{D_0} \right)^{\frac{1}{\gamma}}$  against creep time for tests at a stress of 24 MPa and different ages  $t_e$ . Values for  $t_0$  are deduced from the gradients of the linear portions. The arrows indicate the limits of short-term creep.
- Figure 4 Plots of  $\log t_0$  against  $\log t_e$  for the short-term regions of creep tests at different stress levels. The gradient gives the parameter  $\mu$  in equation (5) which is assumed to be independent of stress. The parameter  $A$  is derived from an intercept on the  $\log t_0$  axis at  $\log t_e = 0$ .
- Figure 5 Plots of  $t_0(t)$  against  $t$  for creep tests at 24 MPa and different ages  $t_e$  showing reactivation of physical ageing following a period of constant  $t_0$  after application of the creep stress. Solid lines are given by equation (9).
- Figure 6 Comparison of calculated and measured creep curves at 24 MPa and different ages  $t_e$ . Solid lines are derived from equation (13) and the broken lines from the use of the modified expression for  $t_0(t)$  given by equation (12).
- Figure 7 Comparison of calculated and measured creep curves under different compressive stresses and a fixed age of the specimen of 24h. The solid lines are given by equation (13).
- Figure 8 Variation of the parameter  $A$  with stress  $\sigma$ .  $\bullet$  — tensile stresses,  $\circ$  — compressive stresses. The solid line is given by equation (14).

Figure 9 Variation of the parameter  $C$  with stress  $\sigma$ .  $\bullet$  — tensile stresses,  $\circ$  — compressive stresses. The solid line is given by equation (15).

Figure 10 Comparison of calculated and measured creep curves at a fixed age of 240h and at different tensile stresses  $\sigma$ . The solid lines are calculated using equation (13) with the parameters  $A$  and  $C$  derived from equations (14) and (15).

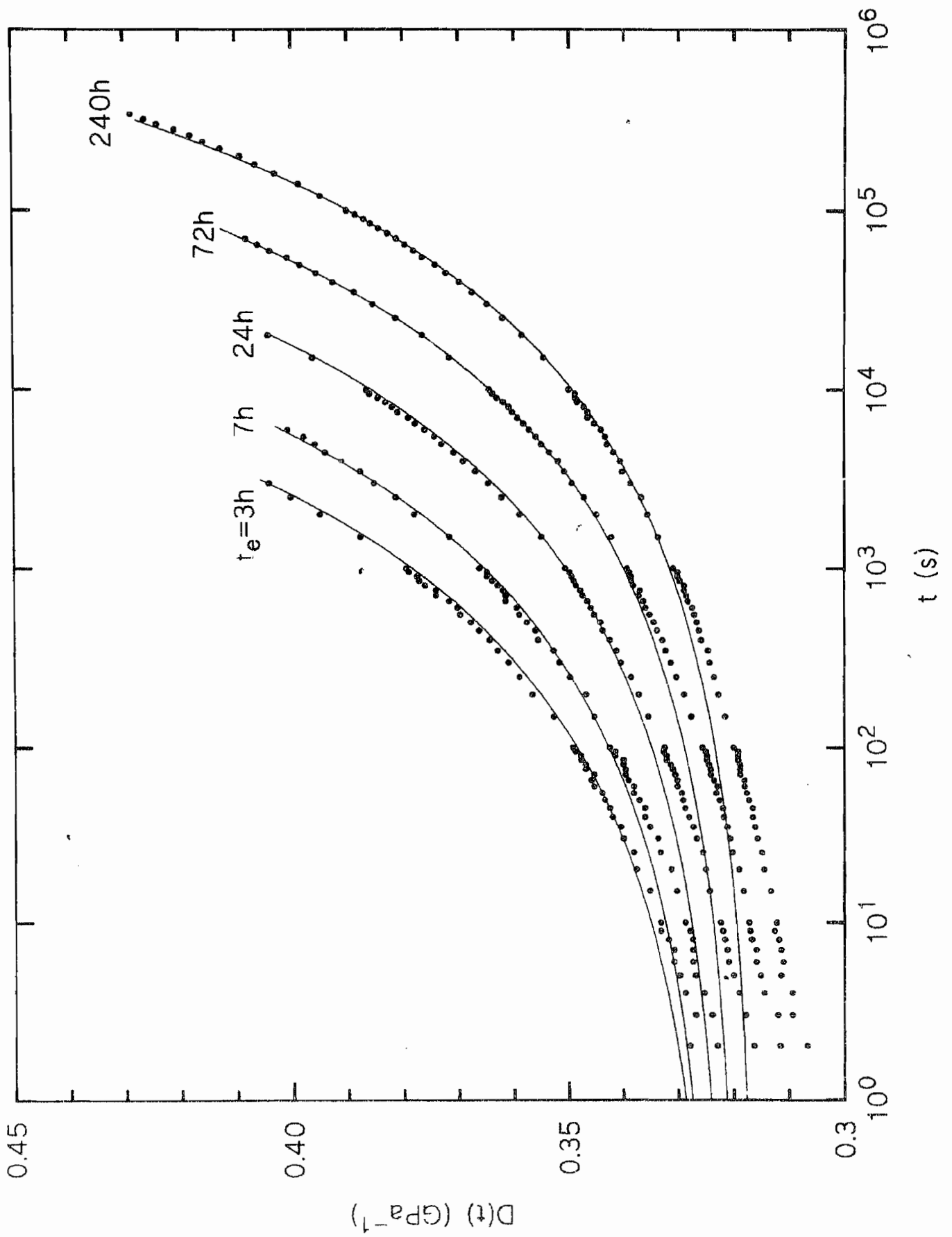


FIG.1

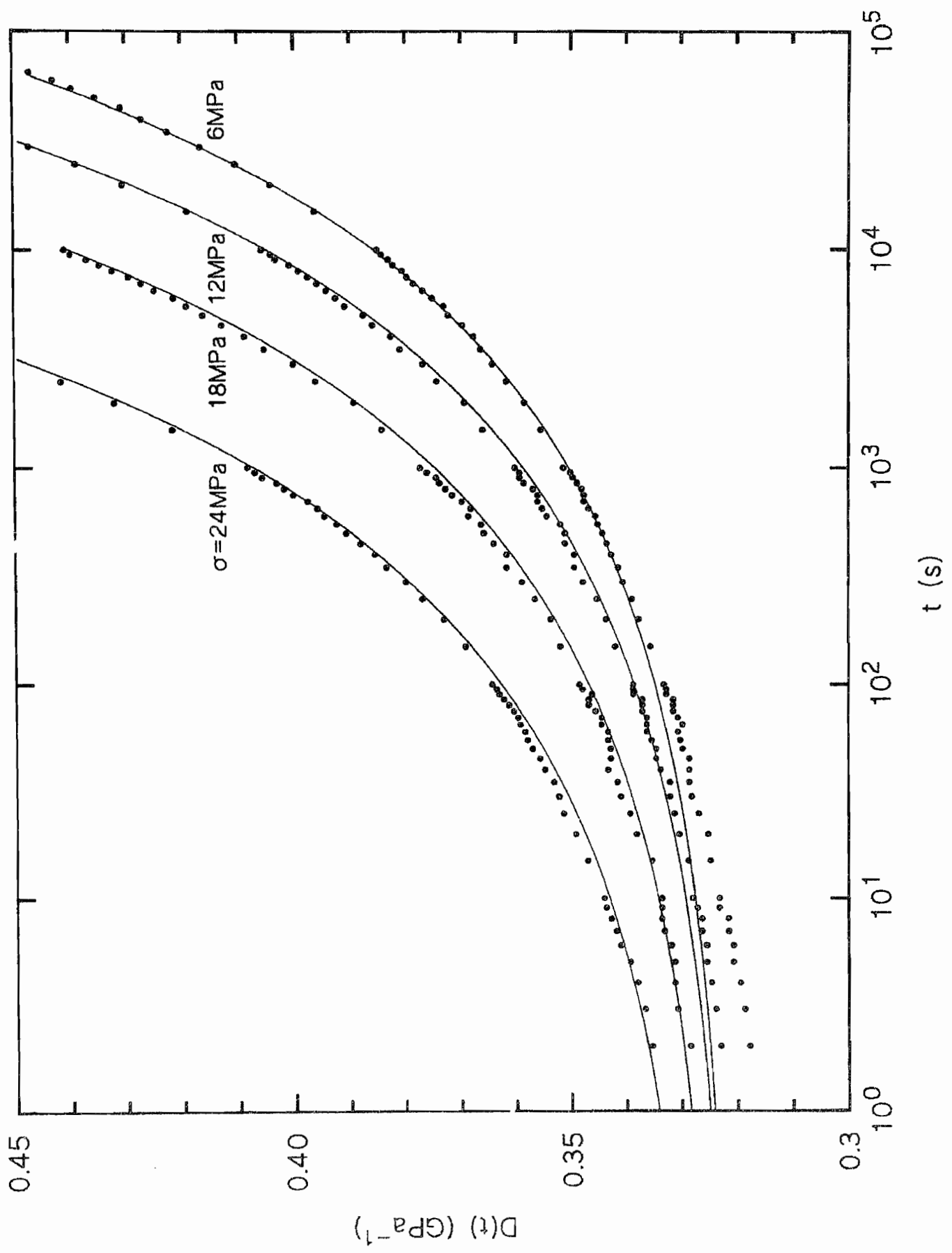


FIG.2

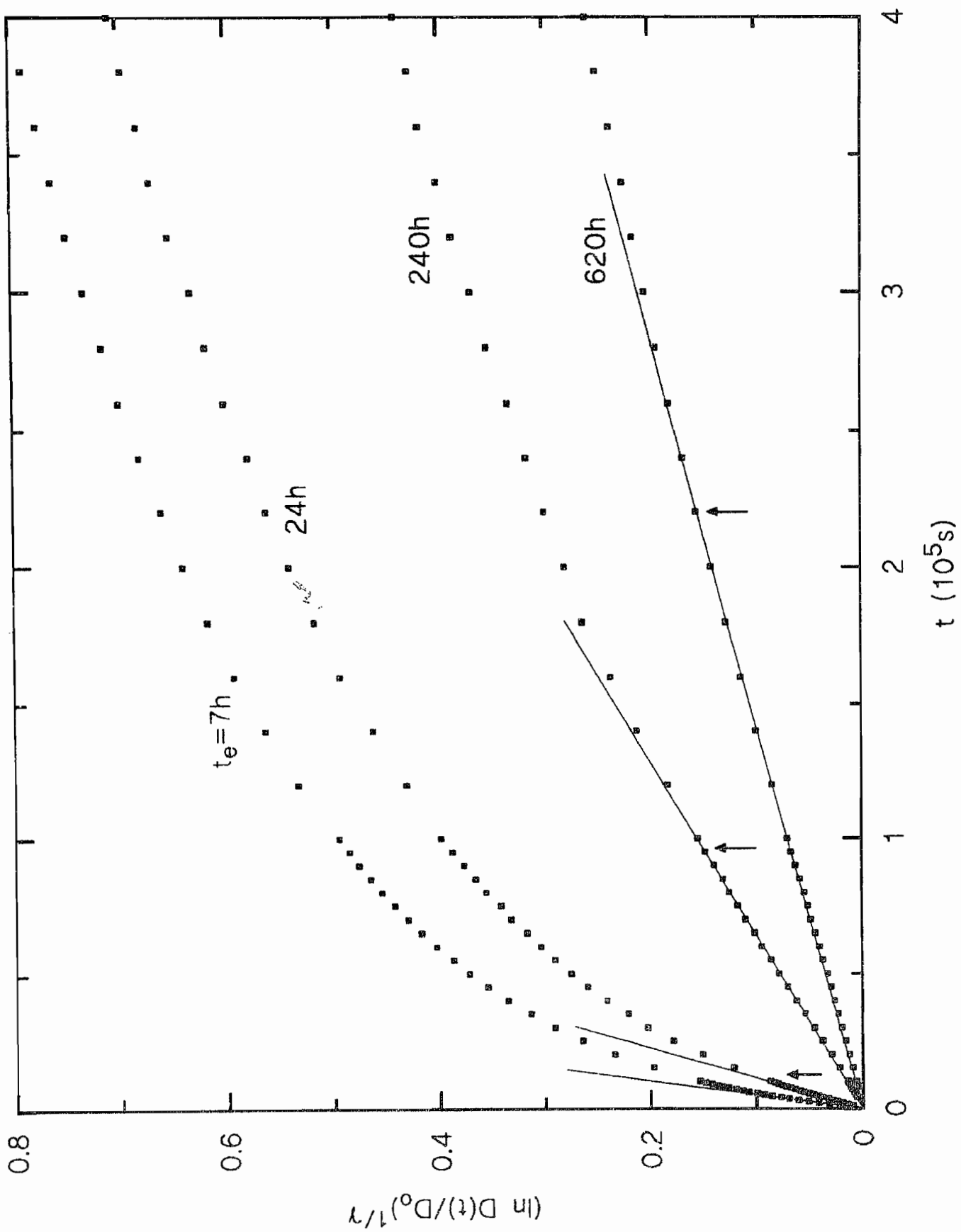


FIG.3

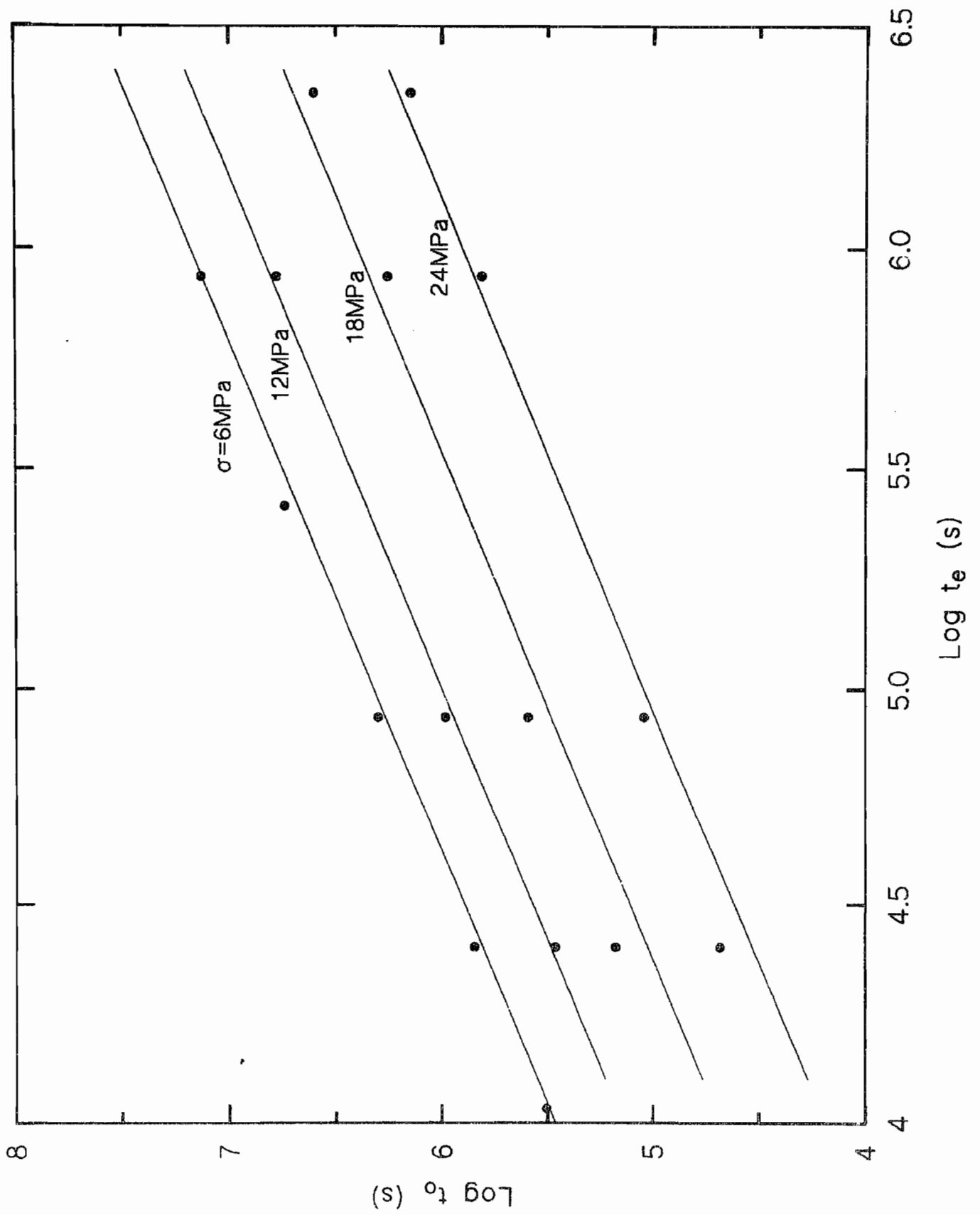


FIG.4

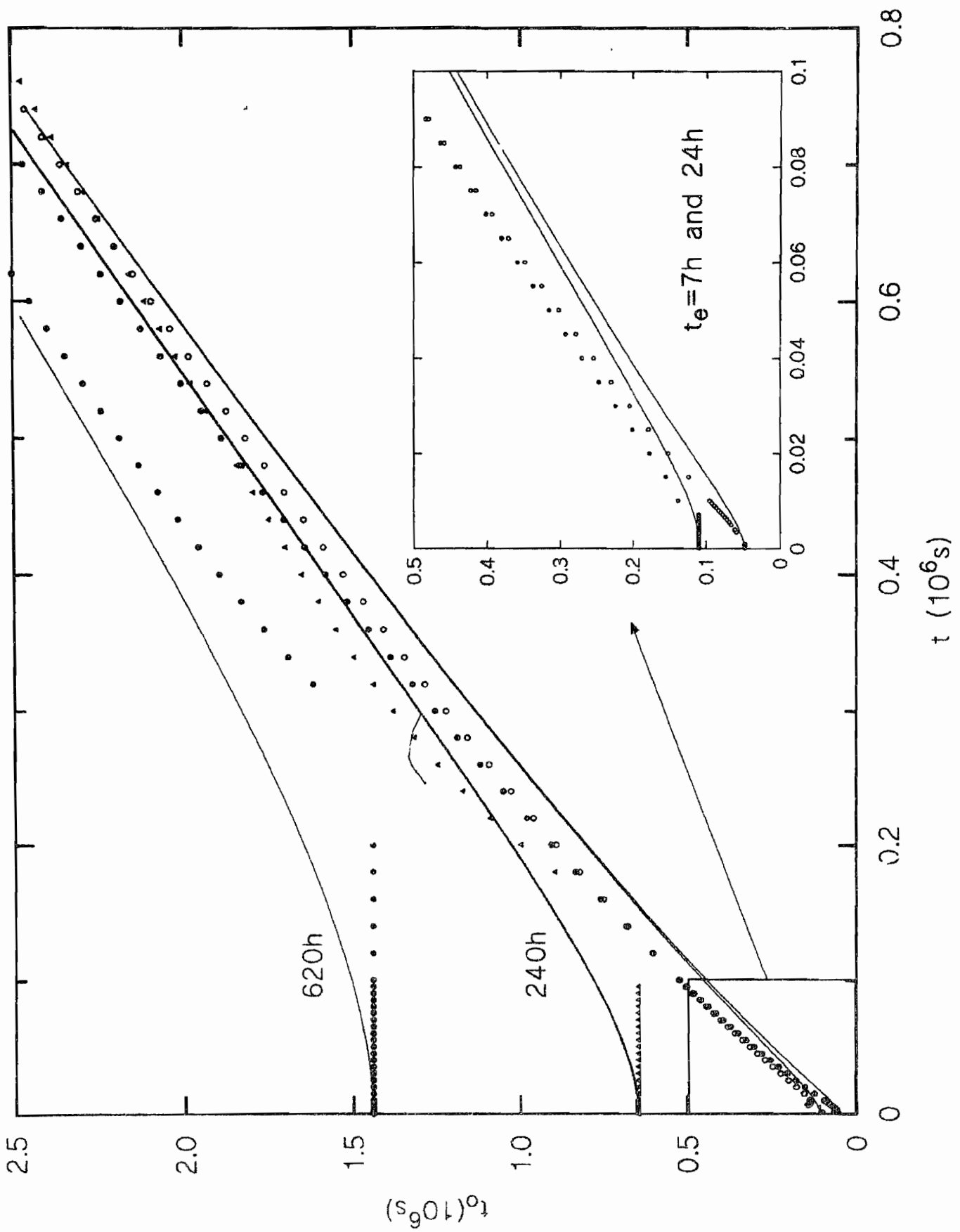


FIG.5



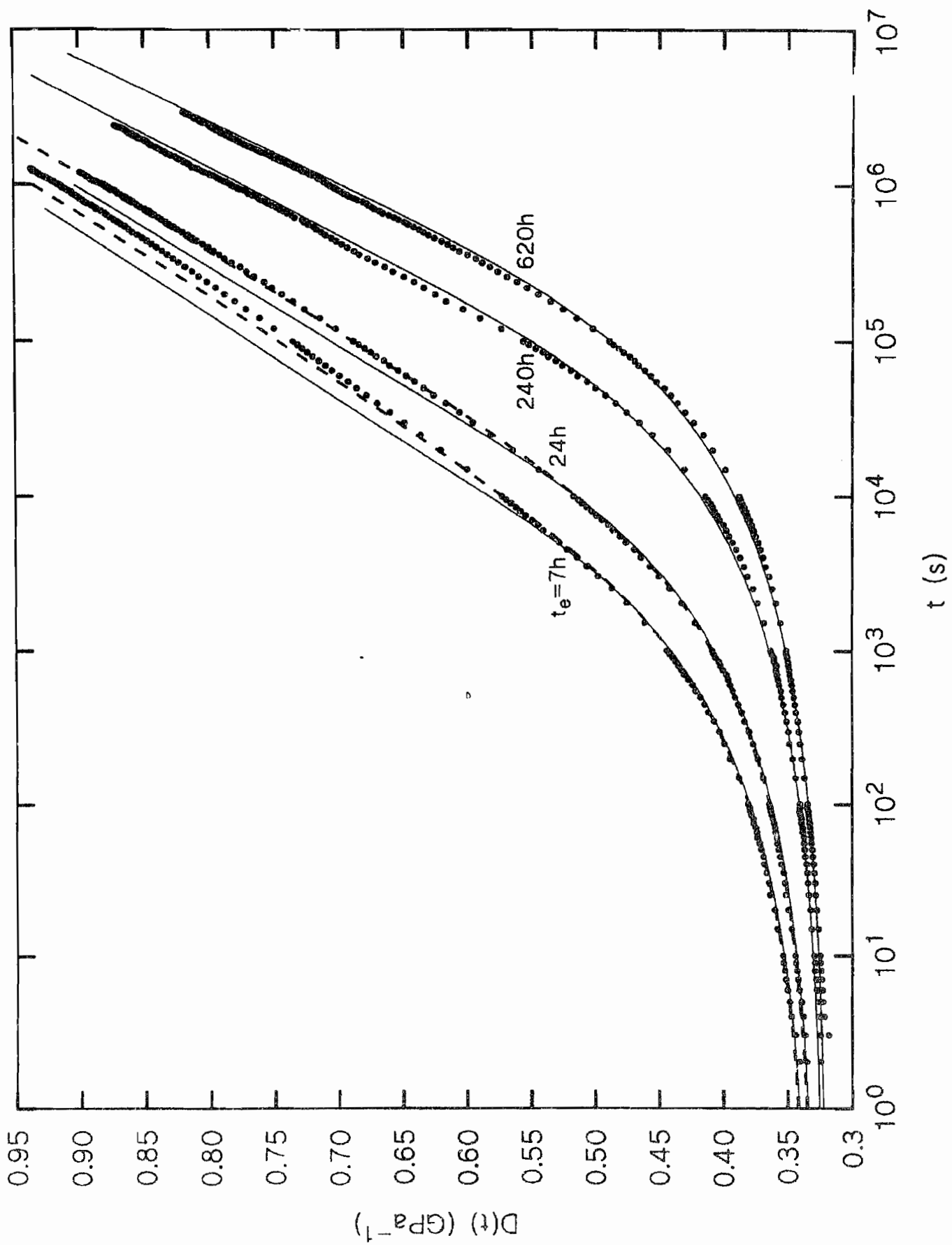


FIG.6

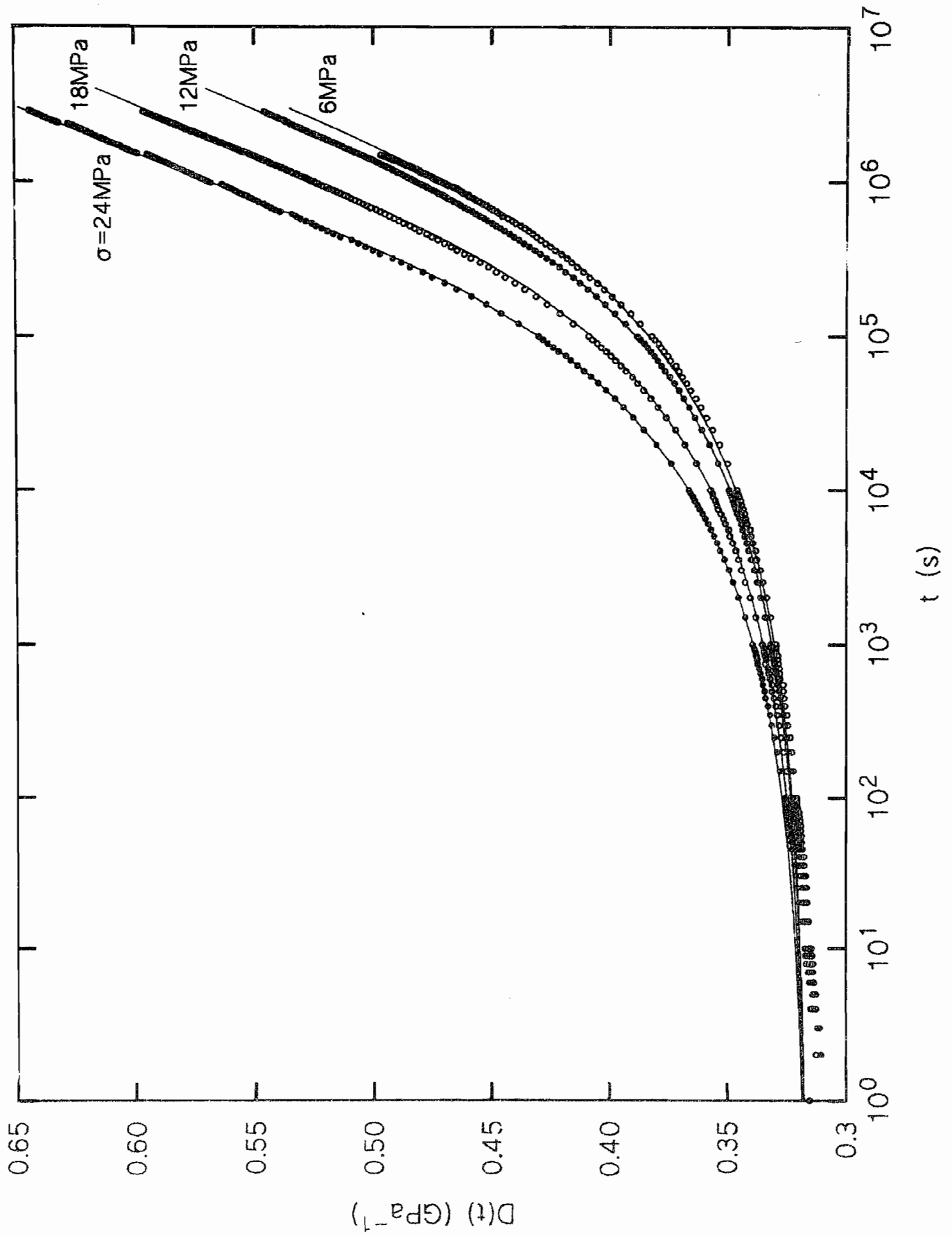


FIG.7

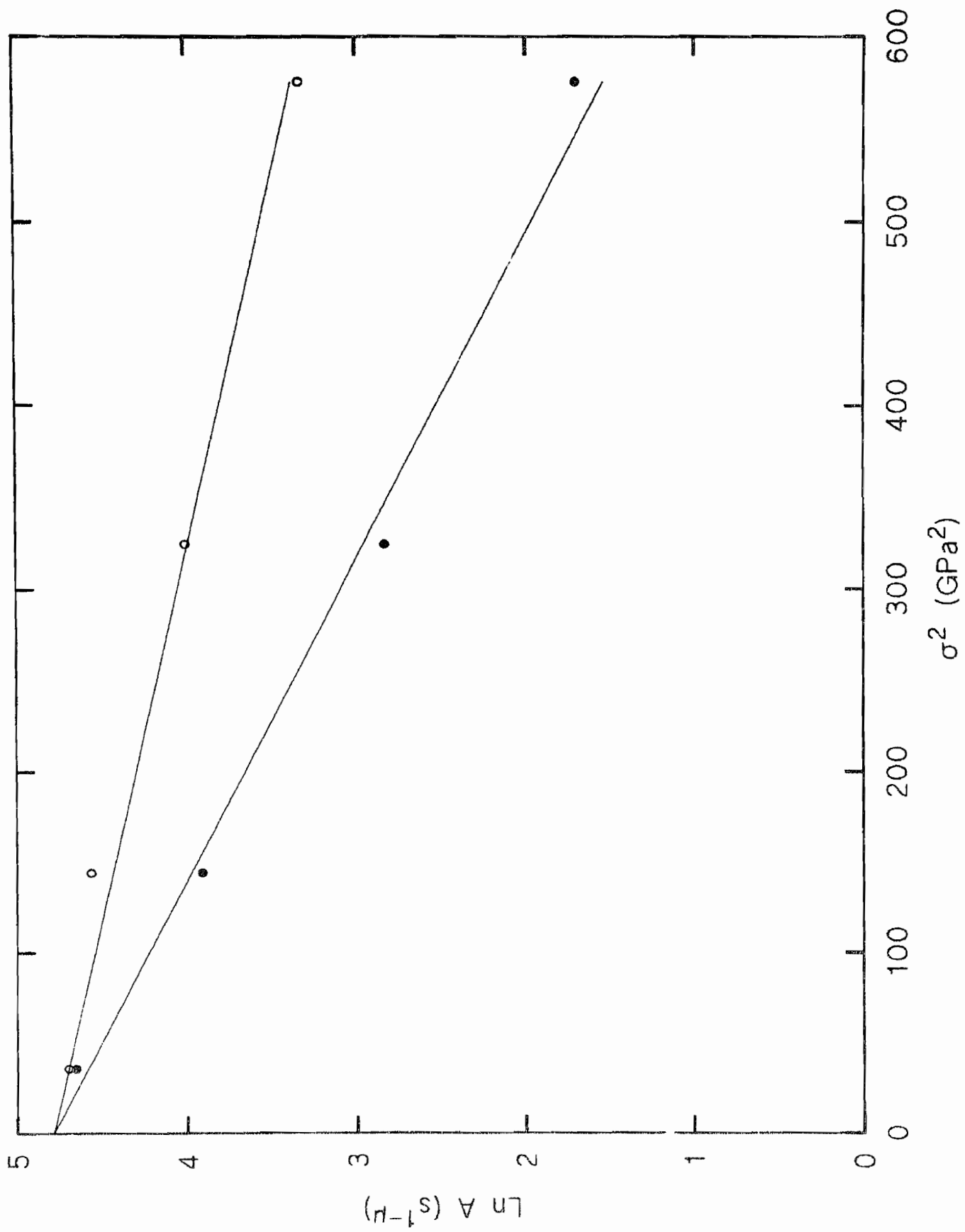


FIG.8

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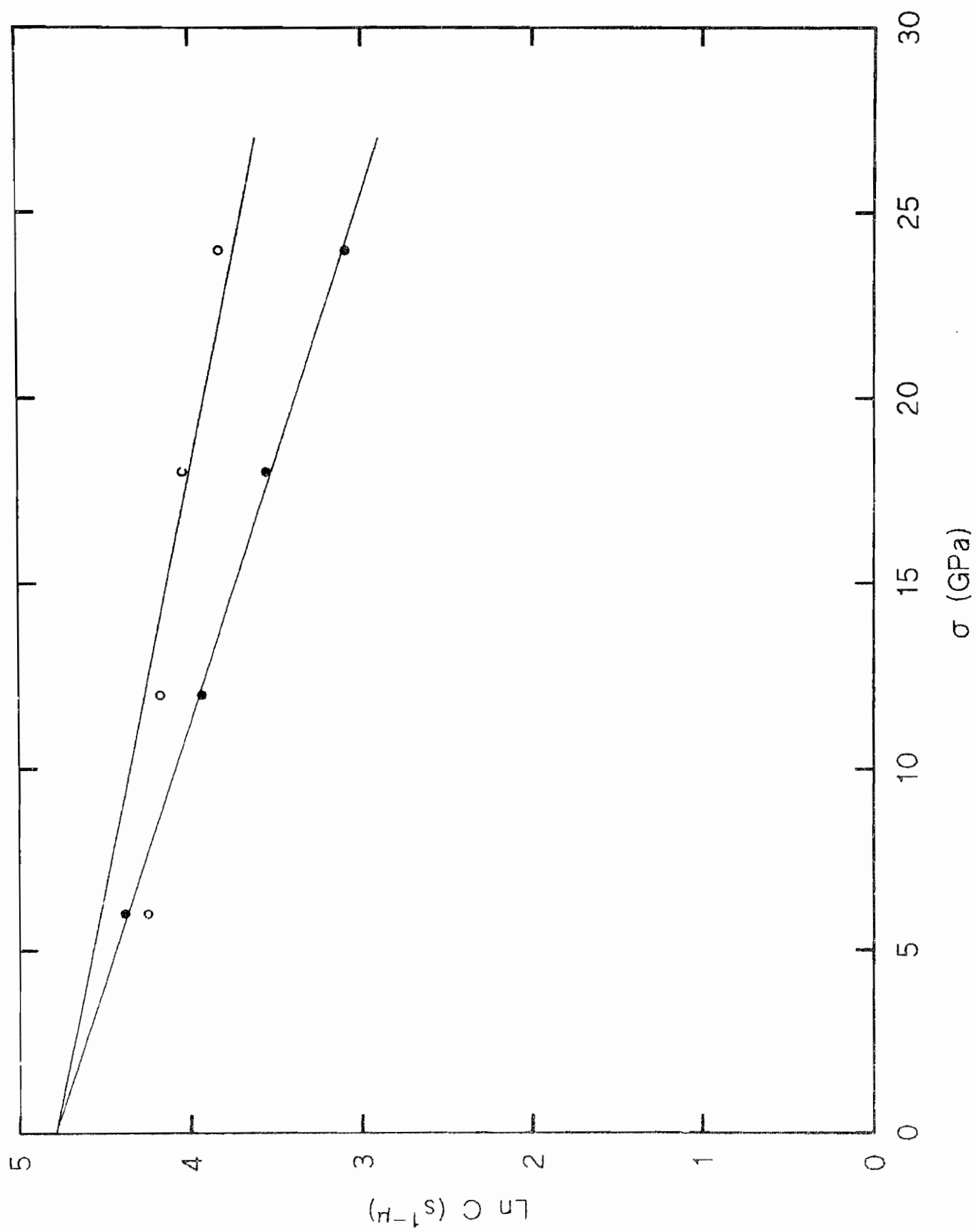


FIG.9

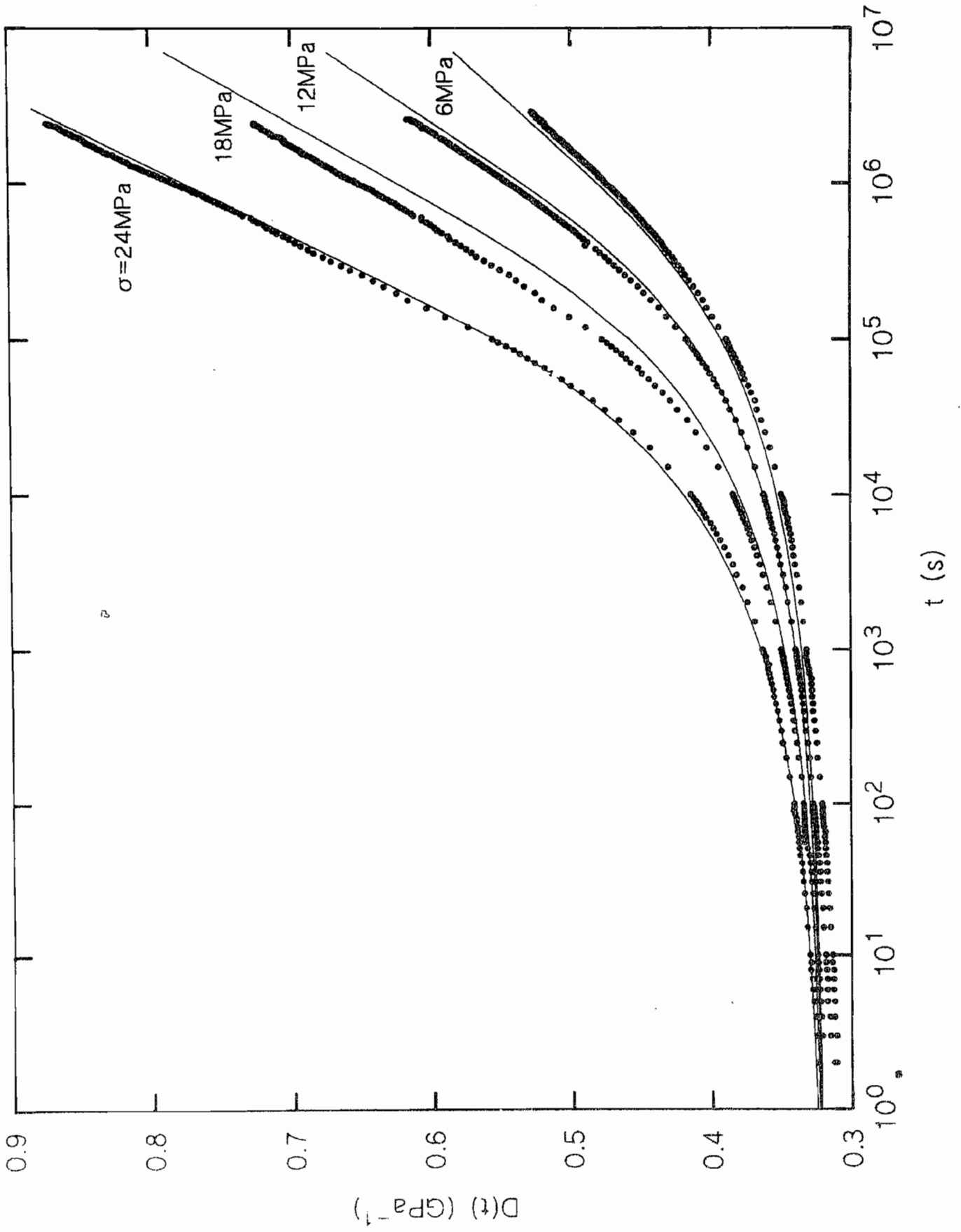


FIG.10