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Kenneth J. Wynne

6. AUTHOR(S)
Jiulin Xia and C.H. Wang

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Nebraska-Lincoln
632 Hamilton Hall
University of Nebraska
Lincoln, NE 68588-0304

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HOLOGRAPHIC GRATING RELAXATION

STUDIES OF PROBE DIFFUSION IN AMORPHOUS POLYMERS

Jiulin Xia[+] *and C.H. Wang*[*]

Department of Chemistry

University of Nebraska

Lincoln, NE 68588

[+] Current Address: Life Technologies, Inc., Gaithersburg, MD 20879

Abstract

Probe diffusion of camphorquinone, thymorquinone and diacetyl is studied by the laser induced holographic grating relaxation (HRG) technique in polymers. It is shown that the probe diffusion coefficient decreases as the probe size increases. The presence of plasticizer enhances the rate of probe diffusion whereas crosslinker retards the diffusion. Probe diffusion is also studied by varying of polymer properties such as Tg, molecular weight and chain conformation. Temperature dependent studies show that except for the very low molecular weight poly(methyl methacrylate), all diffusion coefficients fit well to the WLF equation. Probe diffusion of camphorquinone is found to be much slower in poly(vinyl acetate) than in other polymers. This result is correlated with the outstanding damping property of the polymer.

Introduction

There has been an intrerst in the study of the slow diffusion process of probe molecules in the polymer matrix in recent years. Various techniques including fluorescence photobleaching recovery (FPR) (1-3), laser induced holographic grating relaxation (HGR) or forced Rayleigh scattering (FRS) (4-13), elastic recoil detection (ERD), forward recoil spectrometry (FRES) (14), and small angle neutron scattering (SANS) (15) have been employed in the studies of slow diffusion. Among these methods, HGR and FPR are two optical techniques which are most widely used. These two methods, which have much in common permit the measurement of the probe diffusion coefficient of photochromophore molecules, down to the order of 10^{-15} cm^2/s (16). In additon to diffusion, the photochemical process of these chromophore can also be studied by these methods (17-18).

Since the chromophores used often are large organic molecules, with size comparable to the segmental unit of the host polymer, diffusion of these molecules in the polymer is generally coupled to the polymer chain dynamics. Employing HGR, Wang and co-workers have studied probe diffusion of camphoquinone, and azo dyes molecules in various polymer matrices (19-22). They have found that the diffusion coefficients of these molecules in the polymer are well described by free volume theory (23). Similar findings are also reported by Silescu and co-workers (5), Lodge and co-workers (8) and others (24). Johnson and co-workers (25) and more recently Bloomfield and co-workers (2) have also studied the diffusion of chromophore labeled biological molecules in the polymer system using HGR and FPR, respectively. These studies show the potential of applying these techniques to investigate the biological and controlled drug release systems (26). There are also reports on the probe diffusion of polymer chain in polymer solutions and in melts (13, 27), as well as diffusion of chromophores in polymer gels (9) using the HGR technique. In addition the HGR study of diffusion may also contribute to the field of optical recording materials (28).

In this paper, we report the diffusion study of probe molecules with different size in various polymers using HGR. Effects of polymer properties such as molecular weight, glass transition temperature (Tg) and chain conformation on the probe diffusion coefficient, and effects of polymer crosslinking and plasticising on the same process are also studied.

Experimental

Materials

Camphorquinone (CQ), thymorquinone (TQ) and diacetyl (DA) dye molecules are used as the diffusion probes. They are purchased from Aldrich Chemical Co. Polymers used in the present study are either purchased or free radically synthesized in our laboratory. Sources and the characterization of these polymers are summarized in Table 1. In polymer synthesis, benzoyl peroxide (from Aldrich Chemical Co.) was used as the initiator, and bi-vinyl-styrene (also from Aldrich Chemical Co.) as the crosslinking agent. Monomers of ethyl methacrylate and styrene, purchased from Aldrich Chemical Co., were distilled to remove inhibitors before polymerization.

Table 1.Glass Transition Temperature and Molecular Weight of Polymers

Sample	Name	Tg(°C)	MW	Source
PEMA	polyethyl methacylate	65	$5.0x10^5$	synthesized
C-PEMA	Crossliked PEMA	75-95		synthesized
PMMA	polymethyl methacrylate	7	$1.0x10^3$	Polymer Standard Inc, Germany
PS1	polystyrene	98	$2.8x10^5$	Aldrich
PS2	polystyrene	76	$8.7x10^4$	synthesized
PB1	polybutadiene	-108	$5.4x10^5$	Yianshan Chemical China
PB2	polybutadiene	-108	$1.2x10^6$	Yianshan Chemical China
PVAc	polyvinyl acetate	30	$1.7X10^5$	Aldrich

Methods

Sample Preparation: Samples for HGR measurements were prepared by mechanically mixing 0.5% weight) dye molecules with polymers. After mixing, mixtures were sealed in several test tubes under nitrogen atmosphere. These sealed tubes were then placed in an oven, in which temperature was set 10 degrees above the melting temperature of the polymer. Samples were quenched to room temperature after melting. Homogeneous and transparent rods were obtained. Slices were cut from these polymer rods and polished to pellets of 1-2 mm thicik with good optical quality.

Laser Induced Holographic Grating Relaxation: The pellet was mounted in a specially designed copper holder, which is then placed in a temperature controlled chamber with glass windows to permit transmission of laser beams. A holographic grating is induced by crossing two equal intensity coherent beams from an Ar^+ laser (Spectral Physics 2000) operating at 488.0 nm wavelength and a power of 40 mW. These beams were attenuated by an appropriate factor (2 to 10) before being incident on samples. The writing time was 1 to 5 seconds, controlled by an electronically actuated shutter. The crossing angle θ varies from 3.6 to 15°. At $\theta=3.6°$, it corresponds to a grid spacing of 8.26 μm. Gratings were generated as a result of hydrogen abstraction of dye molecules (29). The optical setup employed in the present study is similar to that used in the previous work(4).

In HGR, the diffracted intensity versus time curve has either a monotonous decay or a decay-growth-decay shape. For the photochemical processes involving unimolecular reactions, one can show that the holographic time dependent signal can be described by a double exponential function as given by (30):

$$I(t) = (a e^{-t/\tau_1} + b e^{-t/\tau_2})^2 \qquad (1)$$

where a and b are optical constants and are functions of refractive index as well as the population of molecules in the ground and excited state. When a and b have the same sign, the signal gives rise to a monotonous decay;o therwise, a decay-growth-decay curve. Values of τ_1 and τ_2 are relaxation times, which are associated with diffusion coefficients (D_1 and D_2) of dye molecules (CQ, TQ or DA) and their photoproducts (CQP, TQP or DAP) according to:

$$D_i = \frac{\lambda^2}{16\pi^2 \sin^2(\frac{\theta}{2})\tau_i} \tag{2}$$

where λ is the wavelength of laser light; subscripts $i=1$ and $i=2$ correspond to the dye molecule and its photoproduct, respectively. Knowing λ and θ, the diffusion coefficient D_i can be calculated from the measured τ_i value via Eq.(2).

Results and Discussion

1. Diffusion Coefficients of CQ, TQ and DA in PEMA

Two types of HGR curves were observed in this study. Figure 1 shows a decay-growth-decay curve obtained for the CQ-PEMA system at T=117°C and θ=3.6°. The curve is well fit to Eq.(1) with a=296.0, b=285.0, τ_1=340.0s, and τ_2=780.2s. In Figure 2, a monotonous decay curve is shown for the DA-PEMA system at T=86°C and θ=12.4°. Values of a=7.0, b=31.9, τ_1=946s, and τ_2= 2000s are obtained by *fitting to Eq.(1) using the best fit to the* observed intensity profile.

Figure 3 shows the temperature dependence of the coefficients of DA and DAP (the photoproduct of didactyl) in PEMA. One bnotes the the temperature dependence of the diffusion coefficients is different above and below T_g. To observe this change the sample nees to be sufficiently aged; otherwise, there will be no discernable change as T_g is travesred. In contrast to the diffusion of TQ in PEMA previously reported(21), the diffusion of DA does not show a rapid decrease when the temperature is deceased toward Tg. This is pressumably due to the smaller size of DA than TQ(31). Above T_g, the diffusion coefficients of both DA and DAP can be fit to the WLF type equation:

$$\log\frac{D(T)T_o}{D(T_o)T} = \frac{C_1^D(T-T_o)}{C_2^D+T-T_o} \tag{3}$$

where $D(T_o)$ is the diffusion coefficient measured at the reference temperature T_o; C_1^D and C_2^D are characteristic constants related to both the diffusant and the polymer. Using $T_o = T_g$, we obtained $C_1^D(DA) = 5.9 \pm 0.3$, $C_1^D(DAP) = 6.2 \pm 0.3$ and $C_2^D(DA) = C_2^D(DAP) = 68.2 \pm 4.5$ K. The C_2^D value is similar to the value obtained from the shear compliance (65.5 K)(32) and the dynamic light scattering result of PEMA(33). Both the agreement with the results of ref. 32 and 33 as well as the analogous C_2^D values obtained for both DA and DAP suggest that the probe diffusion of DA and DAP in PEMA is determined by the visocoelastic property of the polymer. For $T < T_g$, diffusion coefficients show an Arrhenius type temperature dependence with an activation energy of 3.2 Kcal/mole. This is consistent with the result of our previous works(34-35) and that in the literature(5).

According to free volume theory(23), the coefficient C_1^D is equal to $C_1\xi$, where ξ is the volume ratio of the diffusing molecule to the average polymer jumping unit, and C_1 is the usually WLF constant of the polymer for viscosity or shear moduls. For PEMA, C_1 was found to be 17.6(32-33). Thus, we obtained for both DA and DAP that $\xi < 1$, indicating that the size of these diffusion molecules is smaller than that of the polymer jump unit. Since the size of DAP is expected to be larger than that of DA, the ratio of $C_1^D(DAP)/C_1^D(DA)$is 1.06, suggesting that the molar volume of DAP is greater than that of DA by 6%. This is consistent with the geometric models of these molecules.

Measurements of the diffusion coefficients for CQ and CQP in PEMA were carried out at temperatures above T_g. Corresponding results were fit to the WLF equation. The fitting parameters obtained are summarized in Table 2, together with results for DA and TQ(21). The C_1^D values in Table 2 appear to increase with increasing size. Since C_2^D values for DA, TQ and CQ as well as their photoproducts all agree with each other to within experimental uncertainty, the temperature dependence of the diffusion coefficients for these molecules in PEMA can be described by the normalized shift factor according to:

$$\frac{1}{C_1^D} \log a_T = \frac{(T-T_o)}{C_2^D+T-T_o} \tag{4}$$

where a_T is the shift factor defined as $D(T)T_o/D(T_o)T$. Figure 4 shows the normalized curve of diffusion coefficients for these molecules in PEMA.

Table 2 WLF Parameters for the Diffusion Coefficient of Various Diffusants

DAP	6.21	68.2	2.0×10^{-15}
TQ	6.16	70.6	1.9×10^{-13}
TQP	6.68	70.6	1.2×10^{-14}
CQP	8.42	70.6	1.0×10^{-14}(82°C)

2. Diffusion Coefficients of TQ in PS with Varying MW

We have in a recent report on CQ diffusion in PMMA associated the molecular weight (MW) dependence of the probe diffusion with the Tg of the polymer(36). When the MW is sufficiently high for the polymer to reach an asymptotic Tg, the probed diffusion coefficients in such polymers do not change with the MW. Below the asymtotic limit the Tg of the polymer changes with as MW changes, and the diffusion coefficient also adjusts to the Tg change. In this section, we show that the change in the probe diffusion coefficient of TQ in PS with different MW is described by Eq. (4). Figure 5 shows the normalized WLF shift factor for diffusion coefficients of TQ and TQP in PS1 and PS2. For comparison, diffusion coefficients of CQP in PS1 from reference (37) are also plotted in Figure 5. The WLF fitting parameters are given in Table 3. Clearly, the C_1^D value depends on the geometric size of the probe molecule, and C_2^D values agree with the C_2 = 50.0 K(32) obtained from the viscoelastic data of the PS.

Table 3The WLF Parameters of Diffusion Coefficients for TQ, TQP and CQP in PS[1] and PS[2]

Diffusant-Polymer	C_1^D	C_2^D(K)	$D(T_g)$(cm^2/s)
TQ-PS1	4.72	50.2	$2.0x10^{-12}$
TQP-PS1	4.93	50.3	$7.9x10^{-14}$
TQ-PS2	4.34	48.2	$1.0x10^{-12}$
TQP-PS2	4.72	48.6	$5.0x10^{-14}$
CQP-PS1	5.0	49.2	$1.5x10^{-13}$

3. Arrhenius Temperature Dependence of Diffusion Coefficients for CO in PMMA of Low MW

Most early studies (31) on the diffusion coefficients of small molecules in polymers in temperature ranges both above and below T_g have shown an Arrhenius temperature dependence:

$$D = D_o \exp(-E_d / RT) \tag{5}$$

where D_o is the pre-exponential factor, R and E_d are the gas constant and activation energy, respectively. Recent studies (4-5, 8, 10) on the diffusion coefficients of large organic molecules in polymers, however, showed the WLF type temperature dependence above T_g. Below T_g, diffusion coefficients follow however, the Arrhenius type temperature dependence. In contrast to probe diffusion in the polymer of high MW (36), Figure 6 shows the Arrhenius temperature dependence of diffusion coefficients of CQP in PMMA of low MW. The pre-exponential factor and the activation energy are found to be $1.1x10^{-8}$ cm^2/s and 7.0 Kcal/mol, respectively. These values are in the typical range for diffusion of molecules in molecular liquids (31). The reason to observe the Arrhenius type diffusion is due to the low MW polymer. Since in this case the polymer has only about 10 repeat units and has a very low T_g (7°C), abundant free volume is available for the polymer chain motion to take place at T > Tg. Such large free volume would make the probe molecules to diffuse without interference with the segmental motion of the polymer, and the thermally activated mechanism will be the rate determining step for diffusion.

4. Plasticizing and Crosslinking Effects on Probe Diffusion of DA and CQ in PEMA

Since plasticizer increases free volume and depresses the glass transition temperature of the polymer, the probe diffusion coefficient in polymer is expected to increase with increasing the plasticizer concentration. In the HGR experiment, dye molecules serve as the plasticizing agent for the polymer. Table 4 shows the T_g of PEMA as a function of DA concentration. Figure 7 shows the diffusion coefficients of DA and DAP at 95°C as a function of the DA volume fractions, ϕ. One notes a drastic increase of the diffusion coefficient at small ϕ. As ϕ gradually increases, the influence of the DA concentration on the diffusion coefficient becomes less.

Table 4. Glass Transition Temperatures of PEMA as a Function of DA Fraction

Volume Fraction of DA in PEMA	T_g(°C)
0.0016	65
0.008	61
0.036	58
0.065	50
0.13	45
0.2	35

In contrast to the effect of plasticizer, the crosslinking agent decreases free volume and thus increases the glass transition temperature. We, therefore, expect the probe diffusion coefficient to decrease with increasing the crosslinker concentration. Bi-vinylstyrene (BVS) is a common crosslinking agent for vinyl polymers. Table 5 shows the T_g of the crosslinked PEMA as a function of the BVS concentration.

According to Fujita's theory, the probe diffusion coefficient (D) is related to fractional free volume fraction by(38):

$$D = ART\ \exp\left(-\frac{B}{f_o}\right) \tag{6}$$

where A and B are parameters independent of concentration and temperature. Assuming that f_o is linearly proportional to the volume fraction (ϕ) of the crosslinker, we write:

$$f_o = f_a + \beta\,\phi \tag{7}$$

where f_a is the free volume fraction of the pure polymer and β is a proportionality constant, and is positive for plasticizer and negative for crosslinker. Substitution of Eq. (7) into Eq. (6) yields

$$\left[\mathrm{Ln}\frac{D(\phi)}{D(O)}\right]^{-1} = \frac{f_a}{B} - \frac{f_a^2}{\beta B}\frac{1}{\phi} \tag{8}$$

where $D(\phi)$ and $D(O)$ are the diffusion coefficients with and without crosslinker, respectively.

Figure 8 shows the plot of $\{\mathrm{Ln}[D(\phi)/D(O)]\}^{-1}$ vs. ϕ^{-1} for the diffusion coefficient of CQ in crosslinked PEMA at 123°C. The straight line, gives $B = 0.6$ and $\beta = -0.14$ this suggests that Fujita's theory is applicable to the crosslinking case. We have also found that Eq. (8) is also applicable to the probe diffusion in the polymer with plasticizer.

Table 5. Glass Transition Temperatures of PEMA as a Function of Crosslinker Volume Fraction

Volume Fraction of BVS in PEMA	T_g(°C)
0	65
0.011	75
0.022	82
0.033	88
0.052	95

5. Probe Diffusion of CQ in Polybutadiene of Varying Degree of Branching

Figure 9 shows the temperature dependence of diffusion coefficients of CQ in PB1 and PB2, respectively. *Clearly, these diffusion coefficients follow the WLF type of equation.* By fitting the diffusion data to the WLF equation, we obtained $C_2^D = 60.0$ K for both samples, but $C_1^D = 18.8$ and 26.0 for PB-1 and PB-2, respectively. Again the C_2^D value is found to be close to the value obtained from the shear compliance data(32). However, in contrast to the results obtained earlier, we have found that these C_1^D values are greater than $C_1 = 11.3$ obtained from shear compliance data (32). In the parlance of free volume theory, this suggests that the size of CQ are larger than that of the polymer jump unit. Figure 9 also shows that the CQ diffusion is faster in PB-1 than in PB-2, in spite of the fact that these samples have the same T_g. Since molecular weighs for both PB-1 and PB-2 exceed the entanglement MW, we expect to observe similar diffusion coefficient for both samples (36). Instead, different diffusion coefficients with a factor over two were observed. We interpreted this as due to the difference in the molecular branching of the two polymers. Both PB-1 and PB-2 have the same cis-1,4 structure of 96%. However, considering the fact that the degree of molecular branching for PB-2 (6×10^4) is much larger than that for PB-1 (2×10^3)(39), it is apparent that branching gives rise to more molecular entanglement and decreases free volume, which consequently retards the probe diffusion process.

6. Probe Diffusion of CQ in Polyvinyl Acetate

Figure 10 shows the temperature dependence of the diffusion coefficient of CQ in PVAc. The diffusion data are well fitted to the WLF equation. The fit yields $C_2^D = 47.0$ K and $C_1^D = 9.3$, respectively. The shear compliance measurement gives $C_2 = 46.8$ K and $C_1 = 15.6$(32). The C_2^D value is consistent with $C_2 = 46.8$ K, again indicating that probe diffusion is determined by the viscoelastic property of the polymer host. Since C_1^D value is smaller than that of the C_1 it suggests that the size of CQ is smaller than that of the polymer jump unit. However, it should be noted that the rate of diffusion of CQ in PVAc is much slower than that in other polymers, such as in PMMA, PEMA and PS. For example, the diffusion coefficient in PVAc at the temperature of 60°C above the T_g of the polymer is about the same as the diffusion coefficients of other polymers in the vicinity of their T_g's (Table 6). The smaller probe diffusion coefficient may be associated with the outstanding damping property (40) of the polymer. PVAc has been extensively used as a damping material due to the fact that its T_g is close to room temperature, and it has a large tan δ over a wide temperature range. Since acoustic damping is due to scattering of elastic waves in the medium, the slow diffusion coefficient observed in PVAc probably suggests a strong coupling of the probe diffusion process with the low energy elastic waves propagating in PVAc. As a matter of fact, quasielastic light scattering of PVAc shows a considerable low frequency spectrual wing(41) about the laser excitation frequency. In the case of probe diffusion in PVAc, randomizing polymeric structural relaxation could greatly slow down the probe diffusion.

Table 6. Diffusion Coefficients of CQ in PVAc as a Function of Temperature

T(°C)	D(cm^2/s)	T(°C)	D(cm^2/s)
93.0	7.94×10^{-14}	125.5	8.35×10^{-13}
101.0	1.74×10^{-13}	132.0	1.14×10^{-12}
106.0	2.90×10^{-13}	143.5	1.85×10^{-12}
114.5	5.20×10^{-13}	156.0	2.50×10^{-12}
118.0	5.10×10^{-13}	163.0	2.90×10^{-12}

Conclusions

In summary, we have studied diffusion coefficients of camphorquinone, thymorquinone and diacetyl in various polymers. We have shown that the probe diffusion coefficient is significantly correlated with the size of the probes. It increases as the size of the probe molecule decreases. We have also shown that the presence of plasticizer enhances probe diffusion and the crosslinker retards the diffusion. Our temperature dependent results show that, except for the very low molecular weight poly(methyl methacrylate) (PMMA), the diffusion coefficient fits well to the WLF equation for diffusion. We have also shown that all diffusion data of different probes at various temperatures in different polymers can be normalized in accordance with the WLF equation to yield a master curve. We have also shown that probe diffusion coefficients vary with polymer properties such as T_g, molecular weight and chain conformation. Probe diffusion of camphorquinone is found to be much slower in polyvinyl acetate than in other polymers. We have associated this result with the outstanding damping property of the polymer.

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Figure Captions

Figure 1. Decay-growth-decay type of the diffracted intensity curve I(t) as a function of time (t) for the CQ-PEMA system at T=117°C and $\theta=3.6°$. Dots are experimental points, and the curve is calculated according to Eq.(1) with a=296.0, b=285.0, $\tau_1=340.0$s, and $\tau_2=780.2$s.

Figure 2. Monotonous decay type of the diffracted intensity curve I(t) as a function of time (t) for the DA-PEMA system at T=86°C and $\theta=12.4°$. Dots are experimental points, and the curve is calculated according to Eq.(1) with a=7.0, b=31.9, $\tau_1=946$s, and $\tau_2=2000$s.

Figure 3. Temperature dependence of diffusion coefficients of DA (O) and DAP (●) (photoproduct of diactyl) in PEMA. Dots are experimental points, and curves are fits to the WLF equation.

Figure 4. Normalized plot for diffusion coefficients of DA (O), DAP (Δ), TQ (◇), TQP (⊙) and CQP (□) in PEMA.

Figure 5. Normalized WLF shift factor for the diffusion coefficients of TQ and TQP in PS1 and PS2. (□) and (Δ) are for TQ and TQP, respectively, in PS1, (∇) and (⊙) are for TQ and TQP, respectively, in PS2. (O) is for CQP in PS1.

Figure 6. Temperature dependence of diffusion coefficients of CQP in PMMA of low MW. Dots are experimental points, and the line is the Arrhenius fit with pre-exponential factor and the activation energy of 1.1×10^{-8} cm^2/s and 7.0 Kcal/mol, respectively.

Figure 7. Plots of diffusion coefficients of DA and DAP as a function of the DA volume fractions, ϕ, at 95°C.

Figure 8. Plt of $\{Ln[D(\phi)/D(O)]\}^{-1}$ vs. ϕ^{-1} for diffusion coefficients of CQ in crosslinked

PEMA at 123°C.

Figure 9. Temperature dependence of diffusion coefficients of CQ in PB-1 and PB-2, respectively. Dots are experimental points, and curves are fits to the WLF equation.

Figure 10. Temperature dependence of diffusion coefficients of CQ in PVAc. Dots are experimental points, and the curve is fit to the WLF equation.

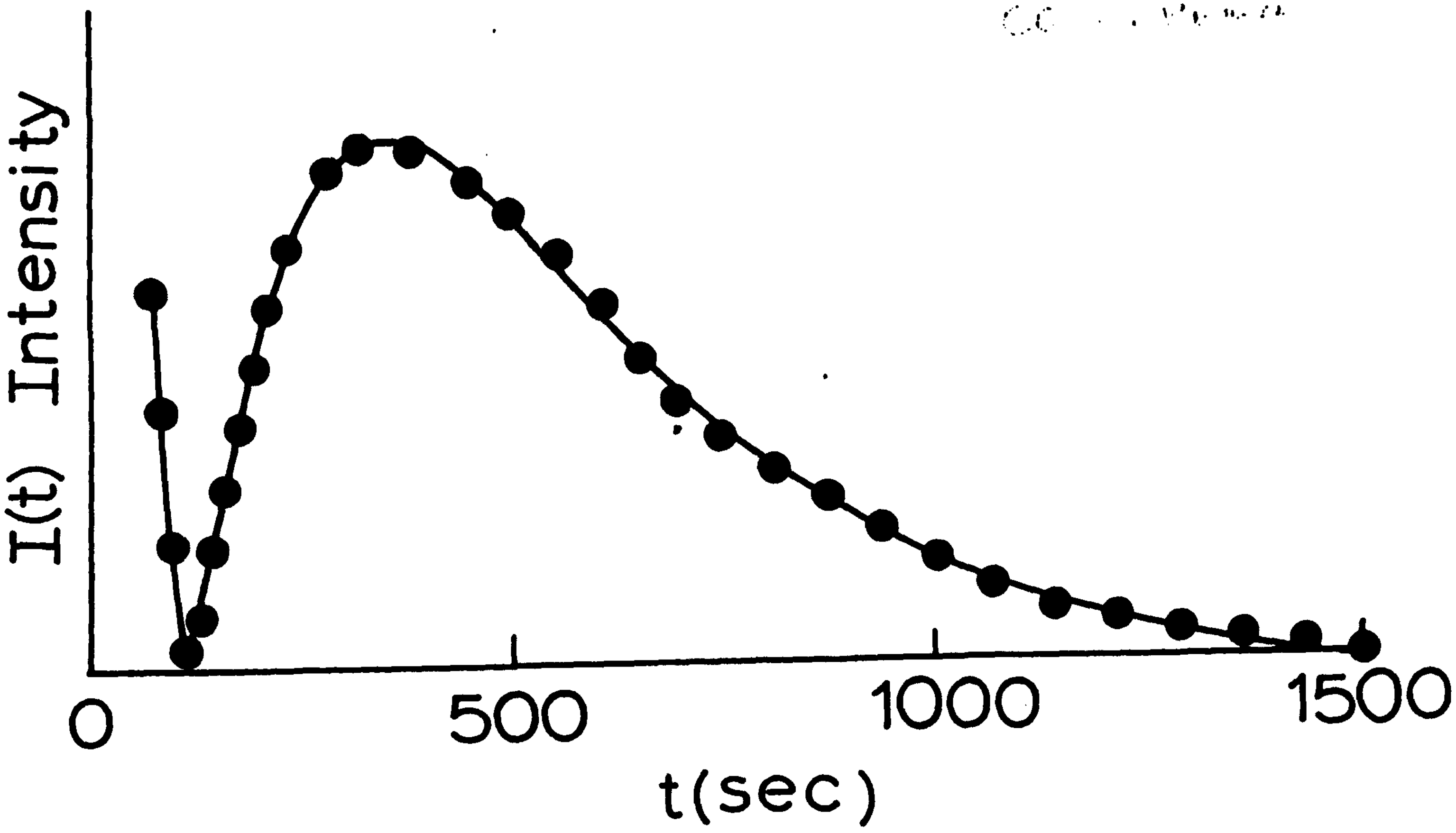
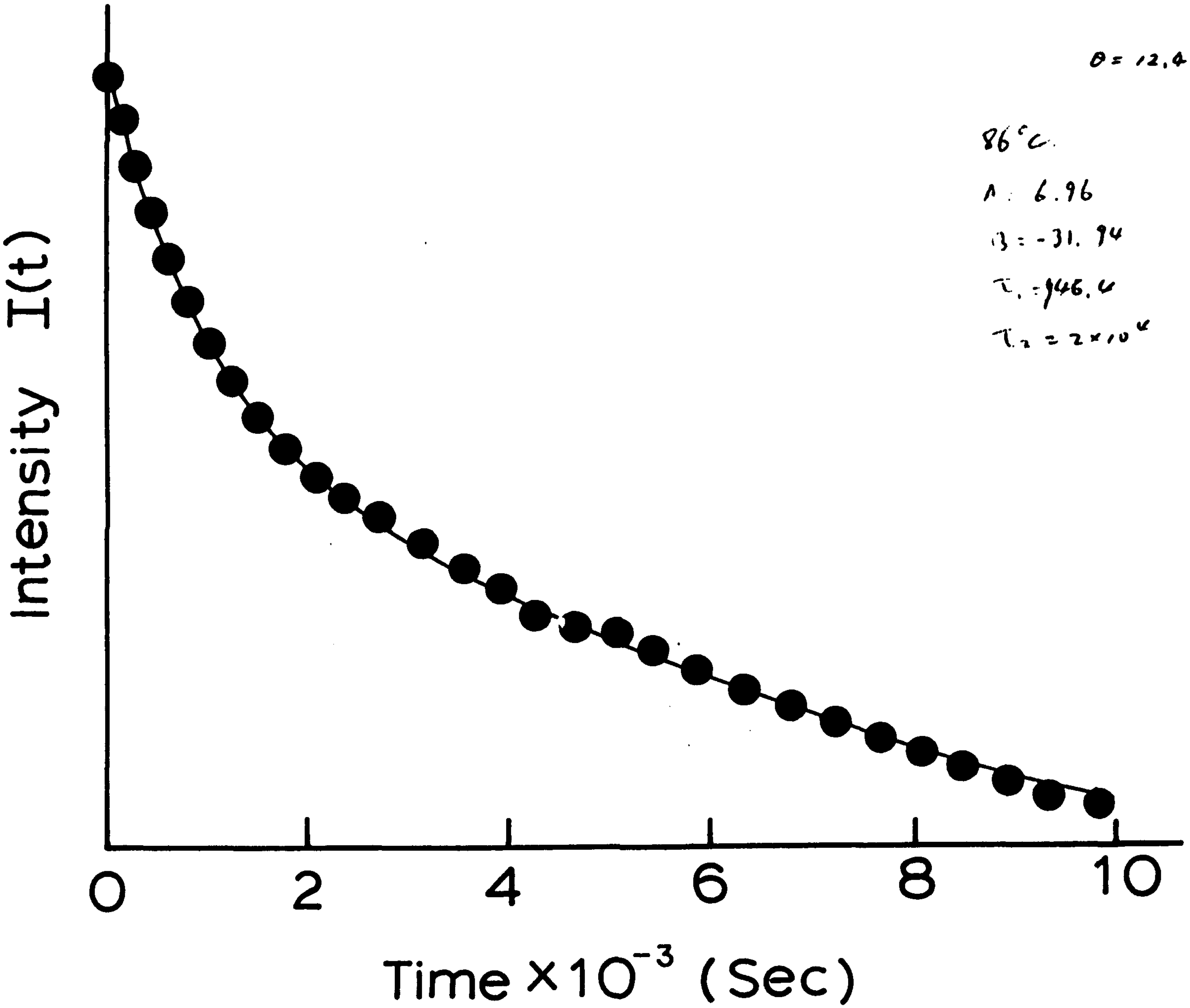


Fig. 1



$\theta = 12.4^\circ$

86°C

$A : 6.96$

$B = -31.94$

$\tau_1 = 946.4$

$\tau_2 = 2 \times 10^4$

Fig. 2

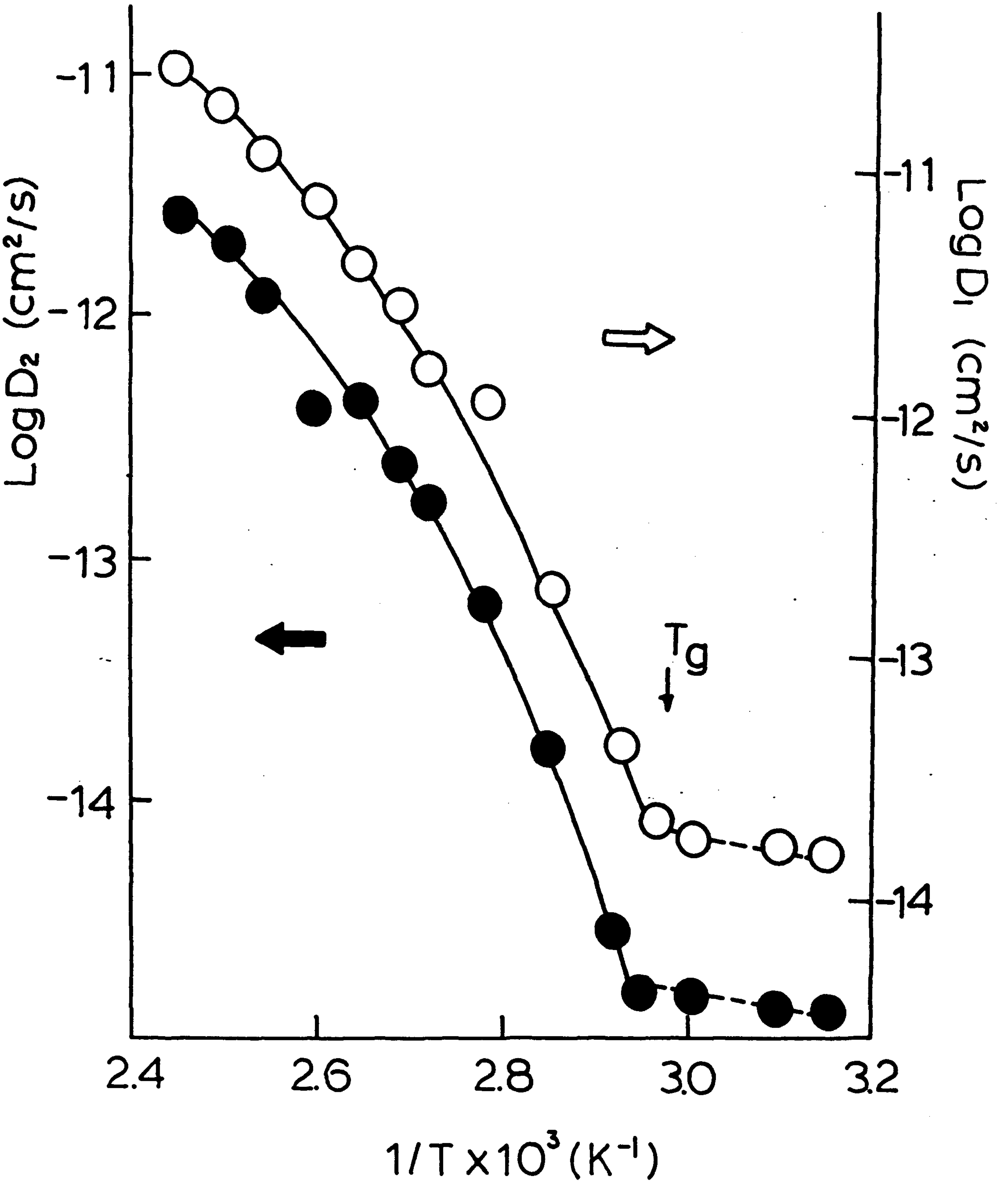

-11
-12
-13
-14
Log D₂ (cm²/s)
-11
-12
-13
-14
Log D₁ (cm²/s)
Tg
2.4
2.6
2.8
3.0
3.2
1/T x 10³ (K⁻¹)

Fig 3

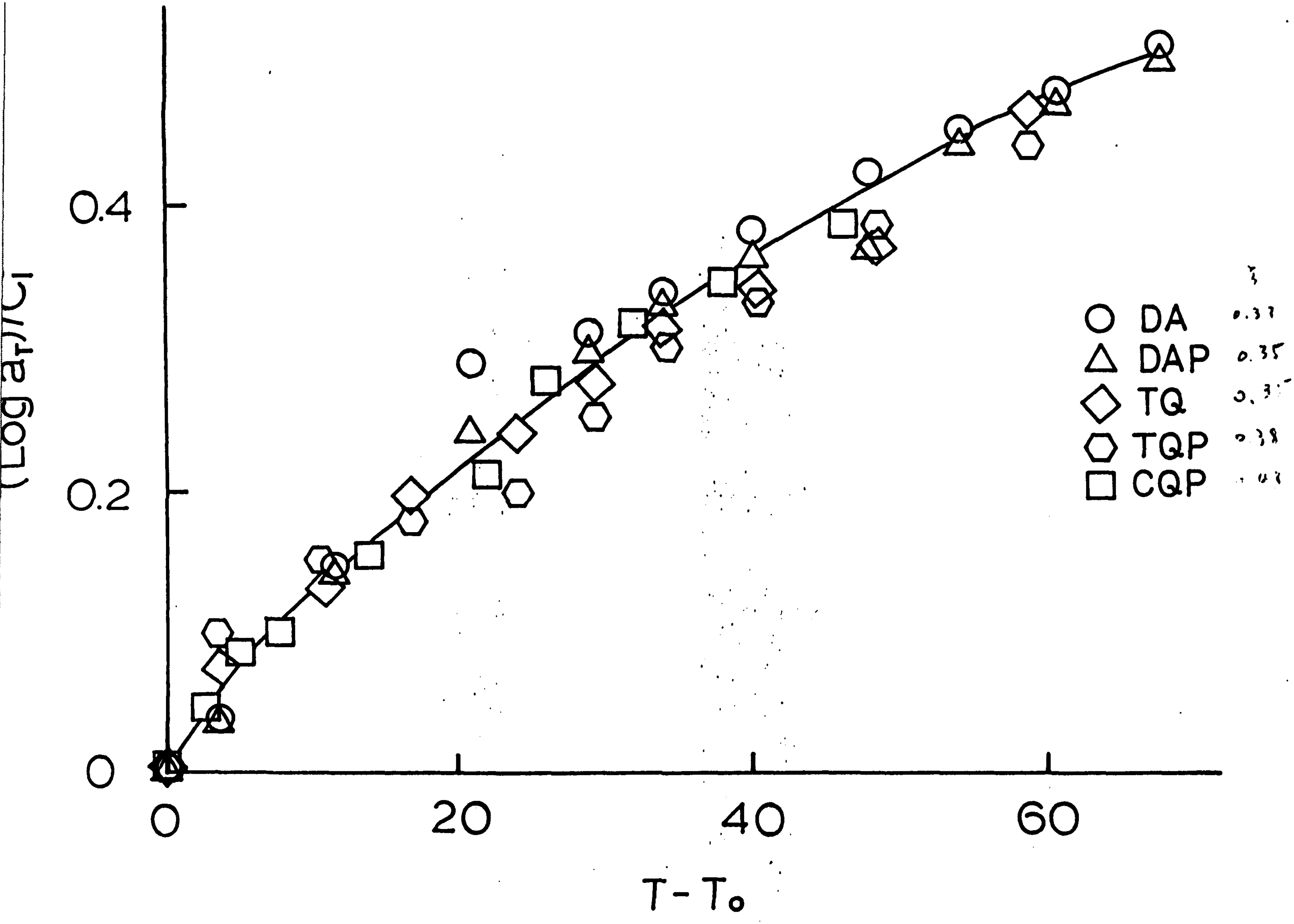

(Log a_T)/C_1
0.4
0.2
0
0
20
40
60
T - T_o
DA
DAP
TQ
TQP
CQP
ξ
0.37
0.35
0.35
0.38
.43

Fig. 4

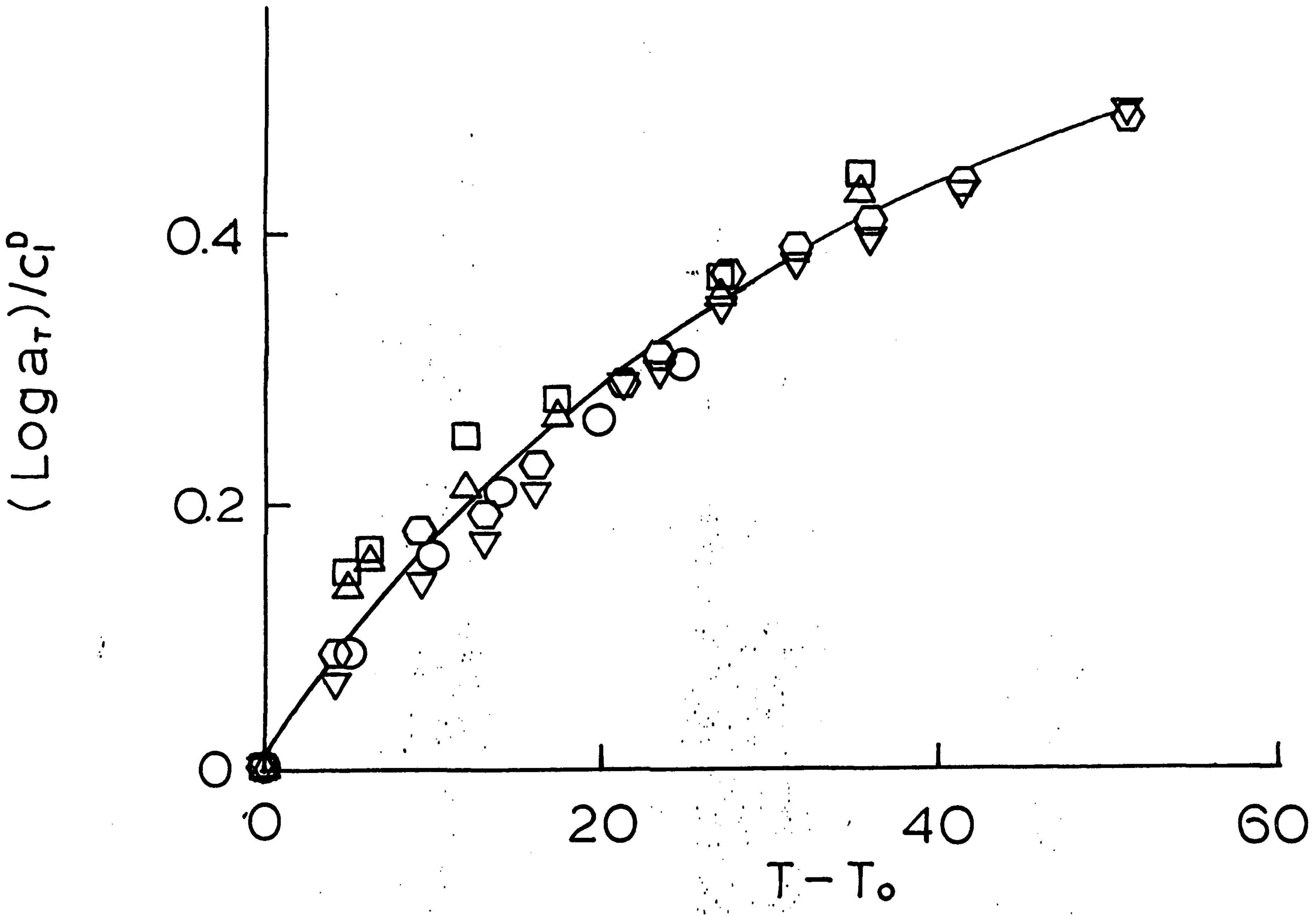


Fig 5

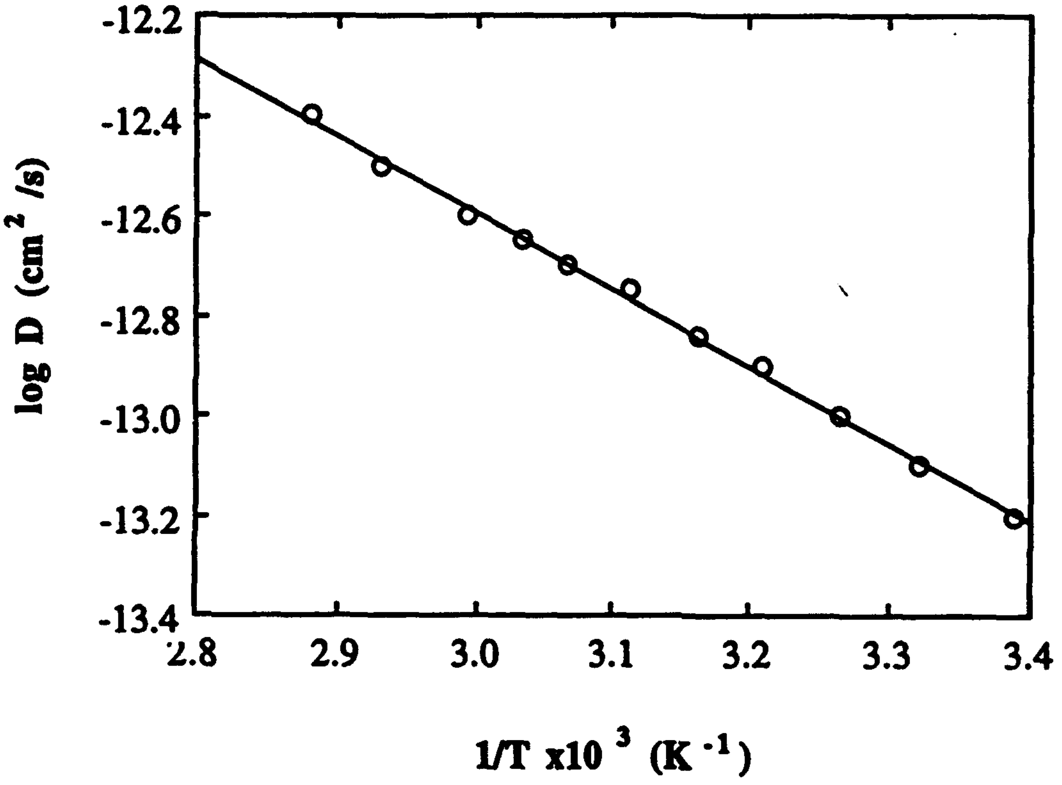

-12.2
-12.4
-12.6
-12.8
-13.0
-13.2
-13.4
log D (cm^2 /s)
2.8
2.9
3.0
3.1
3.2
3.3
3.4
1/T x10 ^{3} (K $^{-1}$)

Fig 6

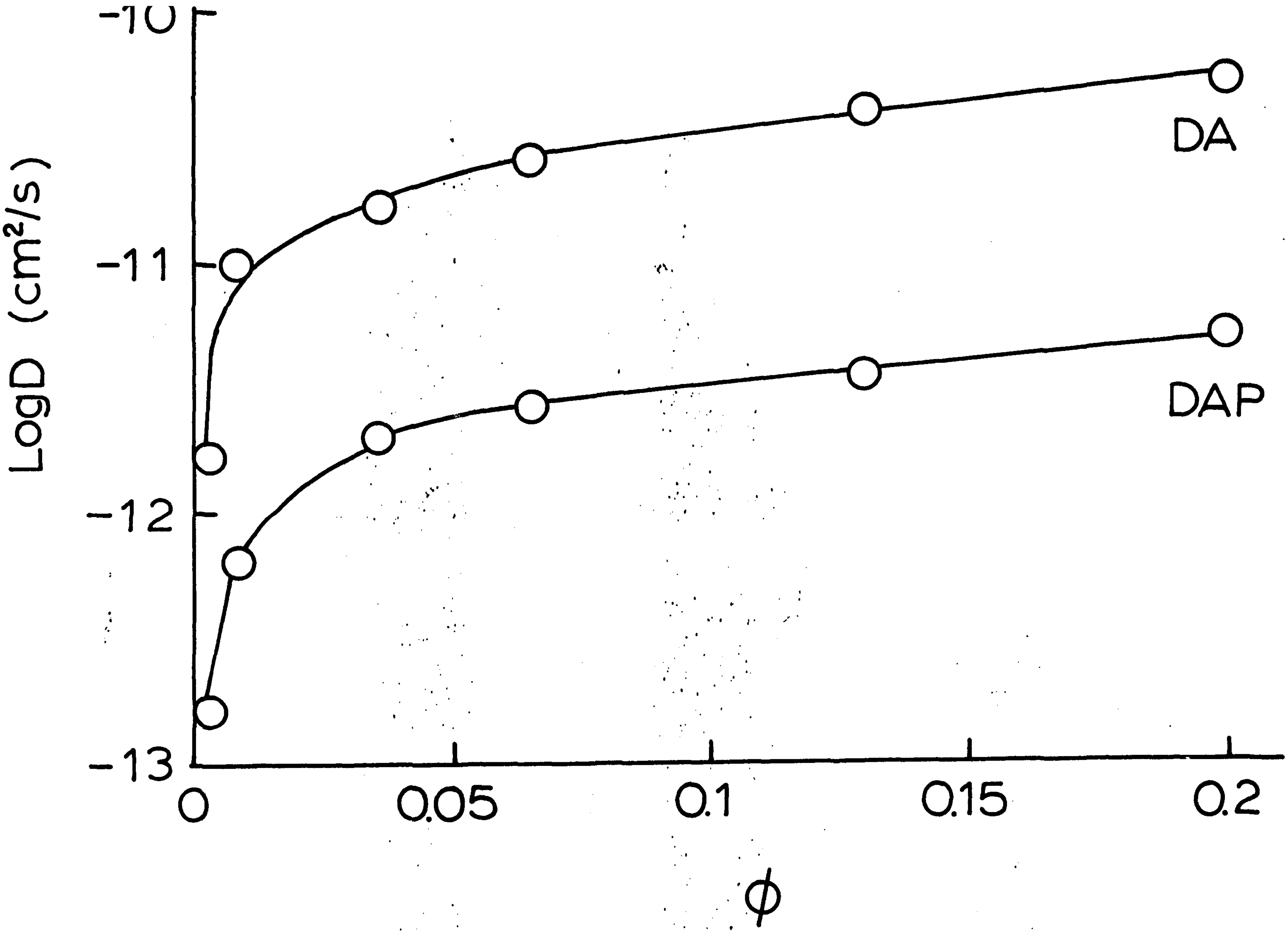
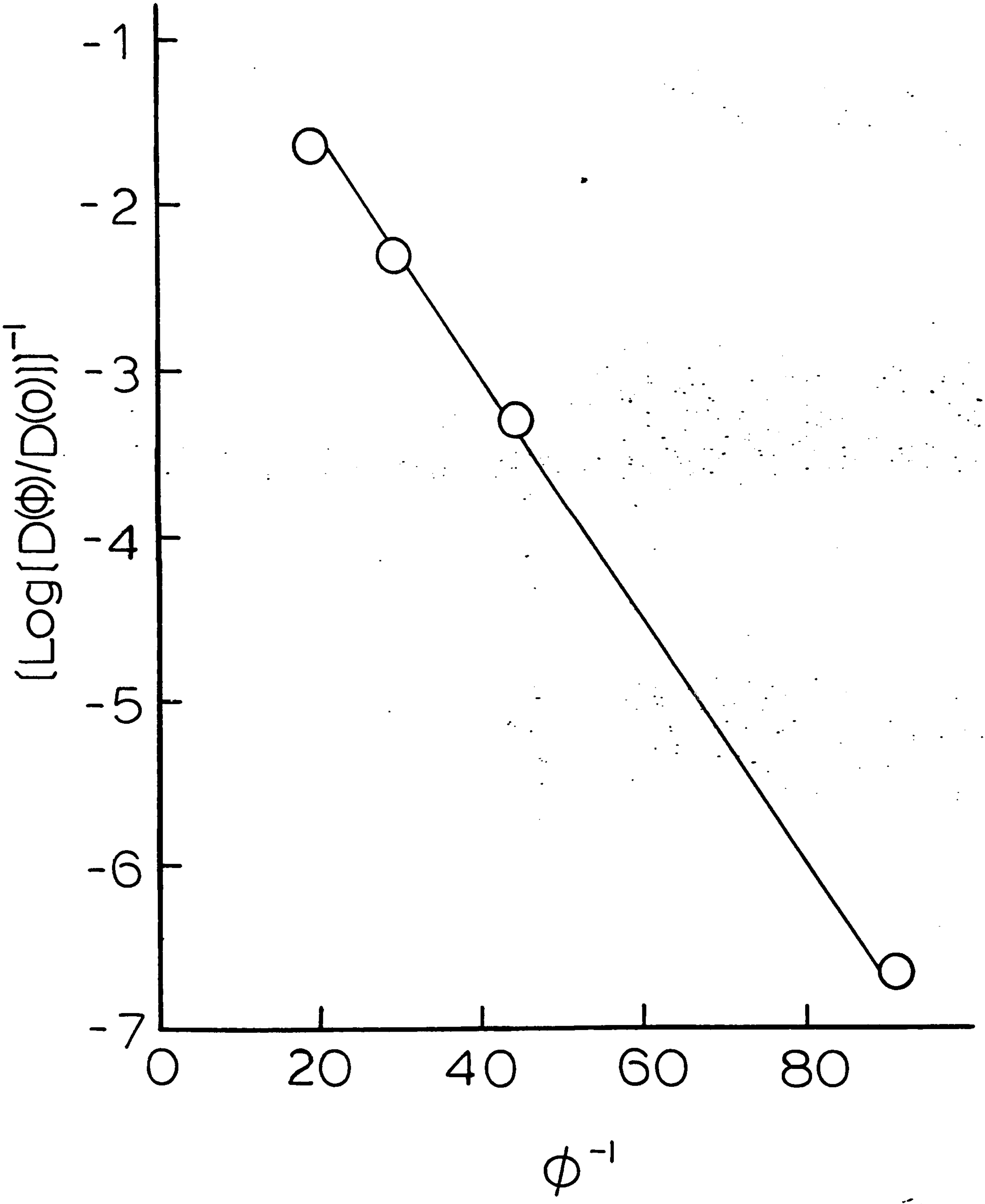


Fig 7.


-1
-2
-3
-4
-5
-6
-7
{Log[D(Φ)/D(0)]}$^{-1}$
0
20
40
60
80
ϕ^{-1}

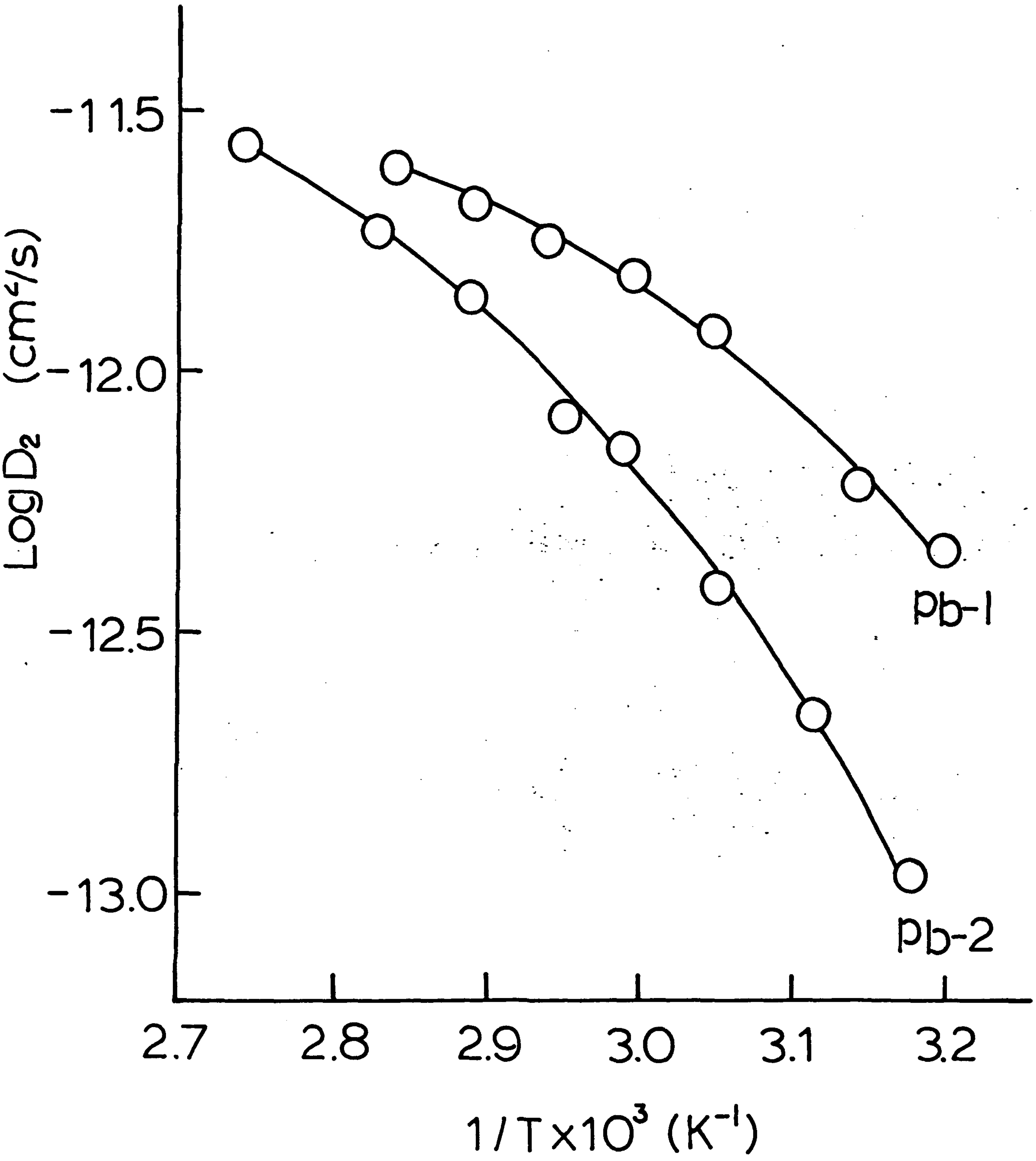


Fig 9

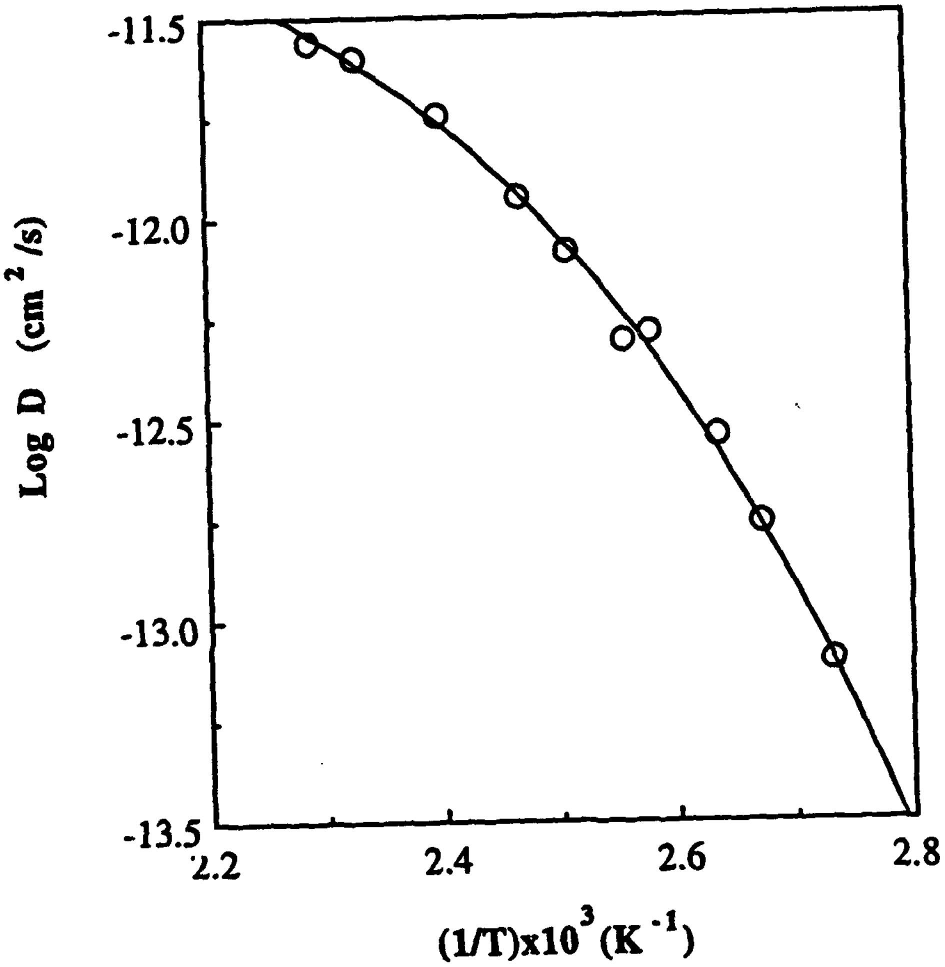


Fig. 12