

Self-diffusion of poly (propylene glycol) in nanoporous glasses by pulsed field gradient NMR. A study of molecular dynamics and surface interactions

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Abstract:

Pulsed field gradient NMR is applied to investigate the self-diffusion of poly(propylene glycol) in nanoporous glasses (pore sizes 2.5 nm – 7.5 nm). In general, the translational motion is slowed down by the confinement in comparison with the bulk state. For native uncoated pore surfaces the stimulated spin echo attenuation or incoherent intermediate dynamic structure factor $S_{inc}(q,t)$ displays a bimodal behavior versus q^2t where q is a generalized scattering vector. This was explained assuming a two-phase model. The slow component is assigned to polymer segments forming an interfacial layer close to the pore wall with an essentially lower molecular mobility than the segments located in the center of the pores. The exchange rate between this different sites was found to be between about 100 ... 200 ms at $T=323$ K.

For silanized pores the bimodal behavior in the intermediate dynamic structure factor disappears but $S_{inc}(q,t)$ shows a stretched exponential decay versus q^2t . The stretching parameter β decreases with decreasing pore size. The effective diffusion coefficient decreases strongly with pore size. Its temperature dependence can be approximated by an Arrhenius law where the corresponding activation energy increases with pore size. The observed behavior can be understood assuming interaction as well as size or confining effects, brought about by the host system. A discrimination between both effects requires additional studies like the investigation of the molecular weight dependence of the diffusion in nanoporous environments.

1. Introduction

During the last decade the behavior of molecules close to interfaces, in thin films and in confining geometries has gained a growing interest [1-5]. On the one hand side this is due to technological interest to know and to control the properties of molecules on a nanometer scale. Some examples therefore are oil recovery, controlled drug release, molecular lubrication, the application of thin films in micro- or molecular electronics or the applications of nanocomposites, for instance in the field of optics. From the theoretical side one main reason for such studies is to investigate the influence of finite size effects on the properties of matter and compare the results with theoretical approaches. In the last decade much attention was paid to investigate glassy dynamics of low-molecular-weight liquids and polymers confined to nanoporous host systems. The underlying question was if there is an inherent length scale responsible for glass transition [6]. By confining molecules to host systems of a few molecular dimensions the relevance of such an inherent length scale responsible for glassy dynamics can be indirectly proven. There are several experimental indications that such a length scale is essential for glassy dynamics.

It is well known that the diffusion in nanoporous systems such as zeolites or nanoporous glasses is dominated by the architecture of the confining host as well as by the interaction of the confined molecules with the internal surfaces [7]. Compared with the large body of literature concerning the glass transition of molecular systems confined to nanoporous hosts only little is known concerning the diffusion of complex organic molecules in nanoporous environments. There are few publications in which the diffusion of low molecular weight molecules [8-10] and polymers [11-15] is investigated.

In general the molecular dynamics of molecules in nanoporous environments is determined by a variety of factors [7]. For the dynamic glass transition a so-called confinement effect is found (for an overview see[16]) which means that the molecular dynamics in the confinement

is faster than that of the bulk. This points to an inherent length scale on which the molecular motion takes place. On the other side, the dynamics of a confined molecular system is also influenced by surface interactions (adsorption effect), which in general would lead to a slowing down of the relaxation times or the diffusion (see for instance [11,16-18]). Adsorption effects should scale with the surface-to-volume ratio of the confining porous systems. But, moreover, also the structure of the pore wall influences the interaction between surface and the confined molecules and therefore its molecular dynamics [19]. Molecular dynamic simulations support this. An increased molecular mobility is observed at the interface of a smooth and weakly interacting wall whereas a small corrugation on a atomic level is enough to reduce the diffusion at the interface [20,21]. The conditions for surface interactions which can be easily constructed in simulations are difficult to meet in experiments. The used porous silica materials have hydrophilic character due to the existence of silanol groups. They form strong interaction sites for polar and H-bonding molecules, which obviously reduces their dynamics at the interface. Silanization of the surface can suppress these interactions but may introduce an increased corrugation of the surface. In addition, the topology of the applied porous system can influence the molecular dynamics of a confined system. In the most experiments Controlled Porous Glasses (CPGs) or Vycor have been used as confining hosts. These mesoporous materials have interconnecting cavities with a broad distribution of sizes and shapes. At the end it should be also mentioned that the density of a confined material can be smaller than that of the corresponding bulk. This implies also that the whole thermodynamic state can be different from that of the bulk material [17]. In this paper the self-diffusion of polymer melt confined to nanoporous Sol/Gel glasses with different pore sizes is studied by Pulsed Field Gradient NMR. To explore surface adsorption interaction in addition to sizes effects the internal pore surface was also silanized.

2. Theoretical Background

Pulsed Field Gradient NMR (PFG NMR) can be applied to measure the incoherent intermediate dynamic structure factor

$$S_{\text{inc}}(q, t) = \int \exp(iqz) P(z, t) dz \quad (1)$$

which is well known from scattering techniques like Neutron scattering [22]. $P(z, t)$ is the so-called propagator [23] or the probability density for a displacement of a polymer segment over a distance z within the diffusion time t and q is a generalised scattering vector. Assuming a Gaussian propagator

$$S_{\text{inc}}(q, t) = \exp(-q^2 Dt) \quad (2)$$

is obtained. The mean square displacement $\langle z^2 \rangle$ of polymer segments in z direction can be related to the diffusion coefficient D by

$$\langle z^2 \rangle = 2Dt. \quad (3)$$

The NMR signal was generated by the stimulated-echo radio-frequency- (rf-) pulse sequence:

$\frac{\pi}{2} - \tau - \frac{\pi}{2} - t' - \frac{\pi}{2} - \tau - \text{echo}$. The spin echo attenuation $A/A_0 = S_{\text{inc}}(q, t)$ is due to field gradient pulses applied after the first and the third $\pi/2$ -rf-pulse and (see eq.(1)) formally coincides with the incoherent intermediate dynamic structure factor. A and A_0 are the spin echo amplitudes with and without applied field gradients, the diffusion or observation time $t = t' + \tau$ and the norm of the scattering vector $|q| = \gamma \cdot \delta \cdot g$. δ is the width and g the amplitude of the gradient pulse and γ the gyromagnetic ratio. Eq. (2) was derived assuming the so-called narrow-pulse approximation $\delta \ll t$. A detailed description of the technique can be found in refs.[23,24].

3. Experimental

Poly(propylene glycol) (PPG) with a number molecular weight $M_n=2000 \text{ g mol}^{-1}$ (Polydispersity=1.05) was selected as model system. The glass transition temperature T_g was estimated to 206 K by DSC. The radius of gyration $\sqrt{\langle r^2 \rangle}$ of the polymer coil is about 3.3 nm. The PPG was obtained from Aldrich and used without further purification.

As confining host materials controlled nanoporous glasses purchased from Geltech Inc., USA were applied. The specified pore sizes are 2.5, 5.0 and 7.5 nm and according to the manufacturer the pore size distribution is narrow. Because these glasses are prepared by a sol/gel process they have also a distribution of pore shapes and interconnected cavities [25]. The glasses are delivered as monolithic cylinders with a diameter of 6 and a height of 2mm. To remove water and other impurities the cylinders were heated to 573 K for 1 h, evacuated to 10^{-5} mbar and kept there for 24 h. Then the cylinder was slowly cooled down to 373 K under vacuum. Two sets of samples have been prepared by different methods of filling. To investigate PPG in uncoated native pores the oligomeric melt was injected directly in the vacuum chamber at 373 K. The pores were filled by capillary wetting at this temperature for 72 h. The internal glass surface contains a large amount of hydrophilic silanol groups which can form hydrogen bonds with the molecules. To modify interaction of the polymer with the glass surfaces the silanol groups were converted into the less hydrophilic trimethylsilyl groups before filling (coated surfaces). 1,1,1,3,3,3-hexamethyldisilazan was injected directly in the vacuum chamber at 373 K and allowed to react with the surface of the pores for 30 min. After that time the surplus amount of hexamethyldisilazan was removed by applying vacuum. This treatment leads approximately to a monolayer of trimethylsilyl groups on the internal glass surfaces. After this surface modification the pores were filled with the polymer melt as described above.

Assuming that the density of the polymer within the pores is the same as in the bulk state from the porosity the amount of the macromolecules within the pores can be calculated and compared with that obtained by weighting. The data show that under these assumptions the

pores are completely filled within an error of 3%. The filled cylinders were placed into stoppered NMR tubes fixed with a cylinder made of Teflon. Dielectric and temperature modulated DSC experiments on the same system have been reported elsewhere [18,26].

The PFG NMR experiments were carried out with a home-built NMR spectrometer [27,28] operating at a ^1H -resonance frequency of 400 MHz. In each experimental run, τ was chosen to be 3 ms, δ and t were fixed and g was incremented. The maximum value of g was 25 T m^{-1} and that of δ 1.85 ms. The accessible length scale of PFG NMR covers a region between $1/q_{\text{max}} \approx 80 \text{ nm}$ to a few μm . The diffusion times t were varied between 13 and 603 ms and so the narrow-pulse approximation is fulfilled. The temperature of the measurement is controlled within $\pm 1\text{K}$. A comparison between dielectric and PFG NMR experiments have been published for PPG [29] with a molecular weight of 4000 g mol^{-1} .

4. Results and Discussion.

Fig. 1 shows the spinecho attenuation versus q^2t for bulk PPG for different temperatures. Only for the highest temperatures the measured data seem to follow eq. 2. This points to a distribution of diffusion coefficients which might be related to the polydispersity of the studied sample. From a formal point of view the well-know Kohlrausch-Williams-Watts (KWW-) or stretched exponential function [30,31] can be used to analyze the data. In analogy to the KWW-function one can formal assume

$$S_{\text{inc}}(q, t) = \exp\left(-[q^2 D t]^\beta\right) \quad (4)$$

(which corresponds to an incoherent scattering function). The stretched exponential parameter $0 < \beta \leq 1$ leads to an asymmetric broadening of $S_{\text{inc}}(q, t)$ for small values of q^2t (short diffusion times) compared to an exponential decay ($\beta=1$). From a theoretical point of view a deviation of the spinecho attenuation versus q^2t from eq. 2 can be understood assuming an anomalous

diffusion characterized by a sub-linear increase of the mean square displacement $\langle z^2 \rangle = 2 \tilde{D} t^\beta$ with time [32]. If the Gaussian approximation is valid one gets $S_{\text{inc}}(q, t) = \exp(-q^2 \tilde{D} t^\beta)$ where \tilde{D} may be considered as a diffusion coefficient in fractal space. However to compare the results obtained for the different samples eq. 4 is used to analyse the data although the Gaussian approximation seems to be violated. In any case the estimated diffusion coefficients have to be considered as effective ones. For bulk PPG $\beta \approx 0.9$ is found.

Fig. 2 compares the incoherent intermediate dynamic structure factor for PPG confined to nanoporous glasses of 5.0 nm with native and silanized (coated) internal surfaces at $T=323$ K. For PPG confined to pores with native surfaces a bimodal dependence of $S_{\text{inc}}(q, t)$ on $q^2 t$ is found. The faster component is similar to the behavior measured for PPG confined to coated pores. This behavior can be explained by a two phase-model. The slow component is assigned to polymer segments forming an interfacial layer close to the pore wall with an essential lower molecular mobility than the segments located in the center of the pores (fast component). This picture is further supported by the fact that $S_{\text{inc}}(q, t)$ vs. $q^2 t$ splits into different curves for different observation times t (see Fig. 3). This should be not the case for homogenous diffusion. In the frame of the discussed two-state model chain segments are adsorbed in the interfacial layer with a lower mobility for a certain time and exchanged after that time with the regions of higher mobility. The bimodal character of $S_{\text{inc}}(q, t)$ versus $q^2 t$ disappears for observation times greater than 103 ms (see inset Fig. 2) So it can be concluded that the time constant for exchange process is between 100 and 200 ms for PPG confined to 5.0 nm pores at $T=323$ K.

For PPG embedded in 5 nm pores with coated internal surfaces $S_{\text{inc}}(q, t)$ does not depend on the observation time (see inset Fig. 3) as expected for diffusion in a spatially homogenous system. Therefore, the self-diffusion of poly(propylene glycol) confined to nanoporous glasses with silanized internal surfaces is analyzed further in detail. Fig. 4a-c shows $S_{\text{inc}}(q, t)$ versus

q^2t for PPG for different pore sizes at different temperatures and Fig. 4d compares $S_{inc}(q,t)$ for different pore sizes at the same temperature including bulk PPG. With decreasing pore sizes the diffusion slows down dramatically and $S_{inc}(q,t)$ broadens. Eq. 4 is applied to analyze the data. Fig. 5 shows the pore size dependence of the stretched exponential parameter β . This strong dependence of β on pore size can be discussed in several directions. Firstly, a distribution of diffusion coefficients due to remaining adsorption phenomena can be assumed. Polymer segments are adsorbed at the wall for a certain time and diffuse after that. Because $S_{inc}(q,t)$ is not bimodal versus q^2t (see Fig. 2) and does not depend on the observation time (see inset Fig. 3) it is concluded that the chains are in fast exchange regime. That means that the exchange time of the chains in both states is lower than the shortest observation time of 13 ms and an averaged diffusion coefficient

$$\langle D \rangle = p_f D_f + p_{ads} D_{ads} \quad (5)$$

is found where D_f and D_{ads} are the diffusion coefficients for the free and adsorbed segments, respectively. p_f and p_{ads} are the corresponding fractions with $p_f + p_{ads} = 1$. Assuming this model with decreasing pore size the fraction of adsorbed segments should increase. On the other hand, a dependence of the shape of $S_{inc}(q,t)$ versus q^2t on the pores size was not found for the diffusion of low - molecular - weight glass-forming systems confined to the same nanoporous system [8]. In principle, for such systems similar adsorption controlled effects should take place. So it can be also discussed that the strong dependence of β on pore size is a confinement-induced effect. Compared to the diffusion of a low – molecular - weight compound the diffusion of a polymer chain is a quite complex process involving a length scale which can be characterized by radius of gyration. With decreasing pore size this inherent length scale of the polymer can interfere with the dimensions of the confining host system. This can change the diffusion from $\langle z^2 \rangle \sim t$ (normal diffusion) to an anormal diffusion

characterized by $\langle z^2 \rangle \sim t^\beta$. To decide between these different pictures requires further experimental work applying well defined host systems and polymers with a low polydispersity.

Fig. 6 gives the pore size and the temperature dependence of the diffusion coefficient. With decreasing pore size D decreases (see Fig. 7) as expected from Fig. 4d. In the investigated temperature range D seems to vary linearly with $1/T$ and therefore the Arrhenius equation

$$D = D_\infty \exp\left(-\frac{E_A}{k_B T}\right) \quad (6)$$

is fitted to the data. E_A is the activation energy, D_∞ is the diffusion coefficient for $T \rightarrow \infty$ and k_B denotes the Boltzmann constant. With decreasing pore size the activation energy increases strongly (see inset Fig. 7). Again interaction effects of the polymer segments with the surface can be assumed to explain the observed behavior. This line of argumentation is supported by the consideration that purely geometric effects should be independent of temperature. But the pore size dependence of both the diffusion coefficient and the activation energy shows a change around 5 nm. This points to the fact that also size or confining effects are responsible for the slowing down of the translational mobility in the investigated system.

The so-called tortuosity [7,33] factor τ describes the influence of the pore architecture and pore interconnections. Furthermore the diffusion is influenced by interactions and confining effects which are summarized in the interaction factor F . Thus, the mean square displacement can be expressed by

$$\langle z^2 \rangle = \langle z^2 \rangle_{\text{Bulk}} \frac{F}{\tau} \quad (7)$$

where $\langle z^2 \rangle_{\text{Bulk}}$ is the mean square displacement for the bulk. The tortuosity factors are estimated measuring the diffusion of the apolar solvent decane [8] assuming that it does not interact with the nanoporous host system. It can be defined as $D_{\text{decane}}/D_{\text{decane,bulk}}$. In Fig. 8a the diffusion coefficient of PPG confined to the nanopores normalized to its value in the bulk is plotted versus inverse temperature. For comparison the pore size dependence of $D_{\text{decane}}/D_{\text{decane,bulk}}$ is given as well. The diffusion of the polymer melt is reduced due to the porous structure of glass. But the reduction of the diffusion is much larger than expected from the tortuosity. Using the estimated values of τ the interaction factor F can be calculated. Its pore size and temperature dependence is given in Fig. 8b. As expected with decreasing pore size F decreases. The increase of F with temperature reflects the increase of the activation energies with decreasing pore size.

5. Conclusion

Pulsed field gradient NMR is employed to study the influence of spatial nanometer confinement on the self-diffusion of poly(propylene glycol). As confining host system nanoporous glasses with specified pore sizes of 2.5, 5.0 and 7.5 nm synthesized by a sol/gel process are used. To study surface interaction in addition spatial confinement effects the hydrophilic silanol groups at the internal surfaces (native surfaces) were converted into the less hydrophilic trimethylsilyl groups before filling (coated surfaces).

As a general result, translational motion is slowed down by the confinement in comparison with the bulk state for both coated and uncoated internal surfaces. For the latter case the incoherent intermediate dynamic structure factor $S_{\text{inc}}(q,t)$ displays a bimodal behavior versus q^2t . This can be understood assuming a two - phase model where segments or parts of the polymer chain adsorb at the internal surfaces due to hydrogen bonds. So a layer with a reduced molecular diffusion is formed closed to the surface. The faster component is assigned to segments which are located more in the center of the pore. For observation times between

100 ... 200 ms the bimodal character of $S_{inc}(q,t)$ versus q^2t disappears at $T=323$ K. So it can be concluded that there is an exchange between the two different states and the exchange rate is in between 100 ms to 200 ms.

For silanized pores the intermediate dynamic structure factor $S_{inc}(q,t)$ shows a stretched exponential decay versus q^2t where the stretching parameter β decreases with decreasing pore size systematically. This is discussed in two directions. Firstly, a distribution of diffusion coefficients due to remaining adsorption phenomena or a distribution of pore sizes which broadens with decreasing pore size can be assumed. Secondly, the mechanism of diffusion of a polymeric chain is more complicated than that of a low – molecular - weight molecule because a length scale is involved (radius of gyration). With decreasing pore size this length can coincidence with the length scale of the confining host system. So a confinement induced change in the diffusion from a linear to a sublinear one can also be discussed. The estimated effective diffusion coefficient decreases with decreasing pore size. Its temperature dependence can be approximated by an Arrhenius law whereas the activation energy increases with decreasing pore size. Again this can be discussed assuming interaction as well as confinement induced effects. A discrimination between both requires further experimental studies on polymer model systems of a low polydispersity as a function of molecular weight.

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Figure Captions

Fig. 1 Spin echo attenuations $S_{inc}(q,t)$ versus q^2t for bulk PPG: ★ - 293 K, ○ - 303 K, △ - 313 K, ▽ - 324 K, ◇ - 335 K. The lines are fits of Eq. 4 to the data.

Fig. 2 Spin echo attenuations $S_{inc}(q,t)$ versus q^2t for PPG confined to pores of 5 nm at T= 323 K: ■ - silanized surfaces, ● - native surfaces. The observation time is 53 ms. The lines are guides for the eyes. The inset compares $S_{inc}(q,t)$ versus q^2t for PPG in uncoated pores for different observation times at T= 323 K: ◆ - 103 ms; ▲ - 203 ms. The lines are guides for the eyes.

Fig. 3 Spin echo attenuations $S_{inc}(q,t)$ versus q^2t for PPG confined to pores with a pore size of 5 nm with native surfaces at T=323 K for different observation times: ● - 33 ms; ▲ - 53 ms; ▼ - 103 ms; ◆ - 203 ms; ◀ - 303 ms. The lines are fits of eq. 4 to the data. The inset compares $S_{inc}(q,t)$ versus q^2t for PPG confined of 5 nm pores with coated surfaces at T=323 K for different observation times: ● - 13 ms; ○ - 33ms; ▲ - 53 ms; △ - 203 ms. The line is a fit of Eq. 4 to all data.

Fig. 4 Spin echo attenuations $S_{inc}(q,t)$ versus q^2t for PPG confined nanoporous glasses. a – 7.nm; b – 5.0 nm; c – 2.5 nm: ● - 298 K, ○ - 303 K, ▲ - 308 K, △ - 313 K, ▼ - 319 K, ▽ - 324 K, ◆ - 330 K, ◇ - 335 K. Lines are fits of Eq. 4 to the data. d - Spin echo attenuations $S_{inc}(q,t)$ versus q^2t for PPG for different pore sizes at T= 313 K: ■ - bulk, ● - 7.5 nm, ◆ - 5nm, ▲ - 2.5 nm. The lines are fits of Eq. 4 to the data.

Fig. 5 Averaged stretched exponential parameter β versus inverse pore size. The line is a guide for the for the eyes. The error bars are the standard deviations of the temperature averaged data. The dashed line indicates the mean squared radius of gyration. The inset gives the temperature dependence of β : ■ - bulk, ● - 7.5 nm, ◆ - 5nm, ▲ - 2.5 nm. The dashed lines indicate the average values.

Fig. 6 Temperature dependence of the self - diffusion coefficients in nanoporous glasses for different pore sizes: ■ - bulk, ● - 7.5 nm, ◆ - 5nm, ▲ - 2.5 nm. The lines are fits of Eq. 6 to the data.

Fig. 7 Diffusion coefficient at T=322 K versus inverse pore size. The line is guide for the eyes. The dashed line indicates the mean squared radius of gyration. The inset displays the activation energy E_A versus inverse pore size. The line is a guide for the eyes. The dashed line indicates the mean squared radius of gyration.

Fig. 8 a - Diffusion coefficient of PPG confined to the nanoporous glass normalized to its value of the bulk versus inverse temperature for different pore sizes : ● - 7.5 nm, ◆ - 5nm, ▲ - 2.5 nm. The solid lines are linear regressions to the data. The dashed lines represents the inverse tortuosity factor $1/\tau$: ○ - 7.5 nm, ◇ - 5nm, △ - 2.5 nm.

b -Interaction parameter F (cf. eq. 7) versus $1/T$ for different pore sizes : ● - 7.5 nm, ◆ - 5nm, ▲ - 2.5 nm. The lines are linear regressions to the data.

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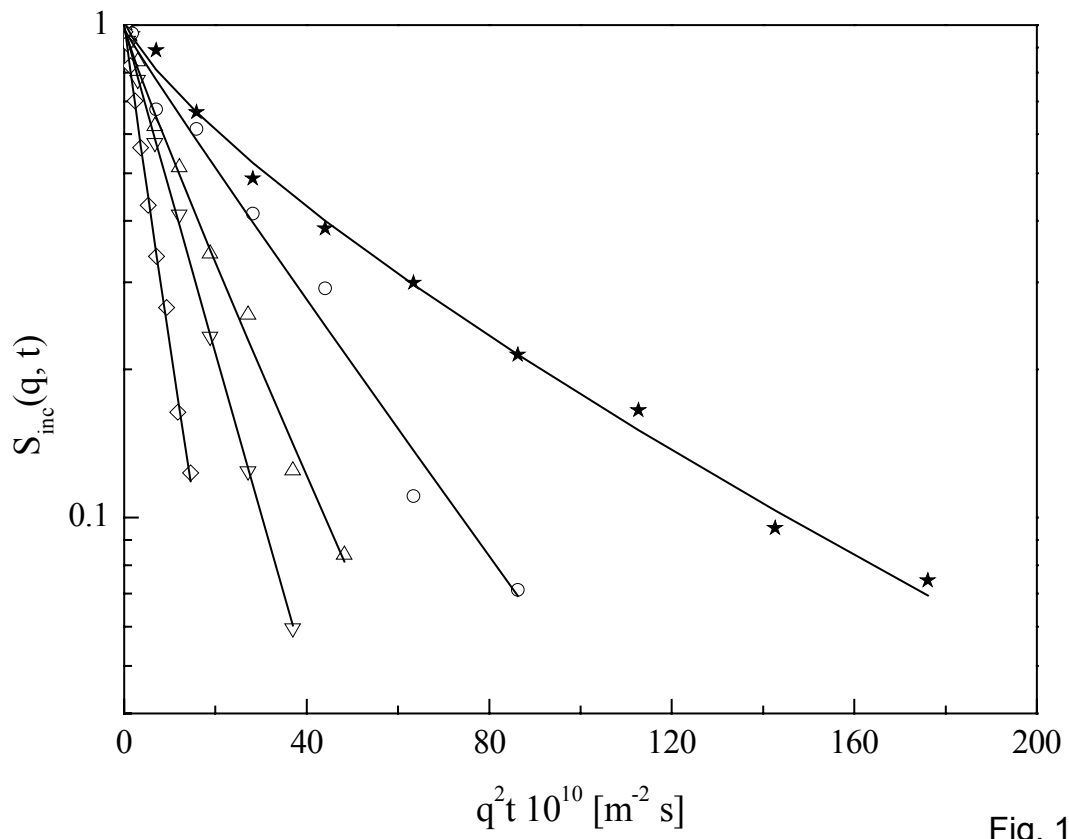


Fig. 1

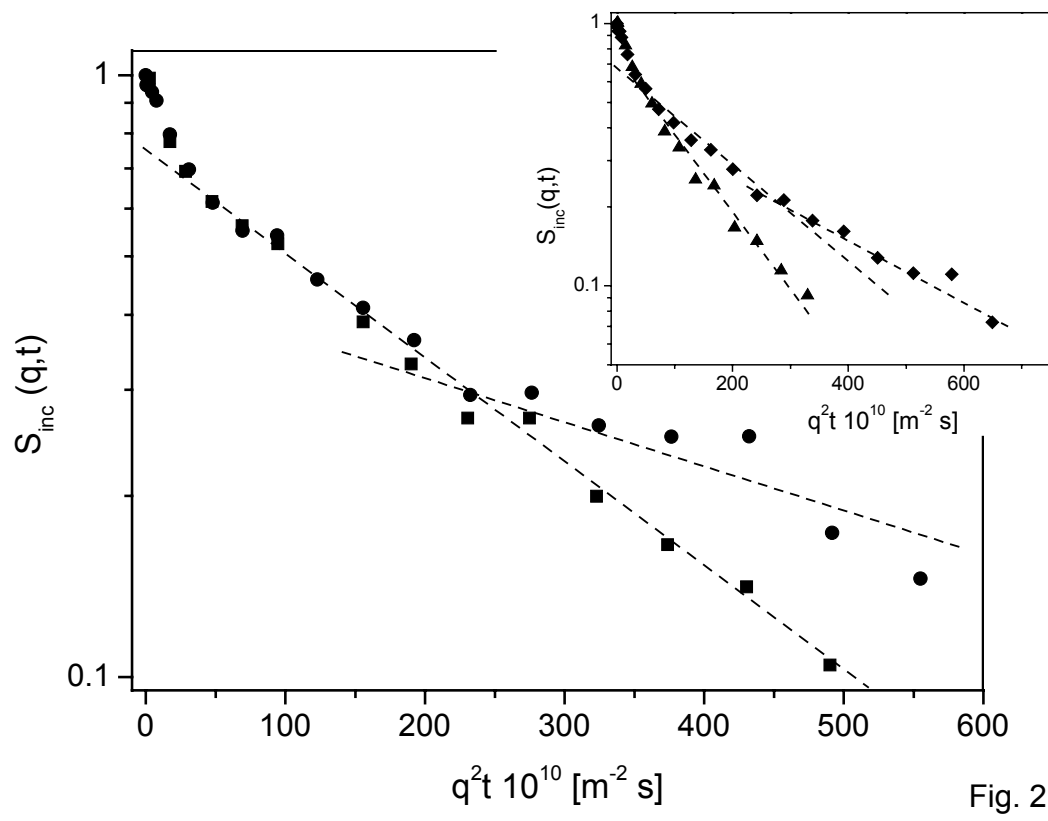


Fig. 2

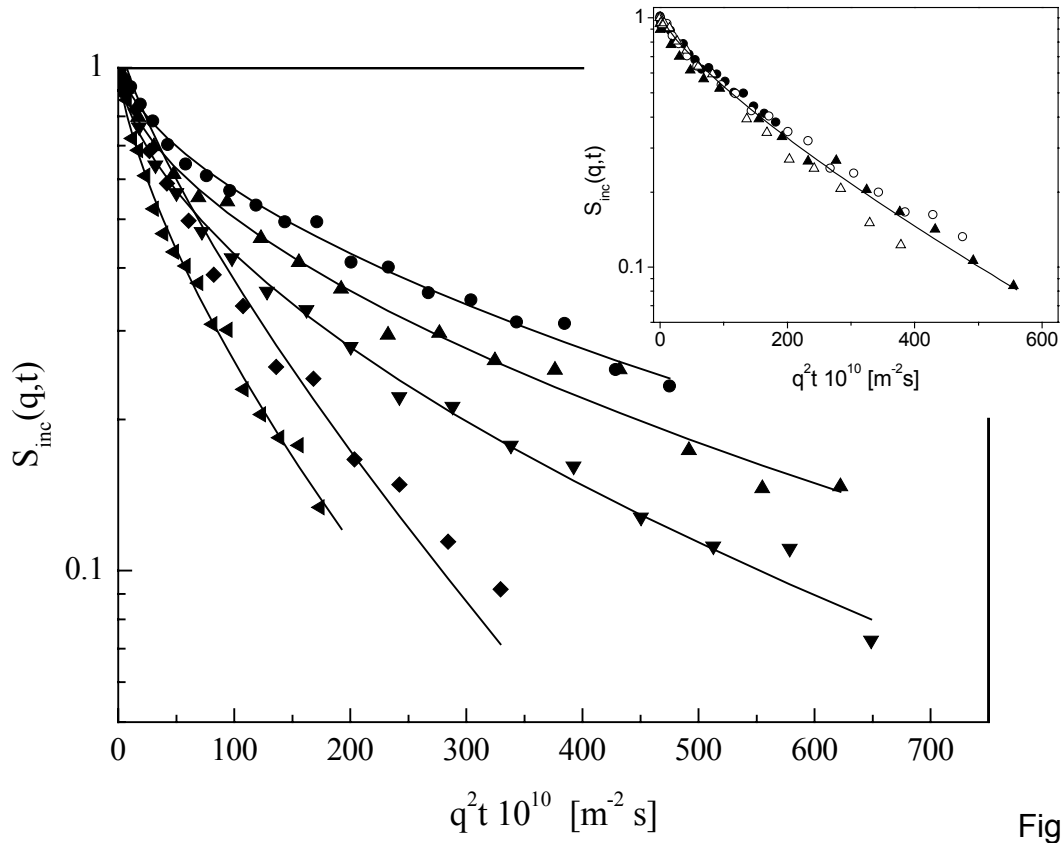


Fig. 3

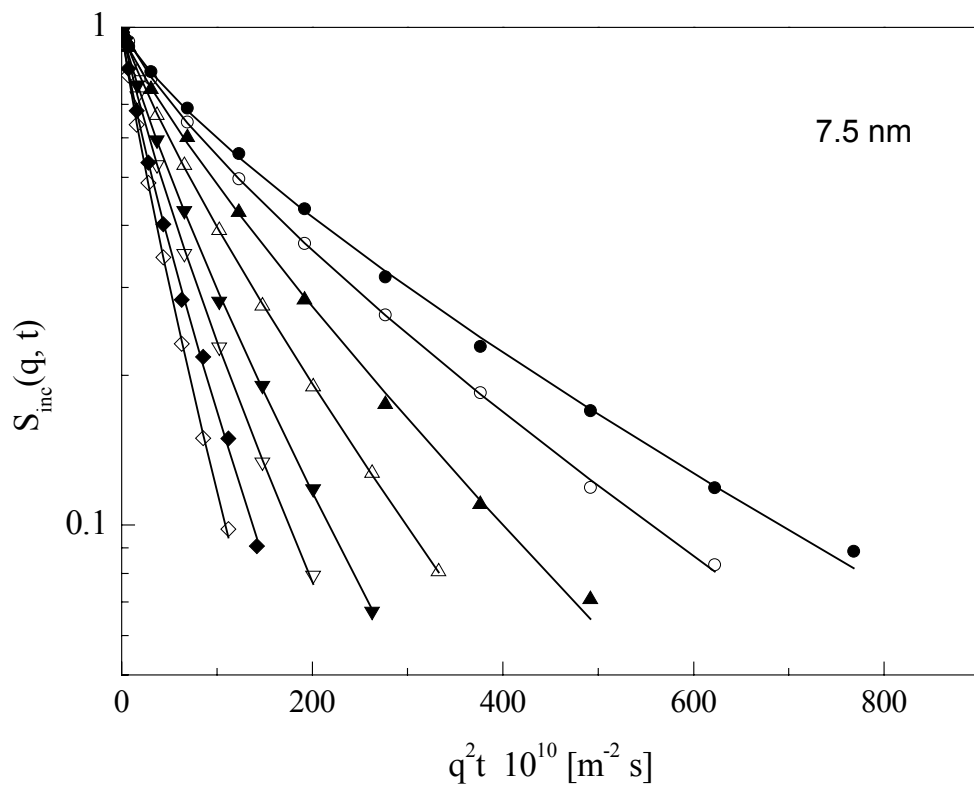


Fig. 4a

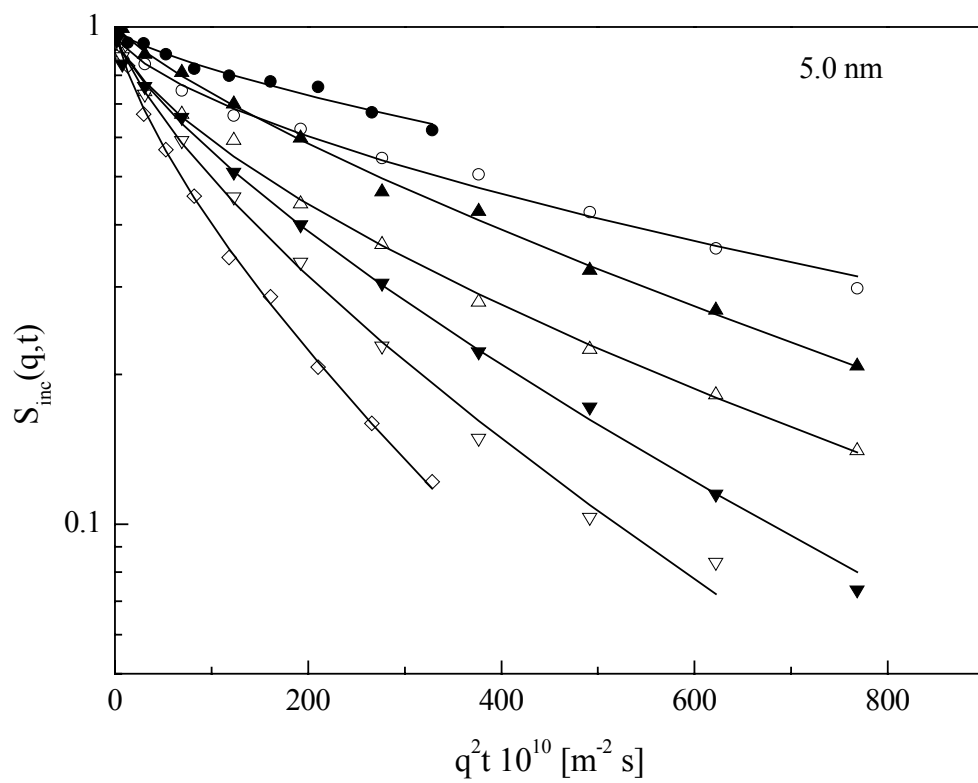


Fig. 4b

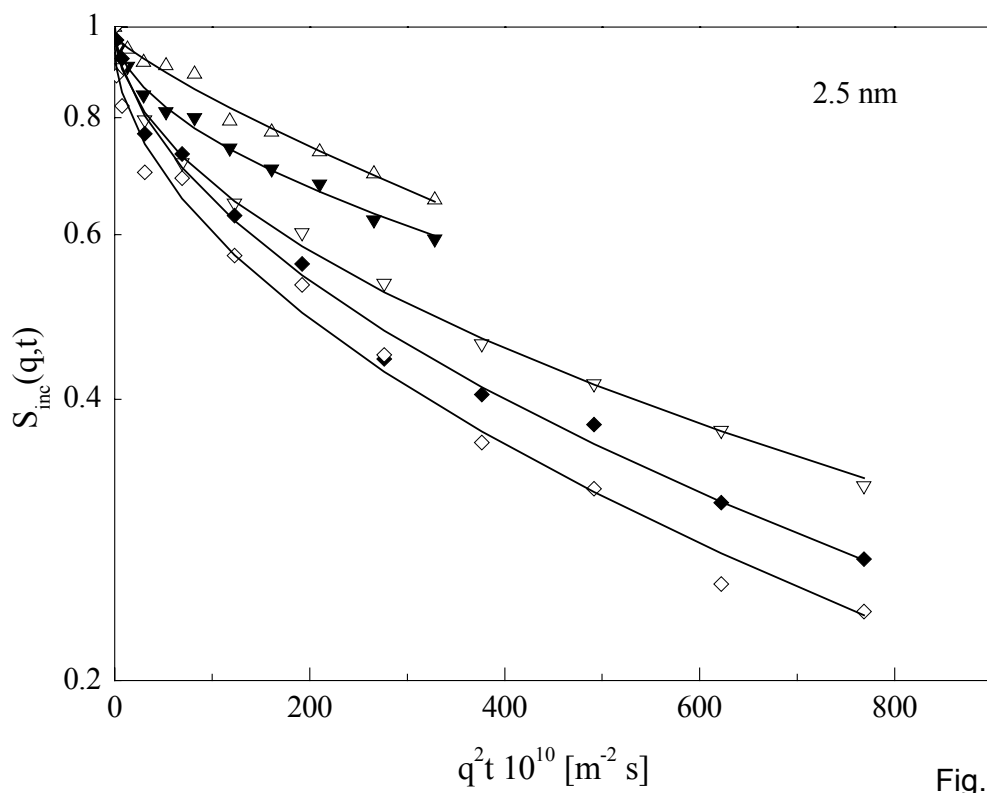


Fig. 4c

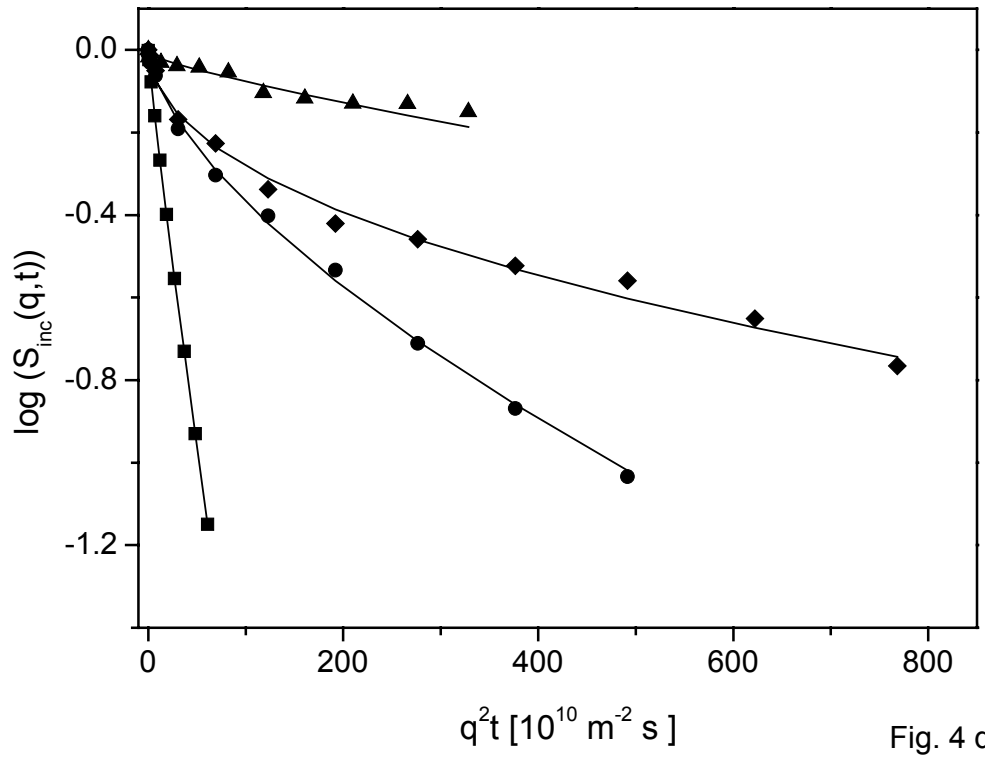


Fig. 4 d

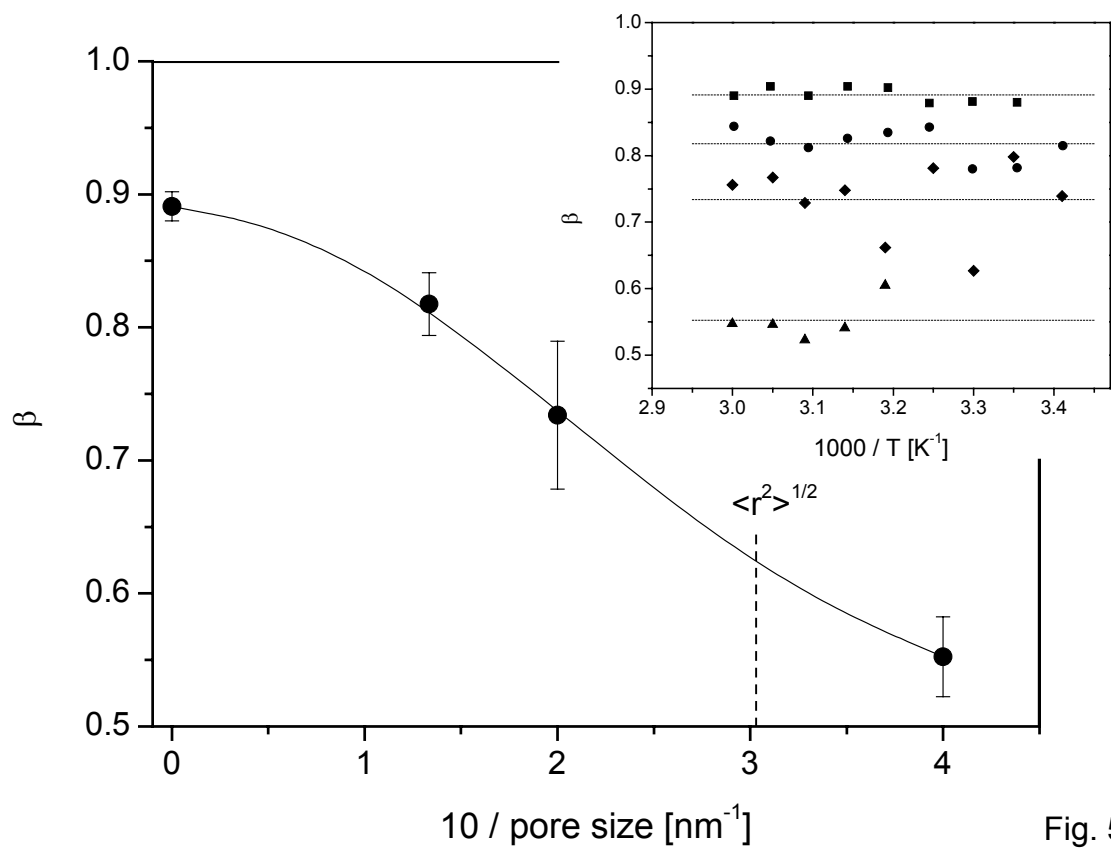


Fig. 5

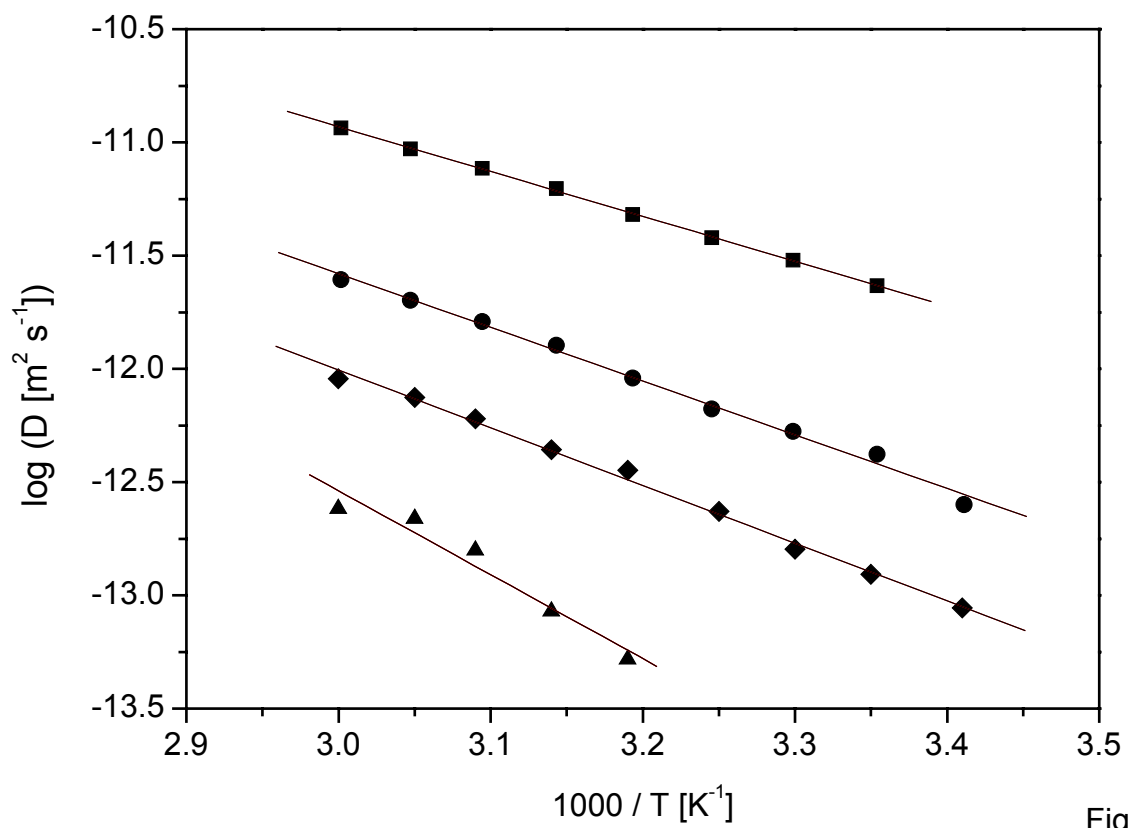


Fig. 6

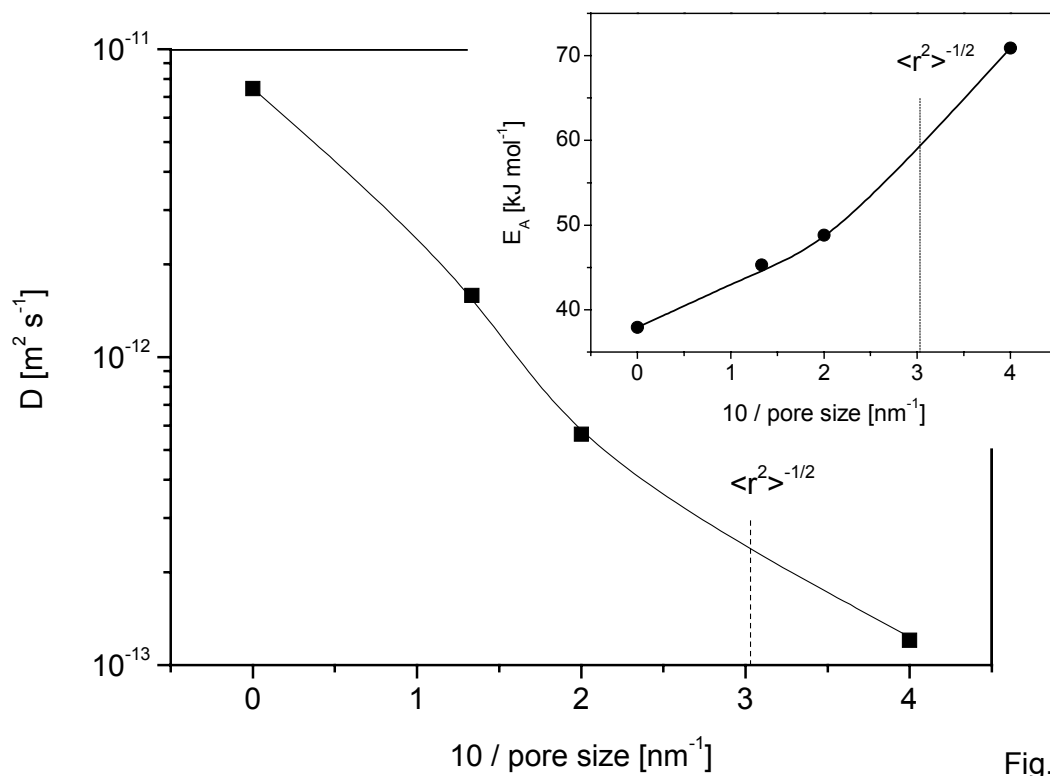


Fig. 7

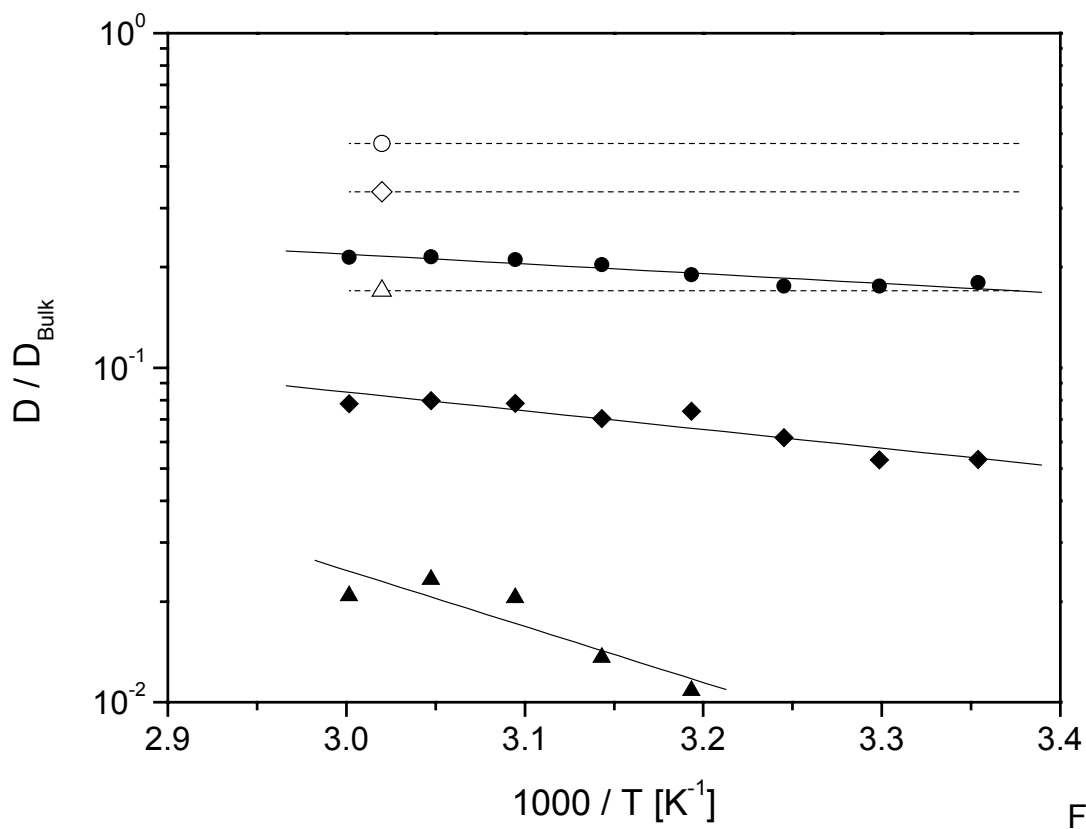


Fig. 8a

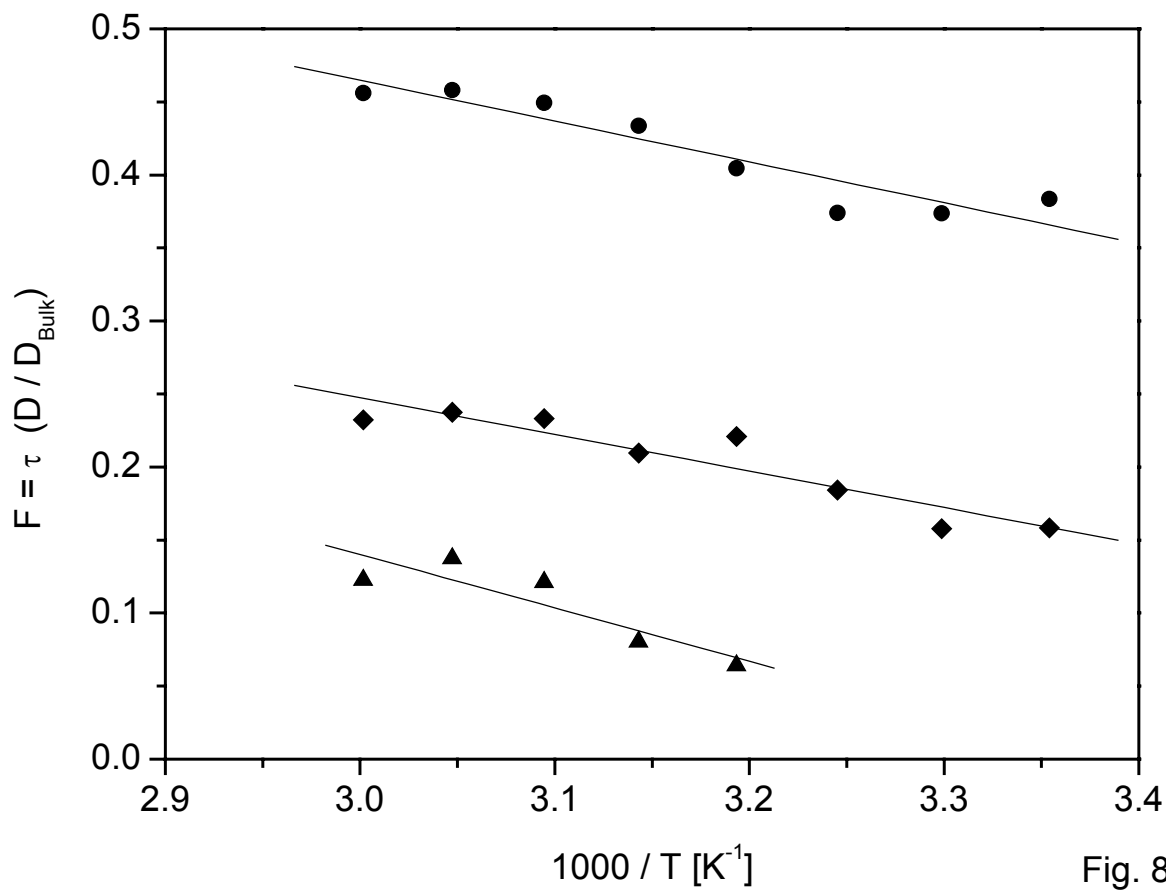


Fig. 8b