On the solution conformation of poly(ethylene oxide). An *FT*-pulsed field gradient n.m.r. self-diffusion study

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Frictional coefficients for short-chain poly(ethylene oxide) have been determined by spin-echo n.m.r. measurements in chloroform, benzene and water. The results do not support an anomalous helical conformation in aqueous media but rather a common structure in all three solvents. Diffusion coefficients for PEO in dextran in NaPSS solutions have been determined. It is found that PEO transport is related to the macroscopic viscosity of the system, i.e. to both the concentration and molar mass of the matrix polymer.

Keywords Self-diffusion; nuclear magnetic resonance; pulsed-field-gradient; dextran

INTRODUCTION

The water-solubility of poly(ethylene oxide) (PEO) is atypical in that the closely-related polyethers are not water-soluble. On the basis of spectroscopic evidence, suggestions have been made that the water-solubility of PEO results from a favourable fit with the water lattice and that the polymer has a more ordered structure in aqueous media than in organic solvents. The methods used range from neutron inelastic scattering[1], n.m.r. and i.r. spectroscopy[2,3] and spin-lattice relaxation (T_1)[4]. One interpretation is the stabilization of a helical structure in aqueous solution resembling that postulated in the solid state[5].

Self-diffusion measurements provide a means of measuring the frictional coefficients to elucidate possible differences in the conformation of PEO. This communication describes the determination of the self-diffusion coefficients of PEO in chloroform ($CDCl_3$), benzene (C_6D_6) and water (D_2O/H_2O), and comprise the same systems and polymer concentrations as those used in the neutron scattering report[1].

Earlier diffusion measurements in ternary (polymer$_1$, polymer$_2$, solvent) systems indicated that anomalous transport is a feature of linear polymers diffusing in a polymer matrix[6-9]. Since the studies referred to were made in the presence of a concentration gradient using a Schlieren technique, it was of interest to examine self-diffusion in such systems under conditions of thermodynamic equilibrium. To this end, measurements were made of PEO transport in dextran and sodium polystyrene sulphonate (NaPSS) solutions.

EXPERIMENTAL

Materials

(1) Polymers

PEO 5700 (Poly(ethylene oxide)) from Polymer Laboratories, Shrewsbury, UK: $\langle M_w \rangle / \langle M_n \rangle < 1.05$.

Dextran 10 $\langle M_w \rangle = 11.2 \cdot 10^3$
$\langle M_n \rangle = 5.7 \cdot 10^3$
$[\eta] = 0.012\ \mathrm{m^3\ kg^{-1}}$

Dextran 110 $\langle M_w \rangle = 100 \cdot 10^3$
$\langle M_n \rangle = 68 \cdot 10^3$
$[\eta] = 0.031\ \mathrm{m^3\, kg^{-1}}$

From Pharmacia Fine Chemicals, Uppsala, Sweden.

Na polystyrene sulphonate (NaPSS)
$\langle M_w \rangle = 3.54 \cdot 10^5$
$\langle M_n \rangle = 1.06 \cdot 10^6$
$\langle M_w \rangle / \langle M_n \rangle < 1.09$

From Pressure Chemicals Co., Philadelphia, USA.

(2) Solvents

Deuterated solvents, D_2O, $CDCl_3$ and C_6D_6 from CIBA-Geigy, (Switzerland).

(3) Solutions

Prior to preparation of solutions, the materials were dried overnight in vacuum at 40°C. All solutions were prepared by weighing.

Self-diffusion measurement

The pulsed-field-gradient nuclear spin-echo measurements were made at 99.6 MHz using improved versions of methods described previously[10], the experiments now being made at a fixed Δ for all δ-values as described in Ref 11. It should be emphasized that the present measurement technique monitors the Brownian displacement of individual molecules during a time $\simeq 0.3$ s, corresponding to diffusion over macroscopic distances of the order of 10^{-3}–10^{-2} mm. To minimize overlap of the PEO signal by the solvent proton signal, deuterated solvents were employed. In the case of water a (50:50) mixture of D_2O and H_2O was chosen to facilitate measurements on HDO-diffusion. D_2O was also required for lock purposes.

Unless otherwise specified, the measurements were made at 25°C except for a selected series in D_2O/H_2O for evaluation of activation energies when additional measurements were made at 50°C and 75°C. The experimental uncertainty in the diffusion coefficients is $\pm 2\%$ ($D \sim 10^{-11}\ \mathrm{m^{-2}\ s^{-1}}$) and $\pm 10\%$ ($D \sim 10^{-12}\ \mathrm{m^{-2}\ s^{-1}}$).

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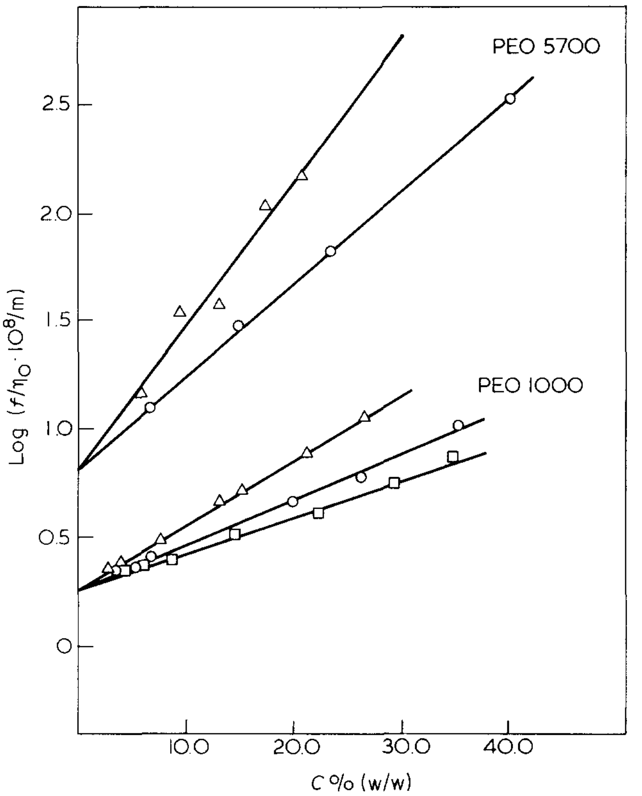

Figure 1 Plot of log (f/η_0) vs. C where f is the frictional coefficient evaluated from the self-diffusion coefficient at 25°C and η_0 is the solvent viscosity. The common intercepts in different solvents correspond to solvent-independent hydrodynamic radii for the two poly(ethyleneoxides). (△) $CDCl_3$; (□) C_6D_6; (○) D_2O/H_2O

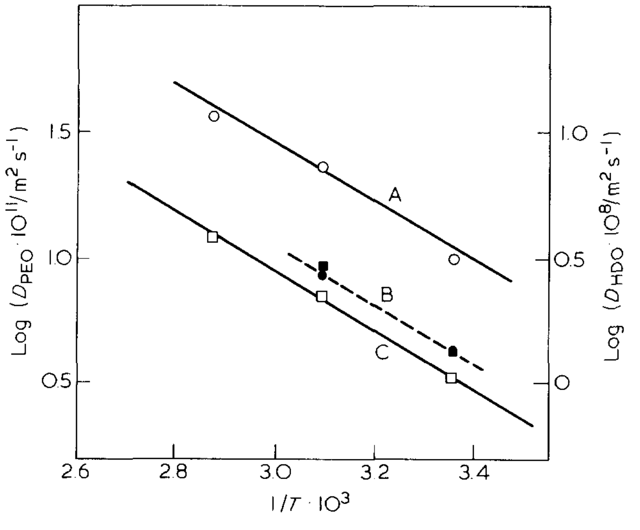

Figure 2 Arrhenius plots for (a) PEO 5700 (D_2O/H_2O; 6.6% w/w) (–○–); (c) PEO 1000 (D_2O/H_2O; 11.9% w/w) (–□–); (b) HDO in PEO 5700 (–●–); HDO in PEO 1000 (–■–). The slope corresponds to an apparent activation energy $E_a \sim 23$ kJ mol^{-1}

RESULTS AND DISCUSSION

Solvent dependence of poly(ethylene oxide) conformation

On the basis of results of neutron-inelastic scattering measurements on PEO in the solid state and in aqueous solutions, Assarsson *et al.*[1] concluded that PEO takes up a helical conformation in aqueous solution similar to that known to exist in the solid state as determined by X-ray diffraction[5]. This was considered to contrast with the conformation in chloroform ($CDCl_3$) and benzene (C_6D_6), using as an index the definition of the maxima in neutron scattering, which was found to decrease with decreasing polarity of the solvent. Subsequently, Liu *et al.*[2], using infra-red and high resolution n.m.r., and Liu and Anderson[3] employing spin lattice relaxation $(T_1)^4$, proposed further evidence that the conformation of PEO in aqueous media is more ordered than in other solvents. Self-diffusion coefficients (and hence frictional coefficients) can be obtained directly through the n.m.r. spin-echo technique. The frictional coefficient of the isolated molecule at infinite dilution provides a sensitive index to differences in the conformation of the molecule as a hydrodynamic entity. For example, the helix–coil transition for poly-γ-benzyl-L-glutamate in dichloroethane/dichloroacetic acid is readily detected by measurement of the mutual diffusion coefficient[12]. The self-difusion coefficient (and hence the frictional coefficient) can be obtained directly through the n.m.r. spin-echo technique over extended ranges of concentration. *Figure 1* shows the frictional coefficient of PEO 1000 $\left(f=\frac{kT}{D_s}\right)$, normalized with respect to the solvent viscosity, plotted as a function of concentration in chloroform, water and benzene. At infinite dilution the frictional coefficients expressed in this way are found to yield a common value and thus correspond to an equivalent radius (through Stokes' law) which is identical in the three solvents. A common intercept is also found for the high molecular weight PEO 5700 in chloroform and water. The differing slopes are mostly a reflection of the solvent densities. When concentrations are expressed in kg m^{-3}, the data are almost coincident for a given PEO sample. One concludes that water does not present any special feature as a solvent at high dilutions compared with the non-aqueous liquids on the basis of this hydrodynamic data. The self-diffusion of PEO in different solvents using a pulsed n.m.r. method has been described by Tanner, Liu and Anderson[13]. These workers concluded that the overall dimensions of a low molar mass PEO are relatively insensitive to the solvent. This was also the conclusion of Molyneaux[14] from a comparison of intrinsic viscosity data in water and a variety of other solvents. It is possible that there is a helical content which is lower than previously supposed and that a low helical content is not revealed in the hydrodynamid parameter at high dilution.

It is also possible that a helical conformation is not preferred at short chain lengths, or at the concentrations used in the investigation. Although the molar mass of the PEO used in the neutron scattering experiments was not given, it may be inferred from the high solubility in benzene that short-chain PEO was employed in the study of Assarsson *et al.*

Temperature dependence of diffusion in aqueous systems

The temperature dependence of diffusion in aqueous solution was also examined over the temperature interval 25°–75°C to see whether there is any evidence for a conformational change for PEO. The common slope for the Arrhenius plots (a)–(c) in *Figure 2* is in close agreement with the activation energy for the viscous flow of water ($E_a \sim 23$ kJ mol^{-1}). These data thus do not support a more compact conformation for PEO 5700 (or PEO 1000) at 75° than at 25°C. The finding that the frictional coefficient is related to the viscosity of the pure solvent is expected for

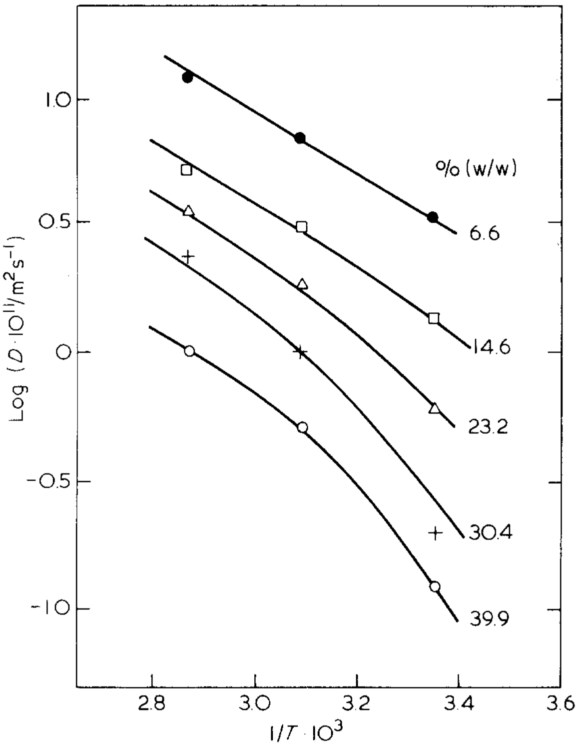

Figure 3 Arrhenius plots for PEO 5700 in water (D_2O/H_2O) at various concentrations. The limiting slope at the lowest concentration (6.6% w/w) corresponds to an apparent activation energy of $E_a \sim 23$ kJ mol^{-1}

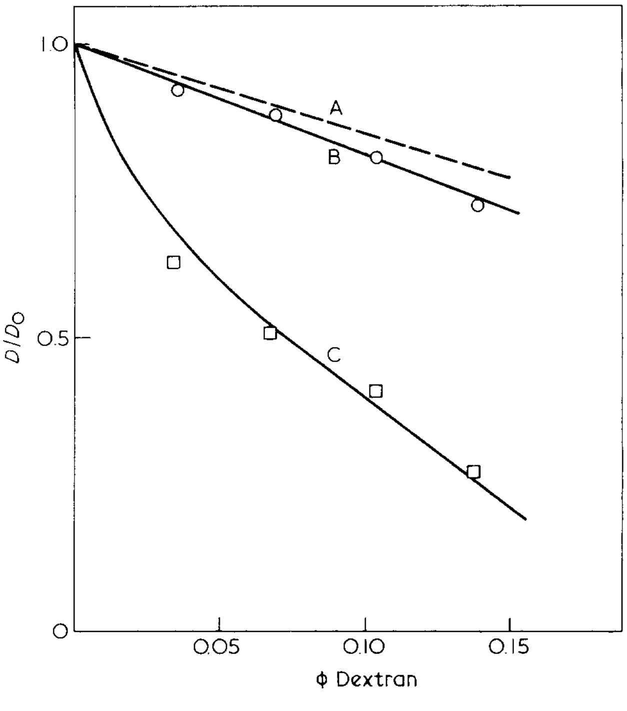

Figure 4 Self-diffusion coefficients for PEO 5700 and water (HDO) in Dextran 10 (M_w = 11.2 · 10^3) aqueous solutions at 25°C expressed as a function of volume fraction Dextran 10, ϕ. (a) According to equation (1); (b) self-diffusion of HDO; (c) self-diffusion of PEO 5700

small solutes at low concentrations according to Stokes' law. It is surprising, however, that the apparent activation energy for PEO 5700 does not reflect polymer–polymer frictional interactions at a concentration of 6.6% (w/w). *Figure 3* shows plots, analogous to those in *Figure 2*, for PEG 5700 at a series of concentrations. At the lowest concentrations the slope corresponds to an apparent activation energy, $E_a \sim 23$ kJ mol^{-1}, i.e. in agreement with the value for water itself. At the higher concentrations there is a pronounced deviation from linearity towards lower temperatures. Similar behaviour has been observed in other polymer–solvent systems[15,16]. The critical overlap concentration $\left(\left(C^* = \frac{1}{[\eta]}\right)\right)$ is approximately 10% (w/w) for PEO 5700 in water; this value approximates the onset of non-linearity in *Figure 3*.

Diffusion of PEO in polymer solutions (ternary systems)

Preston and Snowden[6,7] observed that PEO and polyvinylalcohol are transported unusually rapidly in concentrated dextran solutions, such that D/D_0 (where D_0 refers to diffusion in the pure solvent) greatly exceeds unity. These findings were supported by measurements of Kitchen[8] employing a capillary technique known to yield the self-diffusion coefficient for small molecules in binary systems. These data were subsequently discussed by Laurent *et al.*[9] in terms of the interplay between thermodynamic and hydrodynamic forces operative in diffusion. Recently, however, it has been demonstrated by Preston *et al.*[17] that the phenomenon instead has its origin in concentration inhomogeneities in the vicinity of the initial boundary, leading to local regions of instability ('finger' formation). Since the n.m.r. pulsed-field-gradient

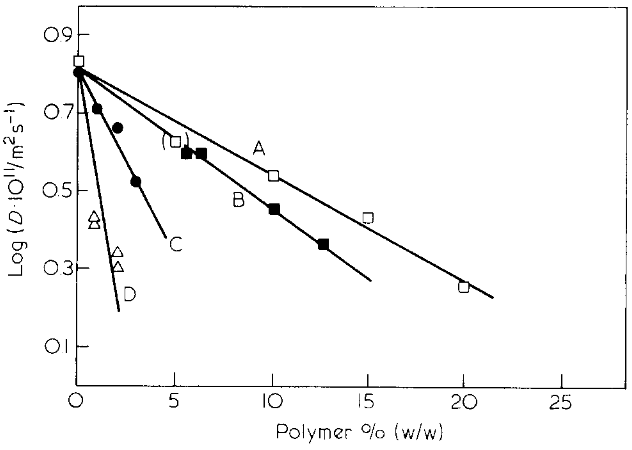

Figure 5 Self-diffusion coefficients for PEO 5700 at 25°C in solutions of: (a) Dextran 10 (M_w = 11 200) (–□–); (b) Dextran 110 (M_w = 100 500) (–■–); (c) NaPSS (M_w = 354 000) (–●–); (d) NaPSS (M_w = 1 060 000) (–△–)

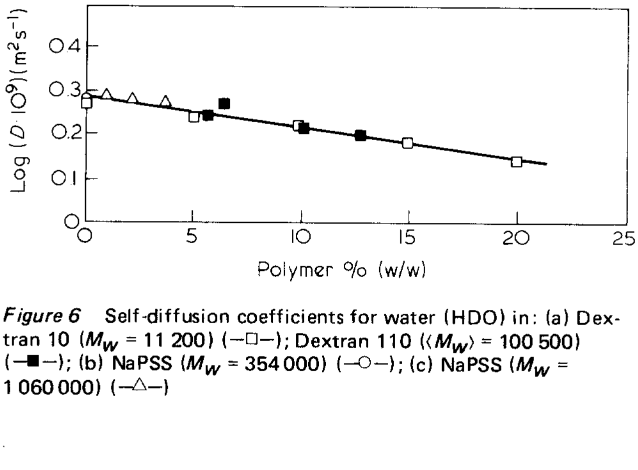

Figure 6 Self-diffusion coefficients for water (HDO) in: (a) Dextran 10 (M_w = 11 200) (–□–); Dextran 110 (⟨M_w⟩ = 100 500) (–■–); (b) NaPSS (M_w = 354 000) (–○–); (c) NaPSS (M_w = 1 060 000) (–△–)

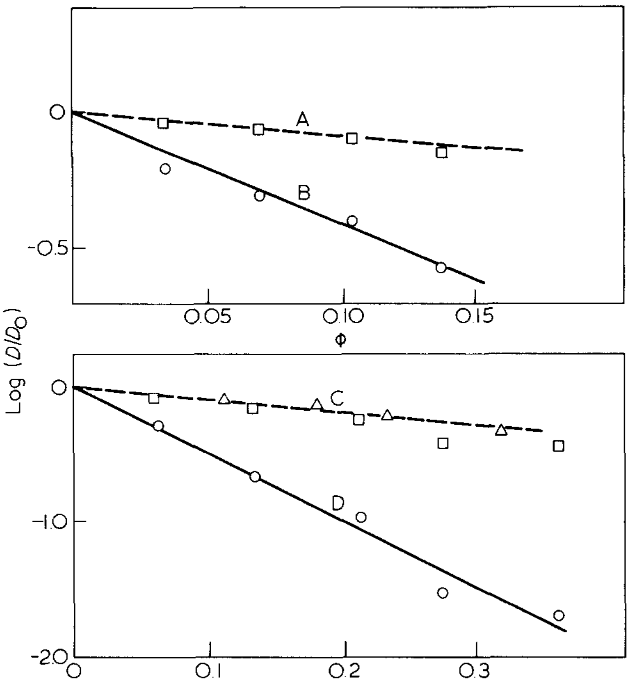

Figure 7 Log (D/D_0) vs. volume fraction polymer, ϕ, for: (a) water (HDO) in Dextran 10 (M_w = 11 200), broken line according to equation (1) (–□–); (b) PEO 5700 self-diffusion in Dextran 10 (–○–); (c) water (HDO) in PEO 5700 solutions (–□–); water (HDO) in PEO 1000 solutions (–△–); broken line according to equation (1); (d) PEO 5700 self-diffusion (–○–); all data at 25°C

technique is used under conditions of thermodynamic equilibrium, it is an excellent method for obtaining true data for the self-diffusion of the components in such systems. Thus *Figure 4* shows the present data for one of the systems investigated by Kitchen[8] using the capillary method, i.e. PEO 5700 diffusing in dextran 10 $M_w = 11.2\cdot10^3$) and for which anomalous transport was found. As expected, D/D_0 for the PEO decreases steeply owing to enhanced frictional interactions as the concentration is increased. *Figure 5* shows data for PEO self-diffusion in concentrated dextran solutions and also solutions of NaPSS of different molar mass. It is to be expected that the diffusion rate of a chain polymer will vary differently with concentration depending on the molar mass of the matrix polymer. Thus the self-diffusion of PEO 5700 in Dextran 110 is strongly reduced in comparison with the diffusion rate in Dextran 10 at a given concentration of polymer matrix. The magnitude of the effect in NaPSS solutions is surprisingly large, however. The corresponding results for water (HDO) diffusion in these systems are of some relevance; *Figure 6*. In both the dextran and the NaPSS solutions the HDO self-diffusion is approximately described by the Wang equation (see below) as is typical for solvents or solutes of low molar mass diffusing in a polymer matrix[22]. However, in the NaPSS solutions, indications were found of the existence of a small fraction of water with a considerably lower diffusion coefficient. This may correspond to solvent occluded in macrostructures present in these solutions. This interpretation finds some support in photon correlation spectroscopy results on this polymer[18]. It was found that the correlation function for NaPSS deviates markedly from a simple exponential function.

Comparison of self-diffusion in binary and ternary systems

When the spaces in a macromolecular solution (or gel) are large compared with the diffusant molecule, the diffusion coefficient is reduced by a function of the volume fraction of the macromolecules present in the system. For example, Wang[19] deduced a simple expression for the diffusion of water in protein solutions which has been widely applied:

$$D = D_0(1 - \alpha\cdot\varphi) \tag{1}$$

where $\alpha = 1.5$ (spherical diffusants) and φ = volume fraction macromolecules. *Figure 7* includes data for water diffusing in PEO solutions where the dashed line represents Wangs[19] equation with $\alpha = 1.5$. The agreement is good.

It may be noted that the data for the self-diffusion of PEO 5700 (*Figure 7D*) coincide with those for the diffusion of this polymer fraction in Dextran 10 (*Figure 7B*), i.e. both sets of data are described by a common function when the concentration of the respective polymer is expressed as the volume fraction ($\varphi = C\bar{v}_2\rho$, where C is weight fraction, $\bar{v}_2$ the partial specific volume and ρ the solution density). This shows that D/D_0 is determined by the excluded volume interactions in the system.

Figure 8 shows that (D/D_0) is smaller for PEG 5700 than for PEO 1000 at the same weight concentration of polymer. This is of course reasonable since it is the polymer–polymer frictional interactions which mainly decide the magnitude of D/D_0 when the diffusant is a polymer molecule rather than a small solute (or solvent) molecule. Thus it is to be expected that D/D_0 will be related to the macroscopic viscosity of the solution and consequently to the molar mass of the polymer. This agrees with the conclusions of Hallett and Gray[20] and Turner and Hallett[21] who studied the transport of polystyrene spheres in polysaccharide solutions and those of Tanner[22] who investigated the self-diffusion of poly(dimethylsiloxane).

CONCLUSIONS

One may conclude that hydrodynamically there is no support for a helical conformation for shortchain

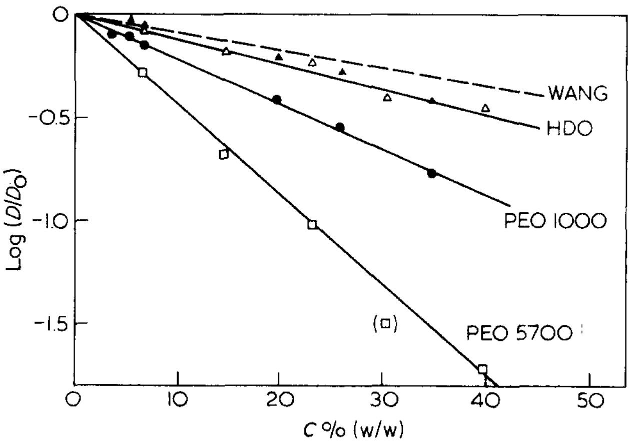

Figure 8 Self-diffusion coefficients for: (a) water (HDO) (–△–); (b) PEO 1000 (–○–); (c) PEO 5700 (–□–); in a diagram of log (D/D_0) vs. C where C is concentration in % w/w. All data at 25°C. The broken line corresponds to equation (1)

poly(ethylene oxide) in aqueous solution. Diffusion data as a function of temperature indicate a common conformation within the temperature interval 25°–75°C.

Diffusion of PEO 5700 in concentrated aqueous solution and in concentrated dextran solutions shows that the transport of a linear polymer chain is related to the macroscopic viscosity of the system. This contrasts with the diffusion of solvent (or small solutes) in a polymer matrix where simple obstacle theories adequately describe the transport process.

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