Self-diffusion of poly(ethylene oxide) in aqueous dextran solutions measured using FT-pulsed field gradient n.m.r.

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Transport in ternary polymer$_1$, polymer$_2$, solvent systems has been investigated using an n.m.r. spin-echo technique. The dependence of the self-diffusion coefficient of poly(ethylene oxide) polymers on the concentration and molecular size of dextran in aqueous solution has been measured. Monodisperse poly(ethylene oxide) fractions ($\bar{M}_w = 7.3 \times 10^4$, $2.8 \cdot 10^5$ and $1.2 \cdot 10^6$) and dextrans ($\bar{M}_w = 2 \cdot 10^4$, $1 \cdot 10^5$ and $5 \cdot 10^5$) have been employed over a range of concentration up to the miscibility limit in each system. It is found that when the molecular size of the diffusant is commensurate with or exceeds that of the matrix polymer, a relationship of the form: $(D/D_0)_{PEO} = \exp{-k(C[\eta])}$ is applicable, where $C[\eta]$ refers to the dextran component and is considered to describe the extent of coil overlap in concentrated solution. (D/D_0) is independent of the molecular size of the poly(ethylene oxide), at least in the range studied ($\bar{M}_w < 300\,000$).

Keywords Self-diffusion; n.m.r.; poly(ethylene oxide); dextran; ternary system

INTRODUCTION

Transport phenomena in polymeric multicomponent systems have attracted considerable attention in recent years. Interest has mainly been directed to elucidating the interactions between mixtures of polymers in a low molecular weight solvent (polymer$_1$, polymer$_2$, solvent). Dextran solutions have frequently been used partly because they constitute a suitable model for the extracellular matrix of connective tissue, (see the recent review of Preston *et al.*[1] for references), but also because of a number of attractive features: dextran is a neutral polymer, available as well-characterized fractions which are soluble in water up to concentrations in excess of 50% (w/w). The present communication deals with the self-diffusion of monodisperse fractions of poly(ethylene oxide) (PEO) in dextran solutions. PEO is highly suitable as a model neutral polymer in n.m.r. spin-echo investigations owing to its favourable transverse relaxation time (T_2). The concentration of PEO has been held at 1 kg m^{-3} in order to maximally extend the range of dextran concentration. The latter extends from the dilute to the semi-dilute regions, up to the limit of miscibility of the two polymers in aqueous solution.

Measurement of self-diffusion coefficients is uniquely important since it allows one to investigate the translational mobility of a molecule in the absence of concentration gradients, i.e. under essentially equilibrium conditions. This is invaluable in elucidating dynamic aspects of polymer solutions and especially those of ternary systems in which thermodynamic factors play a dominant role. Precise measurements of self-diffusion have only been possible on small molecules, but in recent years advances in pulsed field gradient n.m.r. have greatly extended the usefulness of the method to encompass polymer systems[1-5]. This technique monitors the

Brownian displacement of individual molecules during a time ~ 300 ms and for simple random walk behaviour yields the self-diffusion coefficient. This contrasts with, for example, quasi-elastic light scattering which measures the mutual diffusion of solute at finite concentrations. A new technique, also giving the self-diffusion coefficient, is forced Rayleigh light scattering (FRS)[6]. A valuable feature of these techniques is the possibility of exploring the frictional behaviour over extended ranges of molecular weight and concentration where conventional means of following diffusional processes have grave limitations. It may be noted that comparable information is, in principle, also obtainable from sedimentation studies in the ultracentrifuge. However, the experiments are difficult to perform with the required precision at high concentrations and the sedimentation of the matrix polymer is a complicating factor; see the discussion of Laurent *et al.*[7] and Langevin and Rondelez[8].

EXPERIMENTAL

Polymers: Poly(ethylene oxide) (PEO)

PEO 5.7: $\bar{M}_w = 5.7 \cdot 10^3$; $[\eta] = 0.012$ m^3 kg^{-1} ($\bar{M}_w/\bar{M}_n = 1.10$)

PEO 73: (SE-8)*; $\bar{M}_w = 0.73 \cdot 10^5$; $[\eta] = 0.0930$ m^3 kg^{-1} ($\bar{M}_w/\bar{M}_n = 1.02$)

PEO 280: (SE-30)*; $\bar{M}_w = 2.78 \cdot 10^5$; $[\eta] = 0.235$ m^3 kg^{-1} ($\bar{M}_w/\bar{M}_n = 1.05$)

PEO 1200: (SE-150)*; $\bar{M}_w = 1.2 \cdot 10^6$; $[\eta] = 0.650$ m^3 kg^{-1} ($\bar{M}_w/\bar{M}_n = 1.12$)

(* Denotes type according to Toya Soda Mfg. Co. Ltd., Tokyo, Japan.)

Dextran

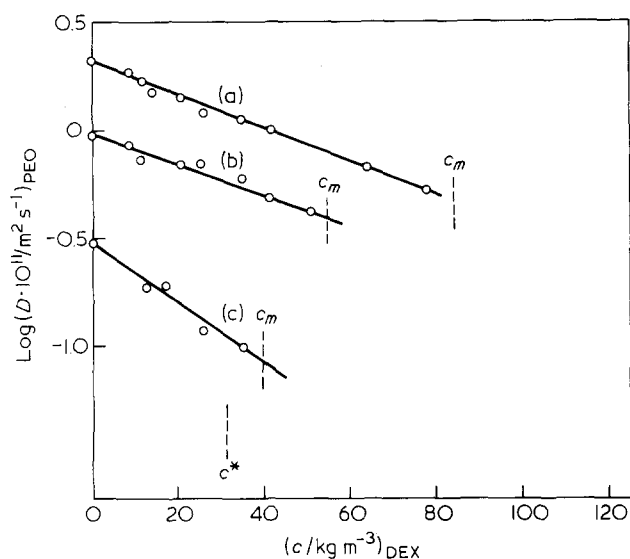(a) DEX 10: $\bar{M}_w = 1.1 \cdot 10^4$; $[\eta] = 0.012$ m^3 kg^{-1}

Figure 4 Relationship between log (D/D_0) for PEO and the overlap parameter $C[\eta]$ [19-21], where the latter refers to the dextran matrix:

	PEO 5.7	PEO 73	PEO 280
in:	DEX 10 (X)	DEX 20 (□)	DEX 20 (■)
	DEX 110 (O)	DEX 110 (△)	DEX 110 (●)
		DEX 500 (▽)	

dilute domains where the critical concentration separating these regions is defined here, following Weissberg *et al.*[12], as $C^* = \dfrac{1}{[\eta]}$. At C^* the macromolecules begin to touch (incipient overlap). The slopes in *Figures 2* and *3* increase with increasing molecular weight of the dextran. As observed by Laurent *et al.*[1] for the diffusion of human serum albumin in dextran solutions of various molar mass, this dependence does not increase in direct proportion to the molar mass of the matrix polymer. As the molecular size of the matrix polymer increases with a given diffusant, the dependence becomes less marked. Tanner[2] made a similar finding for the diffusion of PEO in polydimethyl siloxane.

Exponential decay of D/D_0 is also in keeping with 'obstruction' concepts and the semi-empirical expressions derived for them; see, for example, Ogston *et al.*[13,14], who deduced a relationship of the general form:

$$D/D_0 \propto \exp(-B \cdot C^{1/2}) \qquad (1)$$

where B is proportional to the radius of the diffusing spherical particle and C is the concentration of matrix polymer. Equation (1) was derived for compact solutes, such as globular proteins. However, hydrodynamic expressions applicable to such particles are frequently adequate for chain molecules in a Gaussian segment distribution, which are solvent-impermeable, and for which the intrinsic viscosity follows the Flory–Fox relationship, see, for example, the discussion in ref. 28.

This is possibly a good approximation for the highly flexible PEO chains. An example of the application of equation (1) to extended rod-like chains (Na deoxyribonucleate) is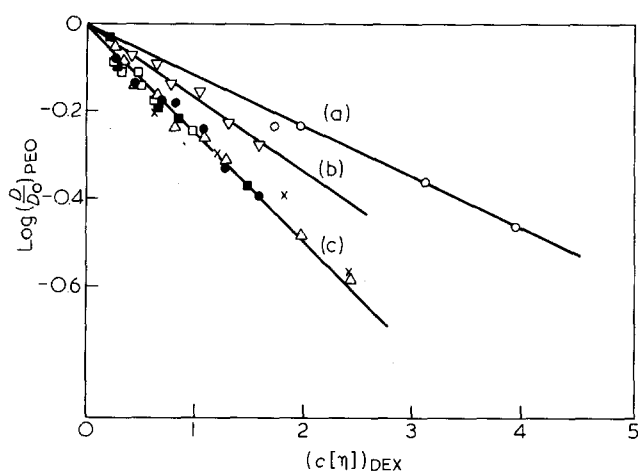 provided in the work of Laurent *et al.*[17] who investigated the diffusion of some u.v.-absorbing polymers in dilute aqueous hyaluronate solutions in the ultracentrifuge. These authors concluded that a relationship of the form of (1) was valid. Their data can, however, in fact be seen to more closely follow an

exponential equation of the type:

$$\frac{D}{D_0} = \exp(-k \cdot C) \qquad (2)$$

as found for the present data. It was also noted by these workers that the hydrodynamic radius calculated from equation (1) was apparently *smaller* than the hydrodynamic radius calculated from the diffusion coefficient in pure solvent. This led them to conclude[17,18] that there was end-on movement of the asymmetric particles in the polymer matrix. This result, however, does not necessarily support a reptation mechanism[31] for the transport of chain molecules in a ternary system. Rather it suggests that, while equation (1) may be valid for solid spheres (globular proteins), this relationship is inadequate for describing the diffusion of a rod-like polymer in a solution of a second linear polymer and does not allow evaluation of the radius of the diffusing equivalent hydrodynamic coil. This should not be expected since the theory[14] underlying equation (1) takes no account of the hydrodynamic interaction between diffusant and the matrix polymer which is unusually large in this case.

The present results are consistent with a somewhat different interpretation. There is a good correlation of log (D/D_0) for PEO polymers with the product $C[\eta]$ for the dextran matrix. The latter parameter is frequently used in unifying data for different concentrations and molecular weights in the same polymer system[19-21]. Frisch and Simha[22] postulated that the dimensionless quantity $C[\eta]$ measures the degree of coil overlap (incipient coil overlap, $C[\eta] \sim 1$) in solution if one neglects changes in coil dimensions with concentration. Since the retarding effect of the matrix polymer on the mobility of the first polymer will depend on some function of the molecular weight and contentration of matrix polymer, it is not surprising that the parameter $C[\eta]$ is a useful one. *Figure 4c* shows that when the molecular size of the diffusing polymer approaches or is *substantially greater* than that of the matrix polymer, there is an excellent correlation between log (D/D_0) and $C[\eta]$. The relationship has the form:

$$D/D_0 = \exp(-0.56\,C[\eta]) \qquad (3)$$

for the present systems. This contrasts with the behaviour predicted by equation (1) which describes proportionality to the radius of the diffusing globular particle. The present results thus show that, for a randomly coiling polymer which is commensurate in size with the molecules of the second linear polymer within which it is diffusing, the diffusional retardation (D/D_0) is determined only by the frictional interactions imposed by the matrix polymer, i.e. there is a relationship to the macroscopic viscosity of the system. It is of course well known that in the limit of very small diffusing molecules (e.g. solvent) diffusing in a polymer solution there is a correlation only with the concentration of matrix polymer according to first-order expressions, such as that of Wang[23], and no dependence on matrix polymer molecular size[11]. Thus the divergent cases shown in *Figures 4a* and *b* apparently indicate intermediate situations where the size of the diffusant is significantly smaller than that of the matrix polymer. As the diffusant size increases relative to the matrix polymer, a correlation with the macroscopic viscosity of the system is observed (*Figure 4c*). Similar observations have been
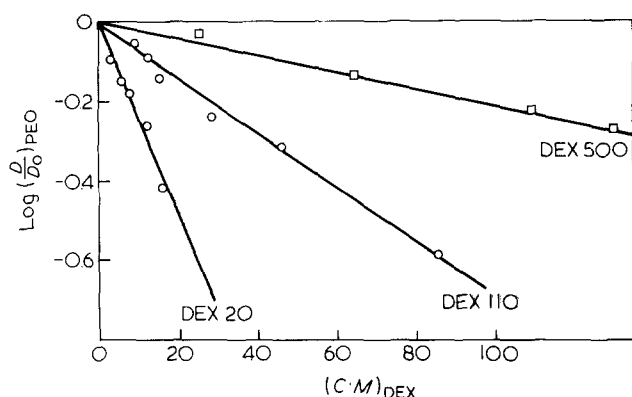
Figure 5 Plot of log (D/D_0) *versus* segment–segment contact parameter $(C \cdot \bar{M}_w)$ according to Bueche[24]. Data are for PEO 73 as a diffusant in solutions of DEX 20, DEX 110 and DEX 500, (compare *Figure 2*)
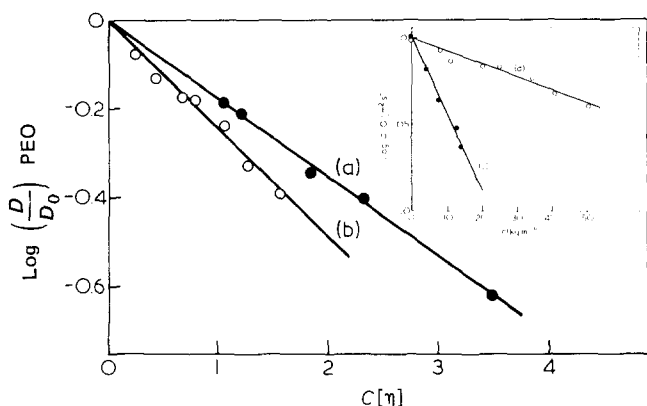

Figure 6 Comparison of diffusion data for binary and ternary systems. (a) PEO 280 in D_2O where $C[\eta]$ refers to the PEO component. (b) PEO 280 in DEX 110/D_2O where $C[\eta]$ refers to the DEX 110 component. Insert: log $(D \cdot 10^{11}/m^2 s^{-1})$ vs. concentration for (c) PEO 280 in D_2O and (d) PEO 280 in DEX 110/D_2O
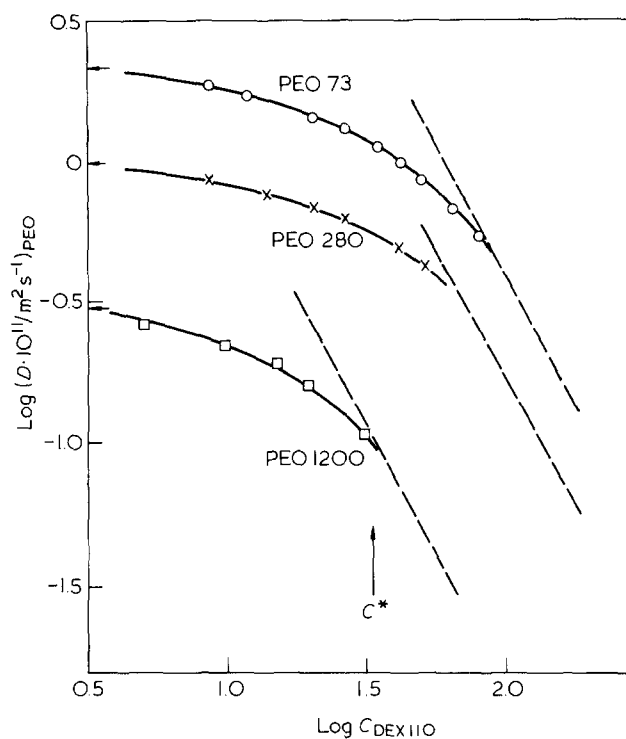

Figure 7 Double logarithmic plot of self-diffusion data for three fractions of PEO in DEX 110. The broken lines have a slope of $\alpha = -1.75$ in accordance with ref. 25

made by Preston *et al.*[1] for the diffusion of various proteins in dextran solutions and by Turner and Hallett[29] and Hallett and Gray[30] who investigated the diffusion of polystyrene latex particles in hyaluronate and dextran solutions.

Bueche[24] has proposed the product $(C \cdot M_w)$ as an alternative correlation parameter which expresses segment–segment contacts in systems of uniform segment density. The product $C \cdot M_w$, however, considerably overestimates the dependence of (D/D_0)—see *Figure 5*.

There is some justification for a comparison between binary and ternary systems. *Figure 6* shows data for PEO in D_2O and also in the presence of DEX 110. The insert shows that the frictional interactions are much greater in the binary PEO/D_2O system than when the same polymer is diffusing in a dextran solution of the same mass concentration. Normalization hydrodynamically using the parameter $C[\eta]$ (main diagram) somewhat overcompensates for the disparate diffusion rates but serves to indicate the dominant part played by the macroscopic viscosity.

It may be noted that scaling theory[25] predicts linear plots of log D vs. log c in the semi-dilute region with a value of slope $\alpha = -1.75$.

The present data, however, only extend into the lower part of the semi-dilute region, as shown in *Figure 7*, owing

to the limitations of polymer compatibility. Hadgraft *et al.*[27] have described QELS measurements of the diffusion of poly(–methyl methacrylate) solutions in benzene over a similar concentration interval and experienced the same problem. Their results have the same qualitative character although these authors give a limiting slope of $\alpha = -0.6$. In *Figure 7* the broken lines have been given a slope of $\alpha = -1.75$ as for binary systems[25]; it is not an implausible limiting value. The same qualitative picture is provided by the results of *Koñák et al.*[26] who measured the diffusion of block copolymer micelles in solutions of polystyrene, also using QELS. These authors also concluded that the diffusion of micelles is governed by the macroscopic viscosity of the system.

ACKNOWLEDGEMENTS

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