Self diffusion of small molecules in aqueous solution of poly(vinylpyrrolidone)

Johan Carlfors and Roger Rymdén

Institute of Physical Chemistry, University of Uppsala, Box 532, S-751 21 Uppsala, Sweden

The self-diffusion coefficients of small penetrants were measured in aqueous solutions at varying concentrations of poly(vinylpyrrolidone). Measurements have been performed using the n.m.r. pulsed-gradient spin-echo (PGSE) technique and the classical gradient diffusion (CGD) method, modified for ternary systems. A good agreement was found between the two, confirming the validity of the latter. The results have been quantitatively analysed by a free-volume approach adapted for diffusion of a solute in moderately concentrated polymer solutions. From this model a linear relationship is predicted between $\ln D/D_0$ and ϕ^{-1}, the reciprocal volume fraction of solvent, which was also found experimentally for all diffusants studied. An enhanced concentration dependence of penetrant diffusion with increasing size of the diffusing molecules was observed. These findings are in agreement with predictions from the free-volume theory.

(Keywords: self-diffusion; poly(vinylpyrrolidone); free-volume theory; nuclear magnetic resonance; solute-diffusion; penetrant)

INTRODUCTION

Self-diffusion of small molecules in polymer solutions is an important process in industrial and biological applications. An excellent review on this matter was presented by Muhr and Blanshard[1] with extensive reference to experimental data and current theories, describing the dependence of diffusion on polymer concentration in gels and solutions. Many of these theories[2-4] have only limited application, however, and many experimental data disagree with their predictions. These disagreements are usually corrected for by adjustment of parameters like; hydration of polymers, shape of obstacles or excluded volume of polymer. In many cases, specific interactions between diffusant and polymer complicate the interpretation of experimental results.

Awaiting a more general solution to this problem, i.e. molecular dynamics (MD) calculations (see for example ref. 5), the statistical mechanical theory of Macedo and Litovitz[6] is quite promising. It combines the free-volume theory[7] with the Eyring rate theory[8] thus regarding diffusion as a jumping process, governed by the probability of the formation of a hole into which the diffusing molecule can jump and the probability that the molecule acquires sufficient energy to overcome the attractive forces, holding it to its neighbours. The Macedo–Litovitz theory thus accounts for both changes of the available space for diffusion and attractive forces present in the system, the latter of which are not included in the other approaches mentioned above.

The free-volume theory was successfully applied to simple liquids[6,7] but has been extended to macromolecular solutions by Fujita[9] and Vrentas and Duda[10,11]. These theories predict the self-diffusion coefficients of both polymer and solvent and their temperature-, molecular weight- and concentration de-

pendences and have been experimentally verified by numerous investigations[9,12-21].

In the present study, we have measured the self-diffusion coefficients of small molecules in aqueous solutions of poly(vinylpyrrolidone) (PVP) to investigate the dependence of penetrant diffusion on polymer concentration. The results have been interpreted using an expression, describing this dependence, based on free-volume concepts.

Self-diffusion coefficients have been obtained by the n.m.r. pulsed-gradient spin-echo (PGSE) method[22,23]. For three of the diffusants investigated, measurements were also performed using the classical gradient diffusion (CGD) technique, modified for ternary systems[24,25].

Since the diffusion of penetrant and polymer occurs on widely different time-scales, the polymer can be regarded as a stationary network through which the penetrant diffuses. From CGD measurements one obtains the mutual diffusion coefficient which approaches the self-diffusion coefficient as the concentration of the diffusing species tends towards infinite dilution.

The two experimental techniques utilized are thus expected to give comparable results at the low concentrations of penetrant used in the present investigation. This would allow us to make a comparison between diffusion data obtained in this work with the diffusion data for corresponding diffusants in aqueous hydroxypropyl cellulose (HPC) solutions from an earlier study[24].

EXPERIMENTAL

Materials

A commercial sample of PVP, K-90, Fluka AG was used. It was purified by repeated dialysis against distilled water, freeze-dried and finally vacuum-dried at 50°C. The

molecular weight, M_w, was estimated to be 880 000 from viscosity measurements ($[\eta] = 128 \ 10^{-3} \ m^3 \ kg^{-1}$ at 25.0°C) using the Mark–Houwink parameters determined by Levy and Frank[26] from subsequent viscosity and light-scattering measurements. Solutions were prepared by weighing, concentrations and volume fractions in H_2O solutions were calculated from density data[27] reported previously. Pertinent density data on PVP in D_2O were obtained using a Kratky digital densimeter, DMA 60, with a cell unit, DMA 601 (Anton Paar K. G., Graz, Austria). The partial specific volume of PVP in D_2O thus obtained was $0.789 \ 10^{-3} \ m^3 \ kg^{-1}$ at 25.0°C.

The diffusants glucosamine-hydrochloride (GA), N-acetyl-glucosamine (NAG) and sucrose (S) of PURISS grade and glucose-6-phosphate disodium salt of PURUM grade purchased from Fluka AG. The diffusant, 1,4-dioxane (D) and deuteriumoxide (used as solvent for the n.m.r. measurements) of high purity were obtained from J. T. Baker Chemicals N. V., Deventer, Holland and Norsk Hydro, Rjukan, Norway, respectively.

Diffusants were added to polymer solutions by weighing to an average concentration of 0.5% (w/w).

N.m.r. self-diffusion measurements

Self-diffusion coefficients were obtained from proton-NMR measurements on a standard JEOL FX-100 standard NMR Fourier transform spectrometer by a pulsed-gradient spin-echo pulse sequence[23]. The self-diffusion coefficient, D, was evaulated from the attenuation of signal amplitude, A, of the observed nucleus as a function of the duration, δ, of the magnetic field gradient pulse, G, (1 Gauss cm^{-1}) according to:

$$A(\delta) = A(0)f(\Delta)\exp[-2\Delta/T_2 - \gamma^2 G^2 D\delta^2(\Delta - \delta/3)] \quad (1)$$

where f is the J-modulation effect, Δ is the time interval between the RF-pulses, T_2 is the transverse relaxation time and γ is the gyromagnetic ratio of the protons. In an actual experiment, Δ is kept constant while δ is varied. The self-diffusion coefficient is obtained by a least-square fit of the observed signal amplitudes to equation (1). A more detailed description of the method is given in the excellent works of Stilbs and Mosely[28-31].

Self-diffusion coefficients were obtained for all five diffusants by this method for PVP concentrations up to about 150 kg m^{-3}. All measurements were carried out at 25°C.

CGD measurements

CGD measurements were performed using an apparatus built at this institute[32]. A diffusion cell of the shearing type[33] was used for the formation of a sharp boundary. The broadening of the boundary was registered by a Schlieren optical system. The temperature was 25.0°C and was regulated to within ±0.01°C by means of a Pt resistor regulated thermostat (Heto, Birkerød, Denmark).

Both compartments of the diffusion cell were filled with PVP solution, with the lower one containing 1% (w/w) diffusant. As described in an earlier paper[24], the PVP concentration in the upper one was slightly lowered in order to compensate for the decrease in refractive index increment of the polymer due to addition of diffusant[25,34].

In the CGD method, by the creation of a concentration gradient, one obtains the mutual diffusion coefficient which is usually different from the self-diffusion coefficient

since the former contains a thermodynamic contribution. However, since the average concentration of diffusant is very low, 0.5% (w/w), one can expect this difference to be small.

CGD measurements have been performed with the penetrants NAG, GP and S in order to compare the results obtained by the CGD and n.m.r. PGSE techniques.

THEORY

The decrease of the diffusion coefficient of a small molecule with increasing polymer concentration is often linear at low polymer concentrations[2,24,35,36]:

$$D/D_0 = 1 - kC \quad (2)$$

where D_0 is the self-diffusion coefficient of the diffusant in pure solvent, C is the concentration of polymer. The empirical constant, k, is a measure of the concentration dependence of the self-diffusion coefficient.

Yasuda et al.[13,16] derived an equation for the diffusion of a penetrant molecule in a polymeric system, based on free-volume concepts[6], given by:

$$D \propto \exp -[(V^*/V_{f,12}) + (E^*_{v,12}/RT)] \quad (3)$$

where V^* is proportional to the volume necessary to accommodate the penetrant molecule, $V_{f,12}$ the fractional free volume in the polymeric system and $E^*_{v,12}$ the activation energy of diffusion. The indices 1 and 2 stands for solvent and polymer respectively. The analogous expression for diffusion in pure solvent is:

$$D_0 \propto \exp -[(V^*/V_{f,1}) + (E^*_{v,1}/RT)] \quad (4)$$

Assuming that the free volumes of solvent and polymer are additive:

$$V_{f,12} = V_{f,1}\phi + V_{f,2}(1 - \phi) \quad (5)$$

where ϕ is the volume fraction of solvent. Then, for large ϕ and since $V_{f,1} \gg V_{f,2}$ (according to Machin and Rogers[37]), equation (5) reduces to:

$$V_{f,12} = V_{f,1}\phi \quad (6)$$

If we further assume that the diffusion proceeds in the aqueous phase of the polymer solution, i.e. no specific interactions exist between diffusant and polymer, the activation energies of diffusion are the same in solvent and polymer solution:

$$E^*_{v,1} = E^*_{v,12} \quad (7)$$

This assumption is a reasonable one at sufficiently low polymer concentration, and has been experimentally verified for the diffusion of several penetrants in aqueous cellulose- and polyacrylamide gels[38,39].

From equations (3), (4), (6) and (7) we obtain the following expression for the diffusion coefficient of a molecule in polymer solution:

$$D/D_0 = \exp -[(V^*/V_{f,1})(\phi^{-1} - 1)] \quad (8)$$

We may thus expect a linear relationship between (ln D/D_0) *versus* ($\phi^{-1} - 1$) with a slope, K, proportional to

V^*. Deviation from linearity is expected at higher polymer concentrations when $V_{f,12}$ is given by equation (5) instead of equation (6). (At high polymer concentrations the theory of Fujita[9] predicts a linear relationship between $(\ln D/D_0)^{-1}$ *versus* ϕ^{-1}.)
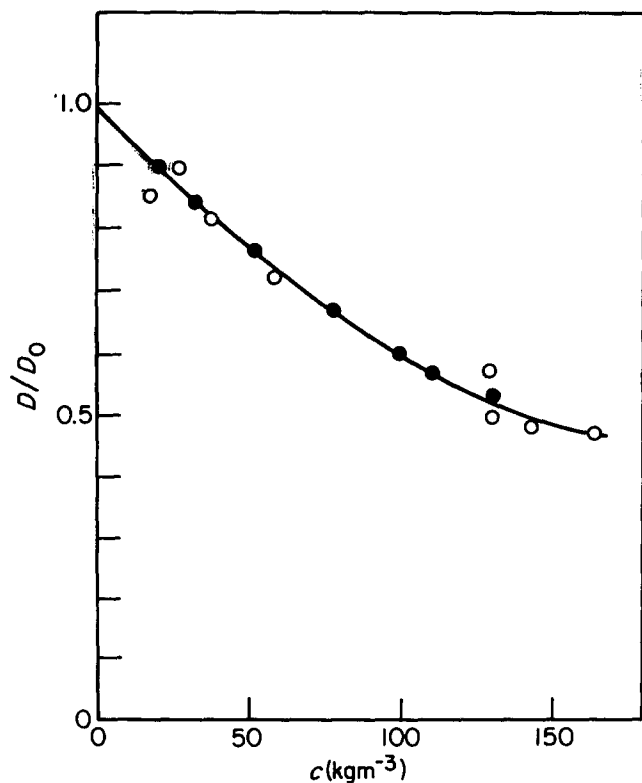

Figure 1 D/D_0 *for* N-acetyl-glucosamine (NAG) *versus* PVP concentration. (●) PGSE measurements; (○) measurements obtained by the CGD technique
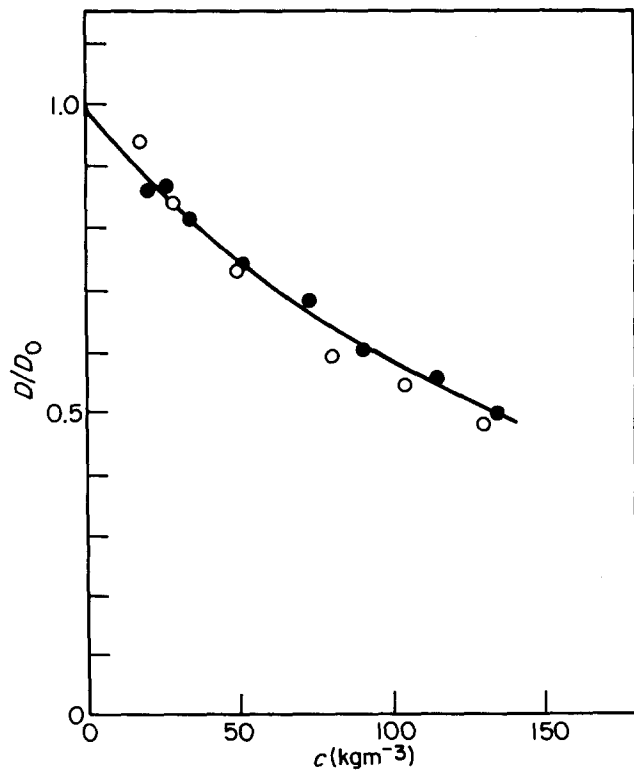

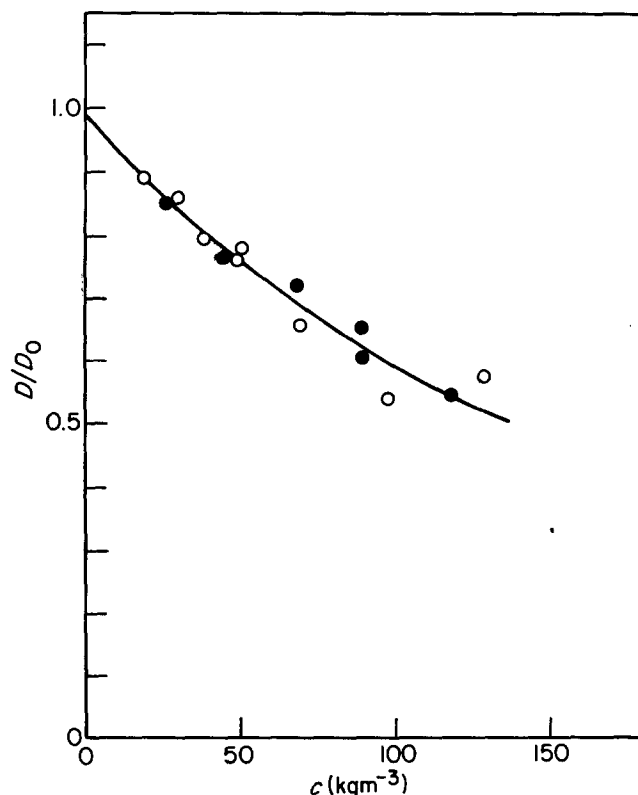**Figure 2** D/D_0 for sucrose (S) *versus* PVP concentration. Symbols as in *Figure 1*

Figure 3 D/D_0 for glucose-6-phosphate (GP) *versus* PVP-concentration. Symbols as in *Figure 1*
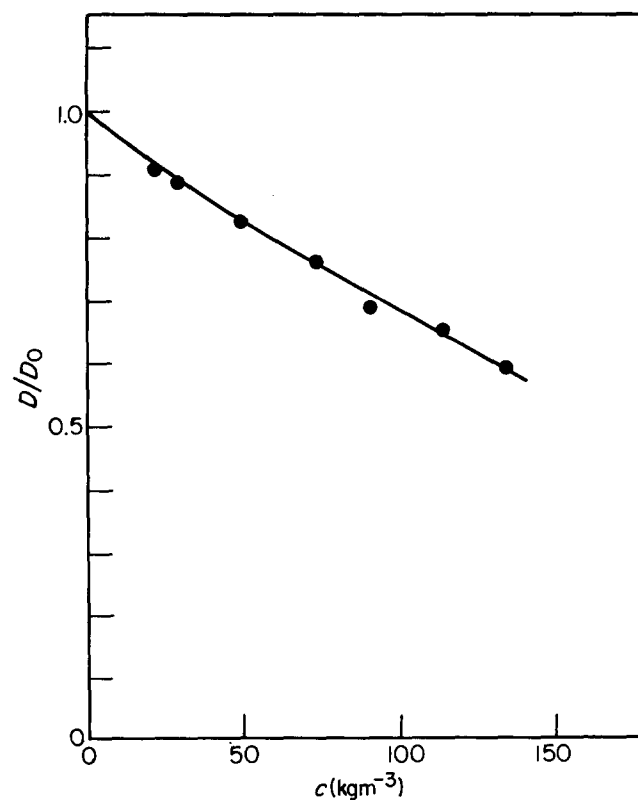

Figure 4 D/D_0 obtained by the PGSE method for glucosamine hydrochloride (GA) *versus* PVP concentration

RESULTS AND DISCUSSION

In *Figures 1–5* we present the diffusion data obtained for the five diffusants in PVP solutions. NAG, S and GP diffusion were studied by both the CGD and the PGSE
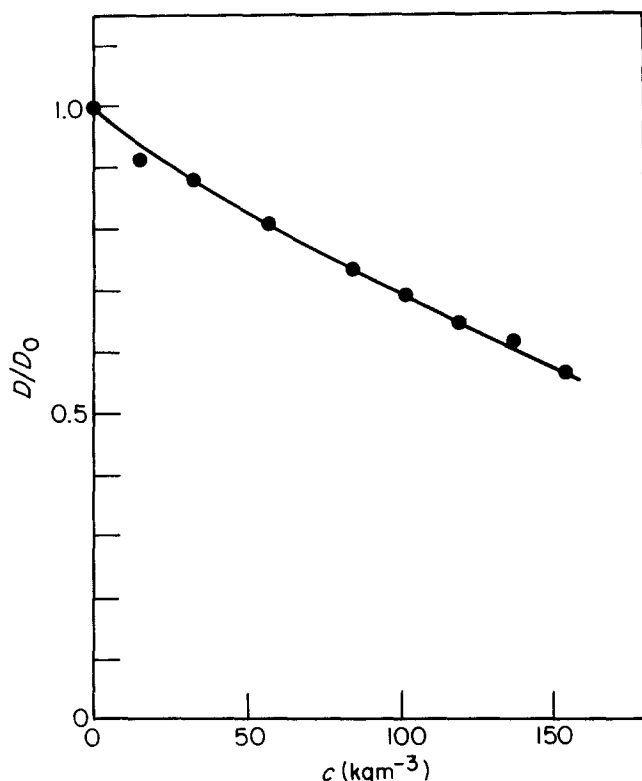
Figure 5 D/D_0 for 1,4-dioxane (D) obtained by the PGSE method *versus* PVP concentration
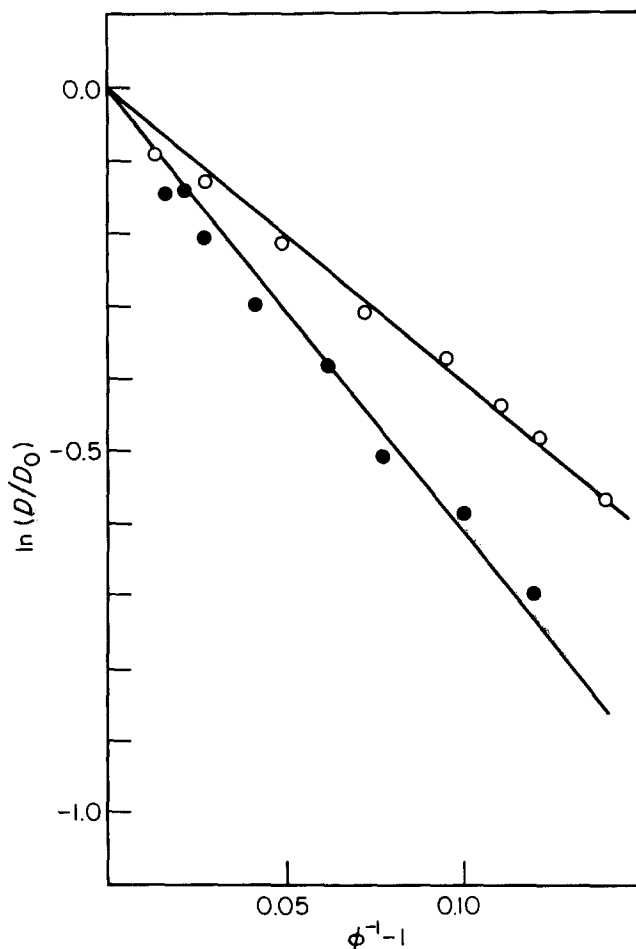

Figure 7 Ln D/D_0 obtained from PGSE measurements plotted *versus* reciprocal aqueous volume fraction -1, $(\phi^{-1}-1)$, for ($\bigcirc$) D and ($\bullet$) S according to equation (8)
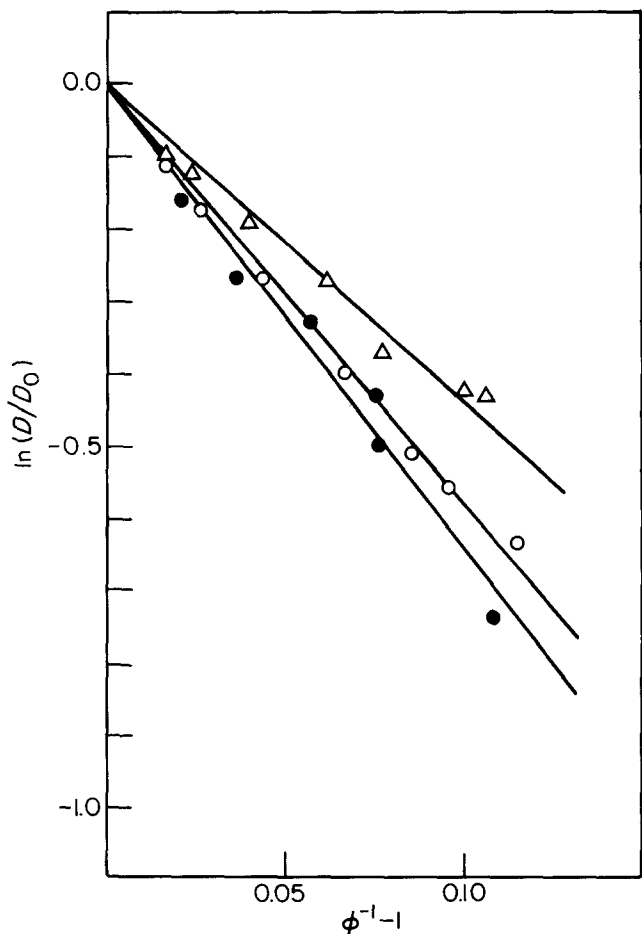

Figure 6 Ln D/D_0 obtained from PGSE measurements plotted *versus* reciprocal aqueous volume fraction -1, $\phi^{-1}-1$, for ($\bigcirc$) NAG, ($\bullet$) GP and ($\times$) GA according to equation (8)

methods. As can be seen from *Figures 1–3*, the agreement between the two techniques is very good.

Plots of ln D/D_0 *versus* $(\phi^{-1}-1)$, according to equation (8), for the diffusants, from the PGSE-data, are shown in *Figures 6* and *7*. A linear relationship was predicted by the free-volume approach, which is also found experimentally for all diffusants.

The quantified results of the diffusion measurements are summarized in *Table 1*. Here are given the diffusion coefficients, extrapolated to zero polymer concentration, which are taken as D_0 values for the penetrants in ordinary and heavy water respectively. We also report k-values for the linear portion of the D/D_0 *versus* PVP concentration curves (i.e. PVP concentration less than 60 kg m^{-3}), according to equation (2). (These values were obtained from CGD data, except in the case of GA and D, and have been calculated by the method of least squares.)

The k-values of GA, NAG and GP increase in the mentioned order. This trend was also observed in a previous investigation[24] where the migration of these diffusants was studied in aqueous hydroxypropyl cellulose (HPC) solution. The similar trends imply that none of the three penetrants exhibit specific interactions with the polymers.

The overall dependence of penetrant diffusion on polymer concentration is, however, more pronounced in solutions of PVP than in those of HPC. The effect of adding polymer can basically be viewed as a competition between polymer and penetrant for the available free

Table 1 Results of the diffusion measurements in PVP solutions

Diffusant	$D_0^{H_2O}$ (10^{-10} m^2 s^{-1})	$D_0^{D_2O}$ (10^{-10} m^2 s^{-1})	k (10^{-3} m^3 kg^{-1})	K
1,4-Dioxane	–	9.28	3.9	4.1±0.1
NAG	6.69[a]	4.98	4.5	5.8±0.1
GA	8.62[a]	5.63	3.5	4.4±0.2
GP	8.22[a]	4.02	4.5	6.4±0.4
Sucrose	5.21	4.36	5.4	6.2±0.2

[a] These D_0 values were taken from ref. 5

volume, making the penetrant diffusion dependent on the relative size of penetrant and polymer jumping unit[10,40]. The present results thus indicate that PVP competes more efficiently than HPC for the free volume available.

The slopes, K, of the lines drawn in *Figures 6* and *7* have been calculated by the method of least squares (the intercepts have been zero-adjusted, since D will approach D_0 at unity volume fraction of solvent) and are given in *Table 1* with 80% confidence intervals. The slopes of the nonionic diffusants increase in the order, D, NAG and S. This is in line with the free-volume model since K should be proportional to the volume of the diffusant which increases in the same order as seen from the D_0 values. In fact, a plot of K *versus* r^3, where r is the equivalent hydrodynamic radius, calculated from the appropriate D_0 value, using the Stokes–Einstein equation, yielded a straight line for these three diffusants. Since, however, the present number of data is rather limited, this relationship needs further investigation.

CONCLUSIONS

It may be concluded that th CGD technique, modified for self-diffusion measurements of small molecules in polymer solution, gives the same diffusion quotient, D/D_0, as the PGSE method.

It has also been shown that the self-diffusion coefficients of small diffusants in moderately concentrated polymer solutions can be quantitatively treated by a free-volume approach. The presented model predicts a linear decrease of ln D/D_0 *versus* reciprocal volume fraction of solvent and an increasing concentration dependence with increasing size of the penetrant. These predictions have been verified experimentally for the present systems. However, more extensive investigations on other systems are needed to further explore the generality of the above conclusions.

It is also desirable to perform a more qualitative analysis by performing measurements in solvents and polymers with known free volumes.

ACKNOWLEDGEMENTS

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