Diffusion and Interaction in Gels and Solutions. 2. Experimental Results on the Obstruction Effect

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ABSTRACT: Studies of the diffusion of monodisperse fractions of poly(ethylene glycol), here denoted solute, in polymer gels and solutions of κ-carrageenan and poly(styrenesulfonate) are reported. We have found that besides the self-evident influence of solute size and volume fraction of obstacles, the solute diffusion is also governed by the thickness and the stiffness of the polymer chains constituting the network, i.e., the structure in the gels or the solutions. Furthermore, when the K^+ concentration in κ-carrageenan gels is increased, which results in thicker chains constituting the network, a faster solute diffusion is found. Also, the solute diffusion is found to increase if the polymer chains become more flexible, as seen in poly(styrenesulfonate) solutions at different ionic strengths. The need for a consistent theoretical explanation of our results is emphasized, and an approach to meet this need is shown in the following paper.

Introduction

The understanding of transport phenomena is the basis of several industrial applications. In the pharmaceutical field, the transport of drugs is a subject of great interest. To find the most efficient pharmaceutical formulation, it is essential to understand how a certain drug is released from a matrix, e.g., a tablet, and how the drug is then transported into the systemic circulation. Both these events are influenced by diffusion processes, which in turn are governed by the physical properties of the drug and its surroundings.

In this work we have focused on solute diffusion in polymer gels and solutions. Let us generally describe the interactions between a solute, e.g., a drug, and its surroundings, e.g., a polymer network, in two different terms, chemical and frictional. The result of chemical interactions then includes the retardation of solute diffusion due to attractive forces, e.g., electrostatic forces between a charged solute and a polyelectrolyte of opposite charge. Chemical interactions sometimes dominate the diffusion process, while in other cases they are almost negligible. On the other hand, solute diffusion will always be influenced by frictional effects, in which we include solvent effects, steric hindrance, hydrodynamics, etc.

In the present investigation we have studied systems in which frictional effects dominate and chemical interactions are insignificant. Numerous studies on the subject have been carried out, and some of these are reviewed by Muhr and Blanchard[1] and by Preston et al.[2] Two main conclusions that can be drawn from their collections of data are the differences between results from the studies of different polymer–solute systems and the lack of a consistent theoretical explanation of the results. First, if results are compared only as a function of the polymer concentration, differences are observed between different polymer–solute systems (see Muhr and Blanchard[1]). This shows that the polymer concentration is not the only parameter governing the diffusion in such systems. Other parameters therefore need to be considered, e.g., the influence of solute size and the geometrical arrangement of the polymer chains in the gel or the solution, i.e., the structure. The influence of chemical interactions must further be quantified, in order to compare diffusion coefficients of different solutes in different polymer gels or solutions. Second, the basic principles of solute diffusion in matrices are a topic of great controversy. Some theories are based on geometrical considerations,[3-5] while others deal with hydrodynamics.[6-8] A comparison between experiment and theory is in some cases quite successful, although it fails for other cases. The intriguing question is then under what circumstances, i.e., what range of solute sizes, polymer concentrations, etc., the different theoretical approaches are most adequate.

In this paper, we report our studies of the diffusion of monodisperse fractions of poly(ethylene glycol) ($300 < M_w < 4000$) in different polymer gels and solutions of a polysaccharide, κ-carrageenan, and in different solutions of poly(styrenesulfonate). An approach to theoretically account for our results, and other results as well, is presented in the following paper.[9]

Experimental Section

Preparation of Monodisperse Poly(ethylene glycol) Fractions. Radioactively labeled poly(ethylene glycol) (PEG) samples were obtained from Berol Nobel Stenungsund AB, Sweden (PEG 400), and from NEN Research Products (PEG 1000, NET-404; PEG 4000, NET-405). Monodisperse fractions were prepared on a thermostated Nucleosil column ($7C_{18}$, 10 × 250 mm) using reversed-phase liquid chromatography. The mobile phase was different mixtures of methanol and water, with methanol concentrations ranging from 30% (v/v) (PEG 400) to 62% (v/v) (PEG 4000). The PEGs were detected by a thermostated differential refractometer (Waters 210) and sampled in plastic vials. The prepared fractions were then concentrated by evaporating the mobile phase in a vacuum chamber and, finally, stored in H_2O at −8 °C.

The molecular weight, M_w, of each fraction was calculated from chromatograms as $M_w = 18 + 44n$, using PEG standards with known M_w. Here, n is the degree of polymerization, which was determined from the peak number in the chromatograms, given n for the standards. The molecular weights of these standards were determined by mass spectrometry. In this work, six different fractions were used with molecular weights 326, 678, 1118, 1822, 2834, and 3978. The purity of each fraction was checked by analysis on a Nucleosil column ($5C_{18}$, 4.6 × 150 mm), and all samples, except the 3978 fraction, were found to be monodisperse (impurities below detection limit). The 3978 fraction

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contained ~5% (mole/mole) of PEG molecules with molecular weights 3934 (=3978 - 44) and 4022 (=3978 + 44).

Purification of κ-Carrageenan. A commercial sample of κ-carrageenan (from *Eucheuma cottonii*; Sigma C-1263, lot no. 87F-0463) was converted to its pure ionic forms, Na^+ or K^+, on an ion-exchange resin (Amberlite IR-120-P, Sigma) at elevated temperature (~80 °C), followed by freeze-drying. The efficiency of our ion-exchange procedure was checked by atomic absorption spectroscopy, which showed negligible amounts of ion impurities in the purified samples. The presence of ι-carrageenan impurities[10] in the ion-exchanged samples was determined to be ~10% (mole/mole) by ^1H NMR measurements at 90 °C.

A chemically cross-linked gel of Na^+ κ-carrageenan was typically prepared by adding 1 mL of ethylene glycol diglycidyl ether (Polyscience no. 1479) to 20 mL of a 2% (w/w) solution of Na^+ κ-carrageenan in 0.5 M NaOH. The cross-linking was then allowed to proceed for 24 h at room temperature. Prior to use, the resulting gel was extensively washed with water to eliminate residues of the cross-linking agent.

The volume fraction, ϕ, of κ-carrageenan in the gels or the solutions (using water as the solvent) was calculated from the partial specific volume (v = 0.50 mL/g) of the coil conformation.[11] Thus, the small volume difference (~1%) between the helix and the coil conformations reported by Gekko et al.[12] was neglected.

Purification of Poly(styrenesulfonate). Sodium poly(styrenesulfonate) (NaPSS) with $M_w \sim 5 \times 10^5$ was obtained from Polyscience (no. 08773). The sample was purified by washing an aqueous solution of NaPSS with H_2O in an ultrafilter (Amicon 4000 with a PM30 membrane) until the impurities were below 0.1% (mole/mole), as determined from the optical density of the eluate. The NaPSS solution was then diluted to the desired concentration. The concentration was determined spectrophotometrically at 224 nm using the extinction coefficient $\epsilon = 9.91 \times 10^3$ M^{-1} cm^{-1}.[13] Finally, the polymer volume fraction, ϕ, was calculated from the monomer weight M_0 = 206 and the partial specific volume v = 0.68 mL/g.[14]

Diffusion Measurements. The measurements were carried out as previously described.[15] Briefly, a 1-mL plastic syringe with the top cut off (Sabre, length ~5 cm, diameter ~4.5 mm) was used. The syringe was filled with a gel or a solution and allowed to equilibrate at 25 °C for 24 h. When solutions were examined, small glass beads were also added to prevent disturbances from, e.g., environmental shaking. The experiment was started by applying a 0.2-μL drop of the radioactive solution on the top of the syringe. At the end of the experiment (after 2–4 days at 25 ● 0.5 °C), the contents of the syringe was carefully pressed out and simultaneously cut into pieces, which were sampled in scintillator vials and analyzed in a β-counter. Prior to analysis, the pieces from K^+ κ-carrageenan gels were dissolved in 1 mL of H_2O at ~80 °C, while the pieces from chemically cross-linked gels of Na^+ κ-carrageenan were hydrolyzed in 1 mL of 0.1 M HCl. All measurements were carried out in at least triplicate, giving standard deviations of less than 5%.

Rheological Measurements. All measurements were carried out at 25 °C with a CarriMed CSL 100 rheometer. The K^+ κ-carrageenan and the chemically cross-linked Na^+ κ-carrageenan samples were investigated by using a 4.0 cm, 1.0° cone-and-plate geometry, while a 6.0 cm, 2.0° cone-and-plate geometry was used for the Na^+ κ-carrageenan solution. The K^+ κ-carrageenan sample was heated to ~60 °C before loading and then allowed to gel upon cooling between the cone and the plate in the rheometer. All measurements were carried out in the linear viscoelastic region of the samples.

Results and Discussion

Results from studies of solute diffusion in polymer gels or solutions are often compared to the diffusion in *the absence of the polymer, i.e., in the solvent*, and reported as the so-called diffusion quotient, D/D_0. This is the quotient between the diffusion coefficients in the gel or solution (D) and in the solvent (D_0). Thus, we first carried out measurements of D_0 on the monodisperse poly(ethylene glycol) fractions in water. The results from these experiments could be summarized as $D_0 = 7.0 \times 10^{-9} M_w^{-0.46}$, where M_w (in g/mol) is the molecular weight of the PEGs and D_0 has units of m^2/s. The diffusion coefficients of the PEGs were measured by using only trace amounts, reflecting the condition of infinite dilution with respect to the PEG concentration. For this case, the PEGs are expected to behave as isolated nondraining chains (Zimm model) and D_0 to scale as $D_0 \sim M_w^{-\alpha}$ ($0.5 < \alpha < 0.6$),[16] which indeed was verified by the results. It can be mentioned that D_0 of the PEGs was not influenced by the presence of added salt below a NaCl or KCl concentration of 0.2 M.

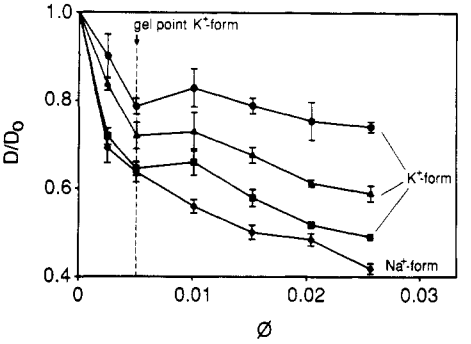

Figure 1. D/D_0 vs ϕ for PEGs of different molecular weights 1118 (circles), 2834 (triangles), and 3978 (squares) in K^+ κ-carrageenan (gels above $\phi \sim 0.005$) and for the molecular weight 3978 (diamonds) in Na^+ κ-carrageenan (solution).

A pure solvent is often treated as a continuum, and the solute diffusion in such a medium is usually described in terms of frictional forces, e.g., as $D_0 = kT/6\pi\eta R_H$. This expression was used when we determined the hydrodynamic radius, R_H, of the PEGs. However, as outlined in the Introduction, in the presence of a network, e.g., a gel, the diffusion of solutes can be affected by both chemical and frictional interactions. As our main interest concerned the frictional interactions, we had to investigate if they dominated the diffusion processes in our systems. Thus, we measured D/D_0 in κ-carrageenan gels at different PEG concentrations, ranging from 0.01 to 10 mM. The results showed that both D and D_0 slightly decreased with increasing PEG concentration. However, the D/D_0 quotients were independent of the PEG concentration within experimental uncertainties. This indicated a negligible chemical interaction between PEG and κ-carrageenan since, e.g., binding would have given an increase in D/D_0 with increased PEG (nonradioactive) concentration. Furthermore, we measured the proton NMR relaxation time T_1 to be 0.7 s for PEG in solutions of sodium poly(styrenesulfonate) (NaPSS) at different ionic strengths (up to 0.2 M NaCl). Thus, a change in ionic strength did not influence the possible chemical interaction between PEG and NaPSS. On the other hand, as will be shown below, the PEG diffusion was indeed influenced by changes in the ionic strengths of the NaPSS solutions, but this was then attributed to an effect of frictional interactions.

The effect of frictional interactions in polymer gels or solutions was then evaluated by measurements of the PEG diffusion in κ-carrageenan at different polysaccharide concentrations. Some results from these studies are presented in Figure 1 for three different PEGs in K^+ κ-carrageenan and for one PEG in the Na^+ form of the polysaccharide. For clarity, the results obtained with the PEGs of molecular weights 326, 678, and 1822 are not shown. The data for these molecules showed similar patterns. All the results from the experiments with the K^+ form showed an increase in D/D_0 when the polymer volume fraction ϕ was approximately equal to 0.005. This is the gel point of K^+ κ-carrageenan and is indicated in Figure 1. However, the results with the Na^+ form showed a monotonic decrease of D/D_0 when the polymer volume fraction was increased,

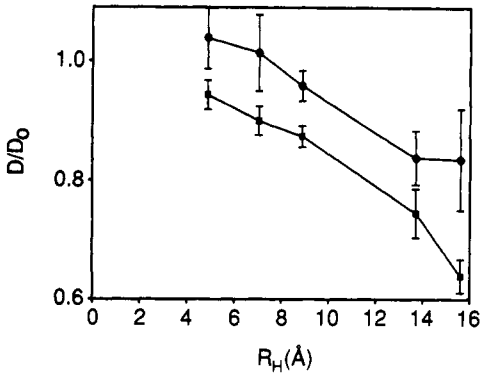

Figure 2. D/D_0 vs R_H for PEGs in 1% (w/w) K^+ κ-carrageenan ($\phi = 0.005$) with 10 mM KCl (squares) and 100 mM KCl (circles).

as expected. Thus, the results showed that the diffusion of PEG was faster in the gel than in the solution of the same polymer. It should be noted that the gelation of κ-carrageenan involves a coil–helix transition and a subsequent aggregation of the helices.[17] These processes are very sensitive to the identity of the counterions. Thus, the K^+ form of κ-carrageenan (without added salt) gels at about 1% (w/w), $\phi = 0.005$, while the gelation of the Na^+ form is known to occur at concentrations higher than those investigated here.[18]

To understand why the PEG diffusion was faster in the gel than in the solution, we performed experiments in 1% (w/w) K^+ κ-carrageenan at two different KCl concentrations, 10 and 100 mM. These KCl concentrations were chosen in light of the studies by Hermansson.[19] She showed with electron microscopy that 100 mM KCl induces an aggregation of the carrageenan chains into rather thick fibers with a diameter around 50 Å, whereas significantly thinner fibers are observed in 10 mM KCl. Results from the diffusion of PEGs in these two gels are presented in Figure 2 as D/D_0 versus the hydrodynamic radius R_H for the PEGs. Figure 2 shows that the PEG diffusion was faster in the κ-carrageenan gel with 100 mM KCl than with 10 mM KCl. This was supported by the electron microscopy pictures, since thicker fibers result in larger spaces between the fibers, and thus a less hindered pathway for the diffusing molecules. These findings might be an explanation of the results shown in Figure 1, since the gelation mechanism of κ-carrageenan is an aggregation process even without added salt. Furthermore, the strongest gel was the one formed in 100 mM KCl, as shown by Hermansson.[19] This indicated that the macroscopic viscosity was no measure of the diffusion of PEGs in these systems.

However, gels and solutions are fundamentally unlike, considering the chain motions at the molecular level.[20] Although polysaccharide chains in aqueous solutions are quite stiff[21] compared to synthetic polymers, polysaccharide gels are almost stationary at the molecular level.[22] It was then interesting to investigate the influence of chain motions on solute diffusion in networks. Thus, we carried out measurements of D/D_0 in the chemically cross-linked Na^+ κ-carrageenan. The results from PEG diffusion in one such chemically cross-linked network are shown in Figure 3, together with the results from the studies in the gels of the K^+ form and in the solutions of the Na^+ form. Figure 3 not only shows the difference in D/D_0 between the K^+ gel and the Na^+ solution discussed above but also that chemical cross-linking of the Na^+ form did not alter the diffusion of the PEGs, provided that the total polymer volume fraction of each system remained the same. Furthermore, the elastic modulus, G', of κ-carrageenan in these three different states was determined at different

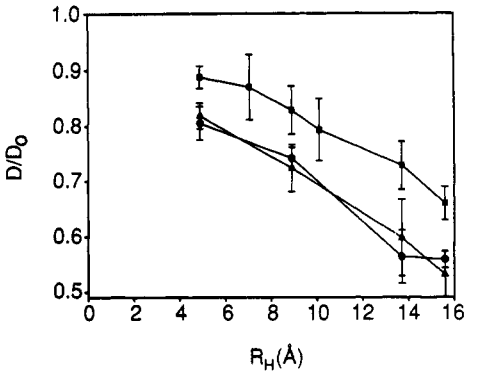

Figure 3. D/D_0 vs R_H for PEGs in 2% (w/w) κ-carrageenan ($\phi = 0.01$) in three different states: as a gel (K^+ form, squares); as a solution (Na^+, circles); and as a chemically cross-linked gel (Na^+ form, triangles).

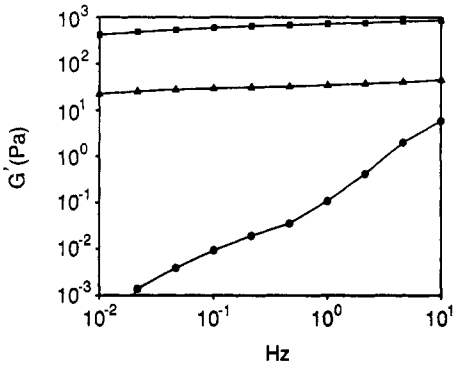

Figure 4. Elastic modulus G' vs the oscillation frequency for 2% (w/w) κ-carrageenan in three different states: as a gel (K^+ form, squares); as a solution (Na^+ form, circles); and as a chemically cross-linked gel (Na^+ form, triangles).

oscillation frequencies using the same polymer concentration as in Figure 3. The results are shown in Figure 4. It is seen that the rheological behavior of carrageenan in these three states was quite different. A nearly frequency-independent G' was found for both gels, while G' for the solution was highly dependent on the oscillation frequency. Using rubber elasticity theory,[23] together with the molecular weight of carrageenan (3.31×10^5),[21] we estimated that each carrageenan chain in the chemically cross-linked gel was on the average involved in only three cross-links. The calculation was based on the assumption of an idealized network with fixed tetrafunctional cross-links. Thus, the degree of chemical cross-linking of the Na^+ form was low and did not alter the total polymer volume fraction.

The results in Figures 3 and 4 clearly show that a macroscopic viscosity by no means could be taken as a measure of solute diffusion in our polymer gels and solutions and that the solute diffusion in such systems could be of the same magnitude despite highly different macroscopic behavior. This agreed with the findings reported by Chen and Ferry.[24] They showed that the diffusion of cetane in rubbers was only marginally influenced by the concentration of cross-links. The explanation we propose is that rheological properties of polymer systems are to a large extent influenced by the presence of cross-links, while the diffusion of solutes is influenced by polymer properties giving rise to different arrangements of the polymer chains. It can be argued that cross-links in a network will act as obstacles for solute diffusion. However, the cross-links will also contribute to the total polymer volume fraction. Thus, when comparing solute diffusion in networks with different cross-linking density, experiments must be carried out at the same total obstacle volume fraction. For low degrees of cross-linking and with

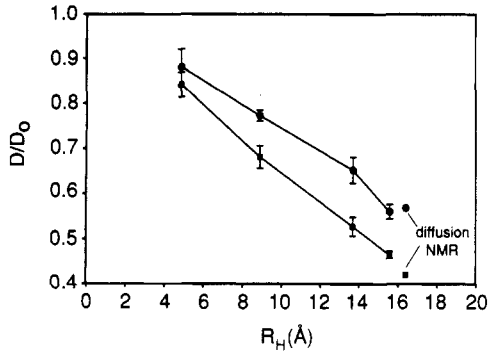

Figure 5. D/D_0 vs R_H for PEGs in solution of NaPSS (ϕ = 0.012) in pure water (squares) and in 0.2 M NaCl (circles). Results from measurements with diffusion NMR, using a polydisperse sample of PEG 4000 in the NaPSS solutions in D_2O, are included for comparison.

small solutes, as used in this work, the net effect on the solute diffusion will be small. On the other hand, the effect might be more pronounced for larger diffusing solutes or for higher degrees of cross-linking, as also discussed by Brown and Stilbs.[25] In any case, the arrangements of the polymer chains were most certainly not altered by the cross-linking used here to transform the Na^+ solution into the gel-like system. Hence, the diffusion of the PEGs was expected not to change between these two Na^+ systems. On the contrary, the gel formation of the K^+ κ-carrageenan includes another mechanism involving chain aggregation, leading to a less hindered diffusion beyond the gelation point, as discussed above.

If solute diffusion is governed by the arrangement of the polymer chains in a gel or a solution, then the chain flexibility, i.e., the persistence length, would be an important factor. Thus, we carried out diffusion measurements of PEGs in sodium poly(styrenesulfonate) (NaPSS) solutions at different ionic strengths. The results are shown in Figure 5. It was found that the diffusion of the PEGs was faster in a NaPSS solution at high ionic strength (0.2 M) than in a NaPSS solution in pure water. This result was also confirmed by self-diffusion measurements with NMR using a polydisperse PEG 4000 sample, 0.1 mM in D_2O (see Figure 5). The persistence length of NaPSS at the concentration used here in water was extrapolated from small-angle neutron scattering data to be 80 Å.[26] In 0.2 M NaCl the electrostatic forces are strongly screened, giving the bare persistence length (12 Å) of NaPSS.[26] Our results thus indicated that a solution of stiff polymers created a greater hindrance to solute diffusion than a solution of random coils at the same concentration and with otherwise similar properties. This might be explained by the fact that flexible polymers tend to coil into spherical domains, giving larger available spaces for the diffusing molecules, as will be shown in the following paper.[9] Furthermore, the results by Ogston et al.[5] show a faster diffusion of albumin in solutions of dextran than in solutions of hyaluronic acid. Their interpretation is that dextran chains might be thicker than the chains of hyaluronic acid, due to the branching of dextran. We prefer to view this as an effect of the different flexibility of the polymer chains,[27,28] which in this case is due to the different monomer linkages for the two polymers. This argument also has implications for the applicability of the viscosity concept in such systems. Solutions of stiff polymers are indeed more viscous than solutions of flexible polymers. Therefore, the macroscopic viscosity has the correct qualitative behavior when compared to solute diffusion in these systems. Despite this, in our opinion the explanation of a faster diffusion in the less viscous systems should basically not be founded on the viscosity concept, since this concept obviously does not give a consistent explanation of the other results presented here or elsewhere.[1,2,5]

Finally, it is appropriate to emphasize the need for a theoretical explanation of our results. Several theories concerning solute diffusion in polymer gels or solutions have been presented, some of which are based on either geometrical considerations[3-5] or hydrodynamics.[7,8] Besides the self-evident influence of solute size and polymer volume fraction, all these theories also predict the observed effect of polymer chain thickness in a qualitative manner, giving higher D/D_0 for thicker chains. The important effect of polymer flexibility has however to our knowledge only been taken into account by Cukier,[7] who differentiated between rods and coils. However, this theory predicts results opposite to our findings, namely, a faster solute diffusion in solutions of rods than in solutions of coils. Furthermore, we indeed wish to emphasize that the observed curvature of a plot of D/D_0 vs ϕ is convex (see Figure 1); i.e., D/D_0 is altered more by a change in ϕ at low ϕ than at high ϕ. On the other hand, a plot of experimental D/D_0 vs R_H is concave (see Figures 2, 3, and 5). The only model that gives the correct behavior for both cases without fitting parameters is the cylindrical cell model,[29] modified to allow a finite size of the diffusing molecule.[9] However, this model does not consider the effect of chain flexibility since the polymer chains are treated as cylinders. Thus, a theory is obviously lacking that consistently accounts for finite solute size, chain thickness, and chain flexibility and also predicts the correct convex and concave curvature of the D/D_0 plots discussed above. In the following paper,[9] we present an approach to account for these effects, using results obtained in the cylindrical cell model. The approach gives a consistent explanation for our results.

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