

Self-Diffusion of Small Molecules in Cellulose Gels Using FT-Pulsed Field Gradient NMR

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Synopsis

Transport in cellulose gels has been studied with ethylene glycol and crown ether (15-5) as "probes" using an NMR spin-echo technique. The cellulose content was varied in range 20-55% (w/w). The retardation of diffusion was found to be adequately described by simple first-order expressions in concentration of cellulose.

INTRODUCTION

Recent investigations of the transport of small molecules in cellulose gels dealt with: (a) the temperature dependence of the diffusion coefficient and the relaxation times (T_1 and T_2) using spin-echo NMR¹ and (b) the mobility of homologous series of small solutes (polyhydric alcohols, oligosaccharides, and polyethylene glycols) using a sorption technique.² A series of earlier papers^{3,4} described measurements of diffusion in various gels using a preliminary form of the latter technique, and these have recently been cited in a comprehensive review of gel diffusion by Muhr and Blanshard.⁵ These latter investigations gave values of D/D_0 , expressing the retardation of diffusion, which were too low owing to deficiencies in both the experimental arrangement and the calculation procedure. The substantially refined sorption technique described in Refs. 2 and 6 gives diffusion coefficients in excellent agreement with those obtained by spin-echo NMR and which harmonize with the overall picture in aqueous gels.⁵

The present note is a complement to the earlier contributions^{1,2} and describes an investigation of the influence of the gel concentration on solute diffusion, the previous studies having been restricted to a single cellulose content. The cellulose concentration has been extended considerably and lies within the range 20-60% (w/w), corresponding to the volume fraction range $\phi = 0.15-0.4$, which is similar to the polymer concentration of commonly used membranes prepared from viscose.

The pulsed field gradient NMR spin-echo technique has been employed. It monitors the geometric displacement of individual molecules during a time 10-1000 ms, depending on experimental conditions (here ~ 100 ms) and for sample random walk behavior yields the self-diffusion coefficient (see, for example, Ref. 7 for a recent review). This is usually written:

$$D_s = kT/f^*$$

where f^* is the friction coefficient and kT the thermal energy of the system. It

may be noted that D_m (the mutual diffusion coefficient characterizing the relaxation of a concentration gradient) measures a different physical process, the corresponding friction coefficient having, for example, a decidedly different concentration dependence.⁸

EXPERIMENTAL

Cellulose Gels

The gels used in these measurements were synthesized at the Swedish Forest Products Laboratory, Stockholm, Sweden. The preparation, which has been earlier described,^{9,10} involved regeneration from cellulose xanthate without addition of crosslinking agents. Prior to preparation of samples with various degrees of swelling, the gel (standard regenerated preparation, 6.70 g H₂O/g cellulose) was equilibrated with the diffusant under study—in the one case ethylene glycol and in the other crown ether (15-5). These probes have strong, well-defined, signals suitable for NMR spin-echo measurements (see below). The water contents shown in Table I were achieved by an extremely slow (2–3 months') drying process under carefully controlled conditions. In this way it was found that homogeneity in the gels could be preserved during dehydration (see Discussion).

The cylindrical samples were thereafter stored, under silicone oil, in the refrigerator.

It was found that, at the low water contents of the gels used, the material could be turned down using a lathe into cylinders 20 mm long which fitted exactly into thin-walled NMR tubes of 5 mm o.d. Measurements were performed immediately after this preparation.

Self-Diffusion Measurement

The pulsed field gradient nuclear spin-echo measurements were made at 99.6 MHz using improved versions of methods described previously,¹¹ the experiments now being made at a fixed Δ for all δ values as described in Ref. 12. All measurements were made at 25°C. The experimental uncertainty in the diffusion coefficient was in the range $\pm 5\%$ at $D \sim 0.2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$.

TABLE I
Cellulose Gel Compositions^a

Sample	% cellulose (w/w)	Sample	% cellulose (w/w)
1	26.3	9	32.3
2	41.7	10	35.7
3	43.5	11	41.7
4	37.0	12	45.5
5	55.5	13	52.6
6	62.5	14	55.6
7	66.7	15	58.8
8	71.4	16	66.7

^a Samples 1–8 equilibrated with ~8% crown ether (15-5); 9–16 equilibrated with ~8% ethylene glycol.

The cellulose and water proton signals were characterized by extremely short T_2 values and were completely absent in the spectra when employing a Δ value of 140 ms.

Ethylene glycol and crown ether (15-5) were purchased from Fluka A.G., Switzerland.

RESULTS AND DISCUSSION

The results for the self-diffusion of ethylene glycol and crown ether (15-5) in the gels are shown as a function of the cellulose concentration in Figure 1. The points for ethylene glycol from the earlier investigation² using a sorption technique are included (filled circles).

The retardation, D/D_0 (where D_0 refers to diffusion of probe in the pure solvent) for a small solute molecule diffusing in a polymer matrix is frequently expressed by equations which are of first order in concentration of the network polymer, i.e., some simple function of the volume fraction of macromolecules, ϕ , in the system.¹³⁻²⁰ Recent reviews of transport phenomena in polymer matrices are those of Preston et al.²¹ and Muhr and Blanshard.⁵ The various models used reflect the assumption that (D/D_0) is dependent only on the frequency of occurrence of obstacles around which the small molecules must make detours. No account is taken of hydrodynamic interactions between diffusant and the matrix polymer. (D/D_0) is thus independent of the network mesh size and diffusant size as long as the latter is significantly smaller than the former. The same reasoning applies to concentrated polymer solutions where the polymeric com-

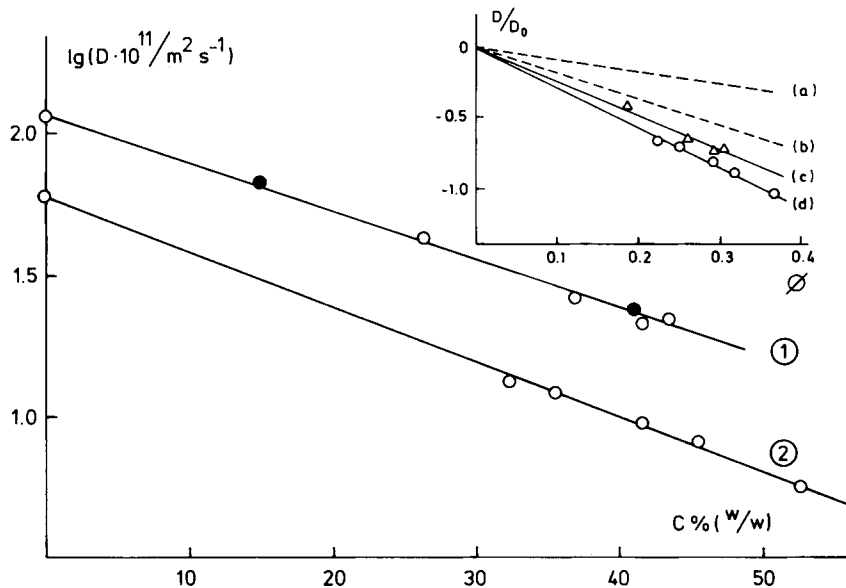


Fig. 1. Self-diffusion coefficients for (1) ethylene glycol and (2) crown ether (15-5) in cellulose gels as a function of concentration (w/w). The filled points are data for ethylene glycol obtained in a previous investigation² using a sorption technique. The insert shows (D/D_0) as a function of concentration cellulose. The broken lines are drawn according to the expressions of Wang¹³ (a) and Mackie and Meares¹⁴ (b); (c) and (d) are the present data, respectively, for ethylene glycol and crown ether 15-5.

ponent is regarded as forming a transient network when the concentration exceeds C^* (i.e., $C \cdot [\eta] > 1$; for a review, see Graessley²²). It is now accepted that diffusion in dilute gels is indistinguishable from transport occurring in polymer solutions of the same concentration.

It is found that the apparent activation energy for diffusion equals the value characterizing viscous flow of the solvent,^{1,2} demonstrating that the frictional properties are those describing the diffusant-solvent pair only. It may be noted that the discontinuities which were a feature of the Arrhenius plots noted in early investigations^{3,4} could not be substantiated^{1,2} and were most probably an aberration. Only for larger solutes (i.e., those approaching the network mesh size) does the apparent activation energy show an increase reflecting the onset of intermolecular hydrodynamic interactions.²³

The expression of Wang¹³ is

$$D/D_0 = (1 - \alpha \cdot \phi) \quad (1)$$

and was derived for diffusion in a continuum in which there are impenetrable and immobile spherical obstacles of volume fraction ϕ . The coefficient α is related to the shape of the diffusant molecule and has a value of $\alpha = 1.5$ for spheres.

The expression of Mackie and Meares,¹⁴ based on a liquid lattice model where a fraction ϕ of the sites are blocked, is

$$\frac{D}{D_0} = \left(\frac{1 - \phi}{1 + \phi} \right)^2 \quad (2)$$

There is some evidence that the Wang equation holds in dilute systems, while eq. (2) is more adequate in concentrated networks.²⁴ The broken lines in the insert to Figure 1 represent eqs. (1) and (2) and the latter is the closest approximation to the present data. It should be noted that energetic interactions between diffusant and cellulose chains (adsorptive, for example) will also reduce (D/D_0); see, for example, the very different diffusivities of the α - and β -cyclodextrins in solutions of poly(methacrylic acid)²⁵. Such contributions are neglected in the approaches leading to eqs. (1) and (2). In real systems the observable value of D at any particular concentration of network polymer will almost always be lower than predicted since an adequate description of weak interactive forces between network polymer and diffusant does not at present exist.

Earlier workers, for example, Nishijima and Oster,¹⁵ explained the reduced mobility of small solutes in gels and polymer solutions by the concept of a microviscosity, describing the local environment experienced by the diffusing particle in the network. Preston et al.,²¹ however, have pointed out that the microviscosity is but an alternative description of the excluded volume interactions between diffusant and matrix polymer.

One concludes that the cellulose matrix has weak interactions with the diffusants used here and that the Mackie-Meares equation¹⁴ gives a fair description of the influence of cellulose concentration. The cellulose gels are, of course, probably far from homogeneous on the molecular level. They are, like agarose gels, composed of intermingled regions of greater and lesser order. This will result in a broad range of mesh sizes within a given gel. An earlier investigation² revealed, however, that essentially all of the water in the gel used was accessible

to the small solutes such as ethylene glycol. The present gels are considerably more concentrated. It was the intention to use the same technique to measure the water mobility, but the transverse relaxation times (T_2) were too short. For the same reason, it was not possible to make measurements on the probes in gels at concentrations in excess of 53% (w/w) cellulose. A forthcoming contribution will describe the diffusion of ions in cellulose gels.

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