

Molecular Motion of Small Molecules in Cellulose Gels Studied by NMR

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Synopsis

Measurements of relaxation times, T_1 and T_2 , and self-diffusion coefficients, D , for small molecules, viz., H_2O , dioxane and *t*-butanol, in the gel system cellulose/ H_2O are reported and compared with those for H_2O in a polyacrylamide gel of the same polymer content. The temperature dependence of T_1 and D can for all the penetrants be represented by Arrhenius type relations which merely are parallel shifts by the same amount, towards smaller values, of those obtained without polymer. The T_2 values for H_2O in both gels pass through a shallow minimum over the considered temperature interval (14°–44°C). Furthermore, relaxation times T_1 of D_2O in the gel system cellulose/ D_2O are reported; in a plot of $\ln T_1$ vs. $1/T$, a plateau region is observed at higher temperatures.

INTRODUCTION

Several papers have been devoted to the interaction between cellulose and water in a variety of cellulosic systems. However, there seem to be few investigations of the mobility of small molecules in cellulose gels.

The principal aim of the present NMR work is to obtain information about molecular motion in cellulosic gels. For this purpose the temperature dependences of the spin-lattice (T_1), spin-spin (T_2) relaxation times, and the self-diffusion coefficients (D) of water and other small penetrant molecules, viz., dioxane and *t*-butanol, were examined in cellulosic gels. By also investigating the molecular motion of molecules other than water, it is possible to establish whether the observed¹⁻⁴ interaction effects in cellulose/water systems depend on properties peculiar to water.

In a forthcoming paper⁵ the diffusion behavior of larger molecules, e.g., polyhydric alcohols in cellulose gels, will be reported.

EXPERIMENTAL

Materials and Preparation of Gels

The cellulose gels used in this investigation were prepared at the Swedish Forest Products Research Laboratory. The gels were synthesized^{4,6} from sodium cellulose xanthate without addition of a crosslinking substance (e.g., epichlorohydrin). The preparation, characterization, crystallinity, and swelling behavior of the used gels have been reported previously.⁶ The degree of swelling is given as g water/g dry gel (g/g). In this series of experiments a heat-treated (at 80°C for 5 days) gel of type O-B (pure regenerated cellulose) swollen to 6.70 g/g was studied. This corresponds to a volume fraction of cellulose of $\phi = 0.093$.

By using a special punching tool the gels were cut into approximately 20 mm long cylinders, which fitted into the NMR tubes used (thin-walled NMR tubes of 5 mm o.d.) perfectly.

Since different probe molecules (water, dioxane and *t*-butanol) were employed in this study, the gels were equilibrated in the respective surrounding medium for at least 2 days before the actual measurement. One gel piece was equilibrated in 100% water, another in 8 wt % H₂O/92 wt % D₂O, a third in 8 wt % dioxane (p.a. Merck)/8 wt % H₂O/84 wt % D₂O, and the fourth in 8 wt % *t*-butanol (p.a. Merck)/8 wt % H₂O/84 wt % D₂O. In addition a polyacrylamide gel ($\phi = 0.131$) containing pure water was prepared directly in an NMR tube. This gel was prepared according to principles discussed elsewhere.⁷

The equilibrated gel pieces were transferred to NMR tubes, open at both ends, and the tubes were then sealed at both ends with teflon stoppers. Great care was exercised in order to avoid trapped air adjacent to the sample.

For the deuterium spin-lattice measurements, 10-mm thin-walled NMR tubes were filled with gel pieces which had been treated repeatedly with pure D₂O.

NMR Measurements

Proton spin-lattice (T_1), spin-spin (T_2) relaxation times, and self-diffusion coefficients (D) are measured in a JEOL FX-100 spectrometer, operating at a frequency of 99.6 MHz. The deuterium spin-lattice relaxation times were measured using a Bruker CXP-90 spectrometer at a frequency of 13.82 MHz.

T_1 was determined by the inversion recovery method and T_2 by the C.P.M.G. pulse sequence, supplied with the JEOL software package for the FG/BG systems. This latter pulse sequence is an FT implementation of the Carr-Purcell-Meiboom-Gill method for the determination of T_2 ; pulse intervals of 10 ms were used in the pulse train.

The Fourier transform proton spin-echo measurements of the solvent self-diffusion coefficient were carried out in accordance with the principles discussed previously.⁸

The temperature was varied by a flow of thermostated dry air and could be controlled to an accuracy of $\pm 0.5^\circ\text{C}$ in the studied temperature range (14–44°C).

The self-diffusion measurements were found to be reproducible to within $\pm 3\%$, while T_1 and T_2 were marred by somewhat larger error.

RESULTS

Figures 1 and 2 show the temperature dependence of the spin-lattice (T_1), spin-spin (T_2) relaxation times, and the self-diffusion coefficients (D) for water in cellulose and polyacrylamide gels, respectively. The temperature dependence of T_1 and D can be represented by straight lines, both with and without the polymer. Both systems show very similar features. The curves representing the T_2 data in the gels exhibit shallow minima. The values of T_1 , T_2 , and D for the respective penetrant in the gels are smaller than the corresponding values in the solvent alone. The observed reduction in T_1 , T_2 , and D as well as the finding that $T_2 < T_1$ when polymer is present are features which are common for most polymer-solvent systems.

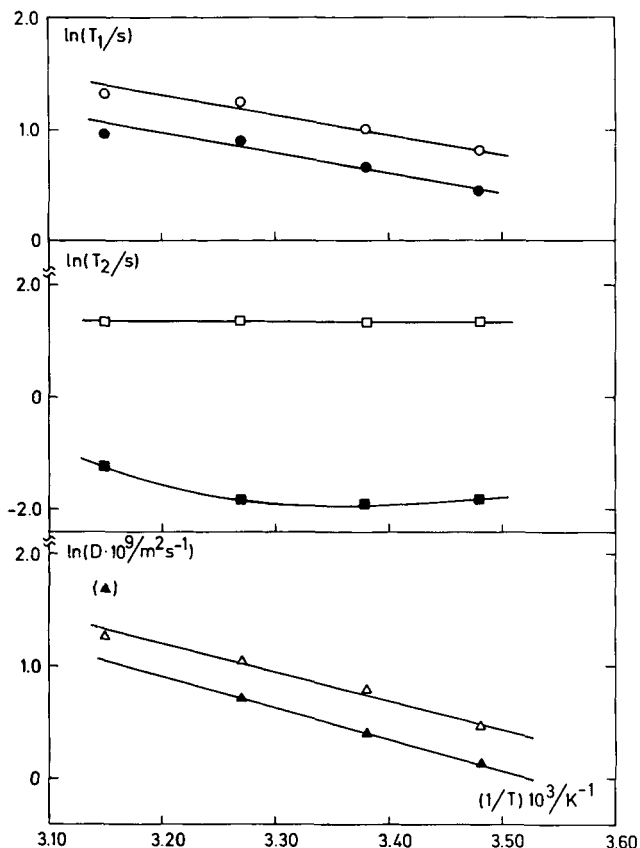


Fig. 1. Temperature dependence of T_1 , T_2 , and D for water in the system cellulose/water. Open symbols represent data in absence of cellulose. Solid symbols represent data in the presence of cellulose.

Furthermore, as can be seen from Figures 1 and 2, there seems to be no significant difference in the behavior of water in the two gel systems cellulose/ H_2O and polyacrylamide/ H_2O .

Figure 3 illustrates the temperature dependence of the *deuterium* spin-lattice relaxation time for the cellulose/ D_2O system. The curve representing the T_1 data for the gel displays a plateaulike region at higher temperatures, which is not observed for the proton T_1 data for the cellulose/water system.

Figure 4 depicts the results from proton measurements on the system cellulose/ H_2O/D_2O , where the composition of H_2O/D_2O is 8/92 wt %. The temperature dependence of D is similar to that for the cellulose/water systems (Fig. 1), whereas the behavior of T_1 and T_2 differs substantially from that in Figure 1. These observations indicate that the behavior of T_1 and T_2 is correlated with the H_2O/D_2O ratio.

Figures 5 and 6 show the temperature dependence of T_1 , T_2 , and D for dioxane and *t*-butanol, respectively, in the multicomponent systems (cellulose/dioxane/ H_2O/D_2O and cellulose/*t*-butanol/ H_2O/D_2O). T_1 , T_2 , and D exhibit similar features in both systems. Furthermore, the behavior of T_1 and D is reminiscent of that for the cellulose/water system, whereas the T_2 process is more complicated for the multicomponent systems.

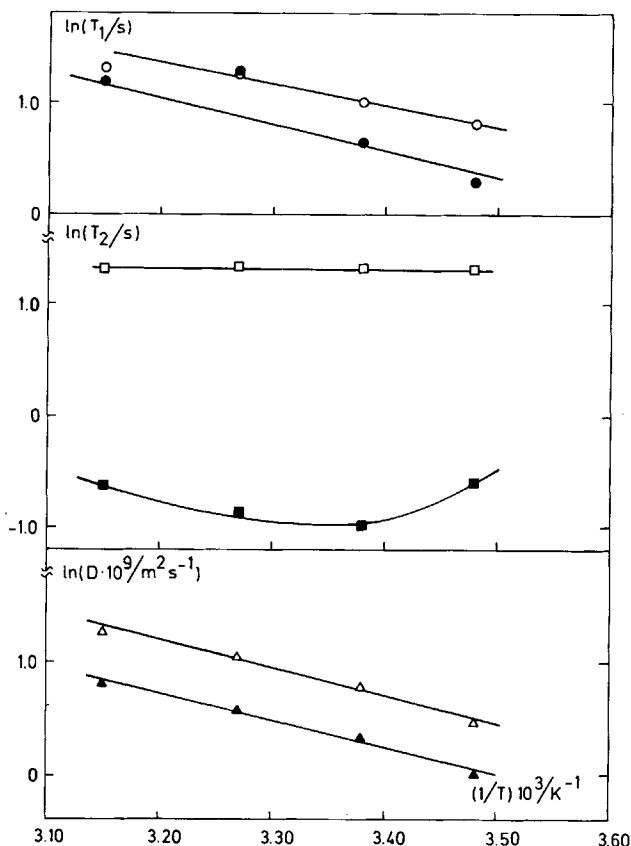


Fig. 2. Temperature dependence of T_1 , T_2 , and D for water in the system polyacrylamide/water. Open symbols represent data in absence of polyacrylamide. Solid symbols represent data in the presence of polyacrylamide.

In these experiments D_2O was added in order to reduce the water peak and to facilitate simultaneous and more accurate evaluation of the signals from the other monitored components (dioxane and *t*-butanol).

DISCUSSION

The interpretation of T_1 and T_2 in gels is by no means simple and straightforward, although attempts at interpretation using simple two-state (or four-state) models have been made. However, there is a conglomeration⁹ of complicating factors such as exchange with specific binding sites, proton exchange processes, spin coupling to polymer protons, spin-rotation interaction, and heterogeneity on a macromolecular scale which together prohibit an unambiguous interpretation in terms of a distribution of correlation times. Thus, it is difficult, if not impossible, to obtain a simple and overall consistent picture of relaxation phenomena in macromolecular systems and in particular for multicomponent systems.

Some characteristic data from the self-diffusion, spin-lattice, and spin-spin relaxation time measurements are summarized in Table I; the data refer to the

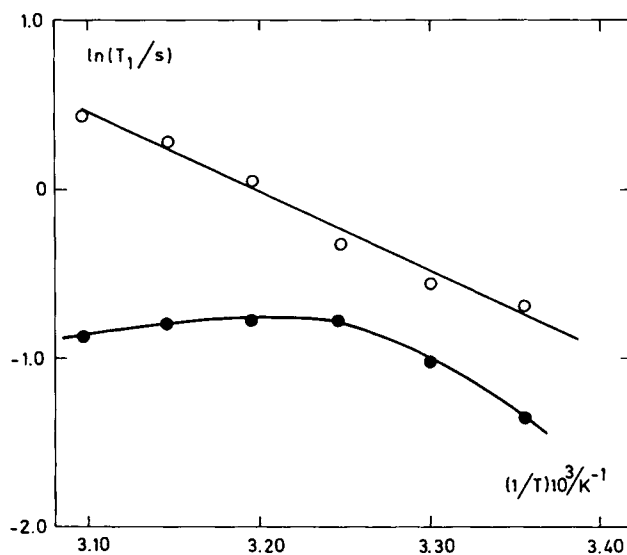


Fig. 3. Temperature dependence of deuterium spin-lattice relaxation time (T_1) for D_2O in the system cellulose/ D_2O . Open circles represent data for pure D_2O . Solid circles represent data in presence of cellulose.

individual components (boldface type) in the systems, with and without (subscript 0) the presence of polymer, respectively, and have been evaluated at the arbitrary temperature of $30^\circ C$ from the curves in the figures. A number of features may be noted: (a) The values of T_1 , T_2 , and D for a given component in the gels are consistently smaller than the corresponding parameters for the component in the absence of polymer. (b) The presence of polymer reduces the value of T_1 and D to approximately the same degree, while T_2 is influenced much more strongly. (c) In the gel systems T_1 is generally much larger than T_2 . (d) Apparent activation energies (E_A) determined from spin-lattice relaxation data and self-diffusion data seem to correlate fairly well. (e) In the gel system in which H_2O and D_2O are both present and the behavior of H_2O is monitored, the T_1 data, in particular, deviate from the general pattern of behavior.

TABLE I
Characteristic Data from Self-Diffusion D , Spin-Lattice Relaxation Time T_1 , and Spin-Spin Relaxation Time T_2 , Measurements for the "Probe"^a

System ^b	$T_1/T_{1,0}^c$	D/D_0^c	$E_A^{T_1}/kJ, mol^{-1}$	$E_A^D/kJ, mol^{-1}$	$T_2/T_{2,0}^c$	$T_{1,0}/T_{2,0}^c$	T_1/T_2
Cellulose/ H₂O	0.70	0.72	15.4	23.3	0.04	0.80	14.4
Polyacrylamide/ H₂O	0.70	0.63	20.0	20.4	0.11	0.85	5.6
Cellulose/ H₂O / D_2O	0.23	0.70	(-3.3)	17.0	0.018	1.6	20.5
Cellulose/ dioxane / H_2O / D_2O	0.71	0.68	13.3	15.0	0.098	0.75	5.6
Cellulose/ t-butanol / H_2O / D_2O	0.91	0.72	20.8	24.1	0.40	1.02	2.2

^a The data are evaluated at $30^\circ C$ from the figures.

^b The boldface type indicates the component monitored in the NMR experiment.

^c Subscript zero denotes the absence of polymer.

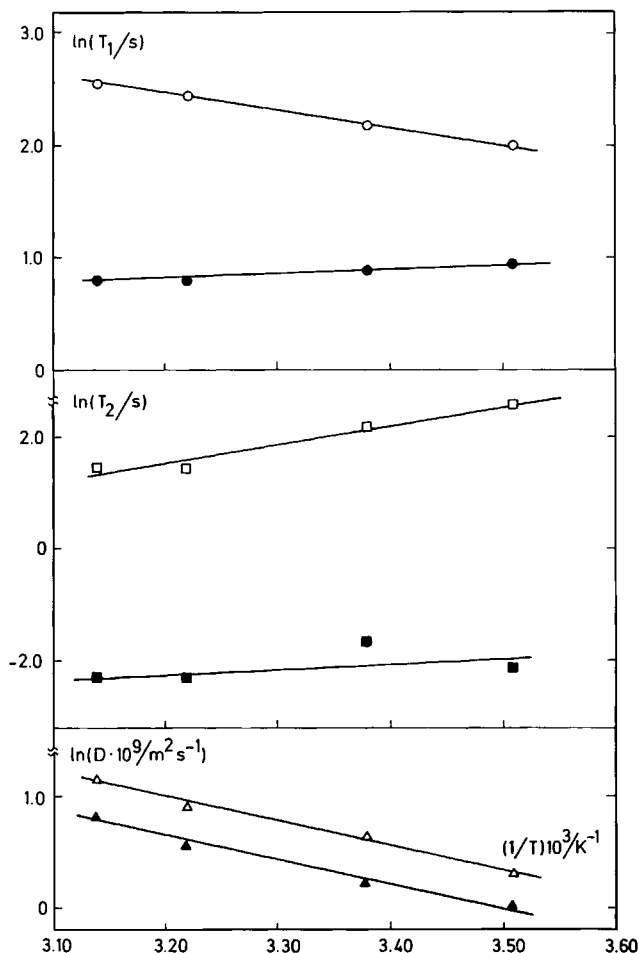


Fig. 4. Temperature dependence of T_1 , T_2 , and D for water in the system cellulose/ $\text{H}_2\text{O}/\text{D}_2\text{O}$. Open symbols represent data in absence of cellulose. Solid symbols represent data in presence of cellulose.

Temperature Dependence of T_1 and T_2

The T_1 data represented in Figures 1, 2, 5, and 6 exhibit an "ordinary" temperature behavior and can be described by an Arrhenius-type equation. Over the studied temperature range it was found that the ratio of T_1 in gel to T_1 in solvent was practically constant and close to the corresponding ratio for diffusion.

The rather complex behavior of the temperature dependence of the deuterium spin-lattice relaxation time for the cellulose/ D_2O system (Fig. 3) is unclear. However, one should note that with ^2H quadrupole relaxation is the dominant mode of relaxation, making the relaxation times directly related to rotational molecular reorientation. Furthermore, the protons nuclei are less sensitive to changes in mobility than the deuterions nuclei.

In this context it may be noted that the flat maximum observed in the T_1 curve in Figure 3 is located at approximately the same temperature as that observed

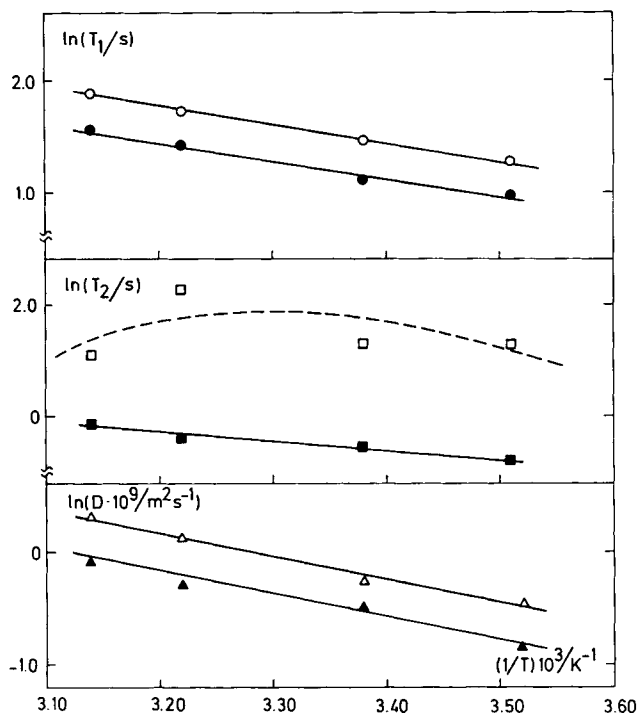


Fig. 5. Temperature dependence of T_1 , T_2 , and D for dioxane in the system cellulose/dioxane/ H_2O/D_2O . Open symbols represent data in absence of cellulose. Solid symbols represent data in presence of cellulose.

by Westman and Lindström¹⁰ in their proton spin-spin relaxation time measurements of water in cellulose gels. They associated their maximum with a secondary transition. However, this coincidence in temperature maximum may be fortuitous.

The difference in T_1 behavior between the systems cellulose/ H_2O (Fig. 1) and cellulose/ H_2O/D_2O (Fig. 4) seems to be associated with H-D exchange processes. This conjecture is favored by the finding that when the T_1 behavior of dioxane (Fig. 5) or *t*-butanol (Fig. 6) (these "probes" have nonexchangeable protons) is monitored in the NMR experiment, no "complications" arise.

The spin-spin relaxation time (T_2) measurements of water in the "simple" systems cellulose/water and polyacrylamide/water show features reminiscent of those reported^{11,12} for agarose gels. The observed shallow minimum was attributed to exchanges of water protons with exchangeable protons on the polymer chains. However, the T_2 data reported by Westman and Lindström¹⁰ for water in cellulose gels revealed a maximum; similar features were observed by Child¹ and Froix and Nelson.³

The general feature that $T_2 < T_1$ (in the presence of polymer) can be anticipated since spin-spin relaxation has other modes of relaxation in addition to those for T_1 . An additional relaxation mechanism for T_2 is frequently proposed to arise from a marked slowing down of translational and rotational diffusion due to interactions of "probe" molecules with the polymer.

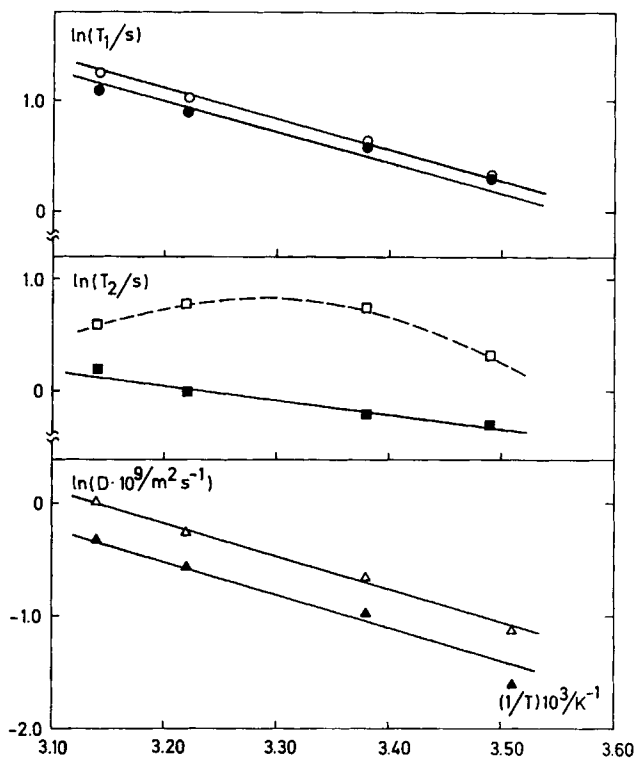


Fig. 6. Temperature dependence of T_1 , T_2 , and D for t -butanol in the system cellulose/ t -butanol/ H_2O/D_2O . Open symbols represent data in absence of cellulose. Solid symbols represent data in presence of cellulose.

Self-Diffusion

The self-diffusion coefficient D is a measure only of the translational motion of the penetrant molecules and, therefore, should be a more direct indication of the mobility than the parameters T_1 and T_2 .

The reduction in D for a small molecule in polymer solution or gel may be attributed to two main factors. (a) The obstruction effect: Because macromolecules are larger and less mobile than the diffusant, they impede the translational motion of the diffusant. "The small migrating species have to make detours around the larger units in solution or gel." (b) Direct interactions between the diffusant and the polymer, e.g., the hydrogen bonding and the ionic interaction: A number of experimental investigations¹³⁻¹⁹ have emphasized the significance of these factors, and a number of theoretical models have been presented in the literature.^{14,16(a),20-23}

By considering, in the zeroth approximation, simple obstruction phenomena, Mackie and Mears treated the problem of gel systems and obtained the relation

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

where D_0 is the diffusion coefficient in absence of polymer and D is the diffusion

coefficient at a polymer volume fraction ϕ . The Mackie–Mears relation is found to account very well for the observed reduction in D for all the diffusants employed in this investigation (see Figs. 1, 2, 4–6), indicating that the obstruction effect is paramount for these systems. It is evident from Table I that the ratio D/D_0 assumes, within experimental error, a constant value irrespective of the system. Recent investigations on the diffusion of a variety of penetrants in polyacrylamide⁷ and cellulose gels⁵ using a sorption technique led to a similar conclusion.

The temperature dependence of D can for all systems be described by a simple Arrhenius-type relation, giving the same activation energy independent of if polymer is present or not. This observation further supports the conjecture that the presence of polymer simply constitutes an obstruction effect. The slopes in Figures 1, 2, and 3 all correspond to a value of $E_A^D \approx 20$ kJ/mol, which is an average value for the viscous flow of water. A similar value is found for D of dioxane and *t*-butanol (Figs. 5 and 6).

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