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Self-Diffusion of Dimethyl Sulfoxide and Dimethylformamide in Solutions and Gels of Cellulose Acetates by Pulsed Field Gradient NMR

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ABSTRACT: Self-diffusion measurements of dimethyl sulfoxide and dimethylformamide in solutions and gels of cellulose acetates have been carried out by pulsed field gradient NMR for different concentrations and degrees of substitution of the polymer. The solvent's diffusion coefficients, D, are found to depend on the time of measurement, indicating the system to be heterogeneous within a space scale of a few microns. D time dependence is more explicit for higher concentrations of the polymer with lower substitution degree.

Introduction

It is now generally accepted that a physical polymer gel is a three-dimensional network of macromolecular chains cross-linked by physical bonds and formed through physical aggregation.[1] During gelation larger and larger macromolecular associates, clusters, are formed, and finally one infinite homogeneous cluster extends throughout the entire volume of the sample. The gel state of polymers has been investigated for many years both theoretically[2–4] and experimentally[1,5–8] by different techniques. The information on the gelation process, the intermolecular interactions and the gel structure may also be obtained by studying the diffusion of micromolecular solute in gels. There has been much progress in the theoretical description of the molecular translational mobility within gels during recent years.[9–13] However, there is still a lack of a general theoretical description quantitatively accounting for the influence of a solute size, the intermolecular interactions, and the geometrical organization of macromolecules on the diffusion of small molecules. Thus, new experimental data on the subject might promote the appearance of a consistent theoretical approach adequately describing diffusion coefficients of different solutes within different gels and polymer solutions.

This work was designed to study the effect arising from the gel or the polymer solution structure on the self-diffusion coefficients of solvent molecules in cellulose acetate (CA)–dimethyl sulfoxide and CA–dimethylformamide systems. The set of CA differing in the number of nonsubstituted OH groups in a polymer unit was examined. In our previous study[14] the rotational and translational mobility of small solute molecules within the CA–solute–dimethyl sulfoxide systems was found to be dependent on the hydroxyl group content of the polymer. In this work the difference in the character of the solvent diffusivities within the gels and solutions of CA with different degrees of substitution was attributed to the difference in the self-organization of macromolecules in the systems. The latter was supposed to arise from the greater number of hydrogen bonds between the macromolecules containing a larger amount of OH groups in a polymer unit. Using the pulsed field gradient spin-echo method the time dependence of the diffusion coefficients of the solvent molecules was studied. This allowed us to conclude whether the systems under investigation could be considered as quasihomogeneous within a space scale of several micrometers, since the distances diffused by the micromolecules during the time of measurement in our experiments were about that long.

Experimental Section

Samples. The fully protonated distilled dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) (Merck, Darmstadt) were used as received. Cellulose acetates with different degrees of substitution, γ, were obtained by saponification and supplied by Polymersyntez (Vladimir, Russia). The value of γ equals the average number of OH groups substituted in a polymer unit and does not exceed 3 for CA. The polymer with a higher γ has a lower amount of hydroxyl groups. The CA samples with γ equal to 0.63, 1.00, 1.66, 2.38, and 2.90 have been investigated. The average degree of polymerization of the samples was within the limit 300–400. The prepared solutions were held at 60 °C for 24 h. A further increase in the holding time did not alter the optical properties of the solutions and the dynamic characteristics of the diffusing molecules. At CA concentrations higher than 150 mg/mL the solutions became viscous, and they stopped flowing at concentrations higher than 300 mg/mL.

Method. Self-diffusion coefficients, D, of DMSO and DMF have been measured using the ^{1}H NMR pulsed field gradient spin-echo (PGSE) method.[15] Normally, PGSE studies the attenuation of the spin-echo signal amplitude, A, with increasing magnitude of the magnetic field gradient pulse, g. If the molecules containing magnetic nuclei undergo Brownian motion, the dependence $A(g)$ will have the form

$$A(g) = A_0 \exp(-2t_d/T_2) \exp(-\gamma_H{}^2\delta^2 g^2 t_d D) \qquad (1)$$

where T_2 represents the spin–spin relaxation rate of the hydrogen nuclei of the solvent, γ_H is the gyromagnetic ratio for protons, D is the diffusion coefficient, δ is the gradient pulse duration, and t_d is the time of diffusion measurement ($\delta \ll t_d$).

For unrestricted diffusional motion D determined from (1) does not depend on t_d. Yet, if we study the diffusion of liquid molecules in systems with spatial heterogeneity, D begins to depend on time due to the nonlinear nature of the time dependence of the molecule mean-square displacement (msd), $\langle x^2(t)\rangle$, along the gradient axis. In such cases experimental results

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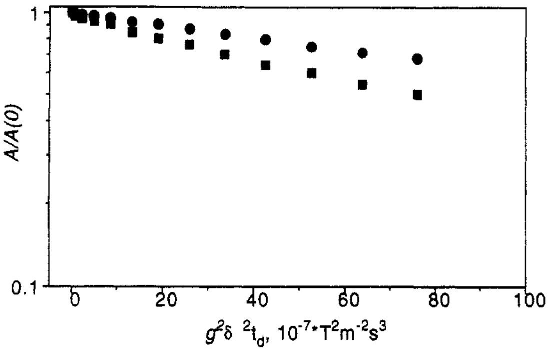

Figure 1. Measured diffusion curves (1) for DMSO within DMSO/CA solutions ($\gamma = 0.63$) at polymer concentration $c = 400$ mg/mL for two different diffusion times: $t_d = 10$ ms (■) and $t_d = 100$ ms (●).

are often represented in terms of an apparent self-diffusion coefficient, D_{app}[16]

$$D_{app}(t_d) = \frac{\langle x^2(t_d)\rangle}{2t_d}$$

where

$$\langle x^2(t_d)\rangle = -\frac{2}{\gamma^2\delta^2}\frac{d(\ln A(g^2,\delta^2,t_d))}{d(g^2)}\bigg|_{g=0}$$

In such an interpretation D_{app} should be determined from the initial parts of the echo decays (1), where the reduction of the amplitude does not exceed 50%. The time dependence of the diffusion coefficients of small molecules has been observed experimentally in swollen polymers, plant tissues, synthetic membrane,[16-20] etc. In polymer solutions and physical reversible gels, however, no $D(t)$ for solvent molecules has been reported yet.

Self-diffusion measurements were made on a home-built NMR spectrometer at the ^1H resonance frequency of 23 MHz. The magnitude of the pulsed field gradient was varied at a constant diffusion time for each measurement in such a way that the echo amplitude did not attenuate less than to about half of its value at $g = 0$. On changing t_d the value of $(\delta^2 t_d)$ was kept constant. Actually, in this work we dealt with D_{app}, but the subscript will be omitted later for simplicity. The T_2 of the protons of the polymer was found to be about 3 ms in the low concentrated solutions and became shorter as the concentration increased. Thus the undesired signal of the polymer protons did not interfere with the signal of those of the solvent, because the shortest t_d used in our experiments was 10 ms. There were different kinds of solvent molecules within the samples under study: free moving bulklike molecules, those bound to the OH groups of the polymer, and motionally-altered molecules moving in the vicinity of the polymer or inside macromolecular cluster. However, the experimental curves (their initial slopes) were single exponential for all concentrations studied. This could be accounted for by (a) rapid exchange between the H-bonded and free molecules (rapid exchange means that the exchange occurs on a time scale that is much shorter than the relaxation times) and b) a small value of population of motionally-altered molecules at small polymer concentrations and the short T_2 of their protons for high concentrated polymer solutions. This means the main contribution to the observed signal was made by the protons of the free solvent moving among the macromolecules and macromolecular clusters. This made it possible to estimate D by using (1). In Figure 1 the amplitude decay of the echo signal is shown in CA with $\gamma = 0.6$ at $c = 400$ mg/mL. The pulse current in the quadrupole coils was 30-A maximum, and the corresponding field gradient was 25 T/m. The temperature was 23 °C. The error in the measurements did not exceed 5%.

The light scattering experiment was carried out in the laboratory of Prof. Sillescu at the University of Mainz and is described elsewhere[21] in detail. Dust was removed by filtering the solution through Millipore 0.45-μm Teflon filters. The deviation of the correlation functions from a single-exponential decay was relatively small, and the decay rates were independent of q^2. A few comparative self-diffusion measurements were made in this laboratory using a ^1H NMR three-pulse stimulated echo method in the (static) stray field gradient of the cryomagnet.[22]

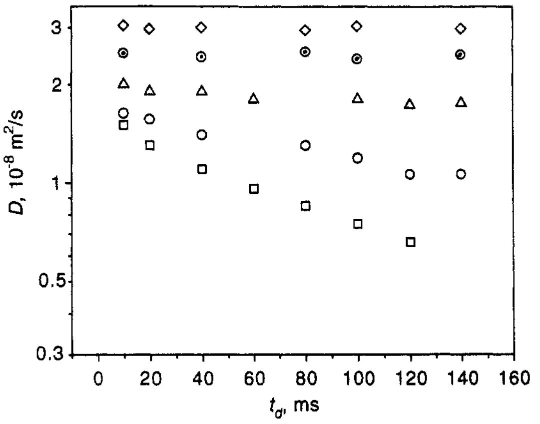

Figure 2. Time dependence of solvent diffusion coefficients within the DMSO/CA solutions ($c = 400$ mg/mL) for different γ: 0.63 (□), 1.00 (○), 1.66 (△), 2.38 (⊚), and 2.90 (◇).

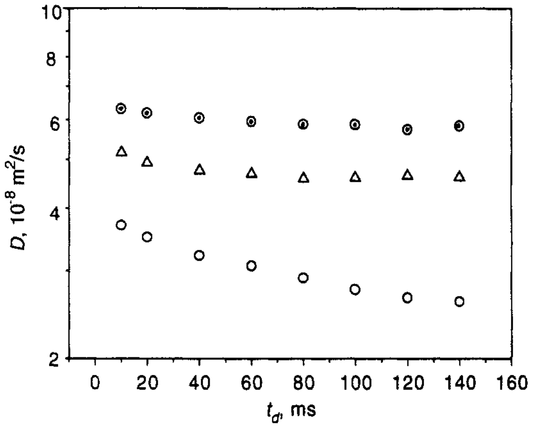

Figure 3. Time dependence of solvent diffusion coefficients within the DMF/CA solutions ($c = 400$ mg/mL) for different γ: 1.00 (○), 1.66 (△), and 2.38 (⊚).

Results and Discussion

In order to study the sensitivity of the character of translations of solvent molecules to the structure of polymer gel, we measured D of DMSO and DMF as a function of time in CA gels of different γ at fixed polymer concentrations, $c = 400$ g/L (the polymer volume fraction ~ 0.25). From the data presented in Figures 2 and 3, one can see that there is a certain time dependence of D within the CA gels of lower γ values. The values of D decreased with increasing t_d but did not always reach the stationary limit due to the T_2 limitations. The decrease of the diffusion coefficients was not large, but it did not appear to be an artifact. The rate of the amplitude decays shown in Figure 1 is substantially higher for measurements with $t_d = 10$ ms than for those with $t_d = 100$ ms, and the decays do not display a downward concavity. The latter means that the residual gradient[23] was of no importance in our measurements. The complete D independence of time in the DMSO/CA gels with $\gamma = 2.4$ and 2.9 at the same experimental conditions also allowed us to conclude that the observed time dependence of the diffusion coefficients of solvent molecules in polymer solutions was not caused by the special characteristics of the spectrometer used. The self-diffusion measurements carried out by using the static gradient stimulated echo method[22] also showed D of the solvent molecules was time dependent, but the

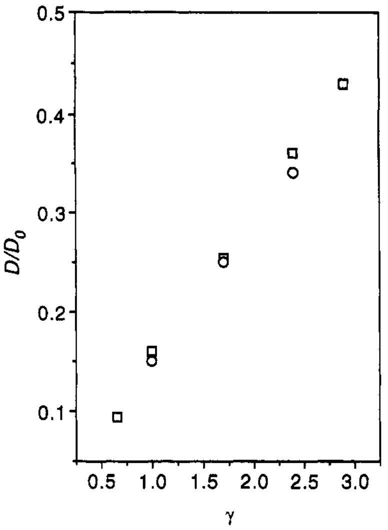

Figure 4. Ratio of solvent diffusion coefficients measured in the pure solvent, D_0, and within the CA solutions at c = 400 mg/mL, D, as a function of γ for DMSO (□) and DMF (○). (D_0 were independent of time; D were determined with t_d = 120 ms.)

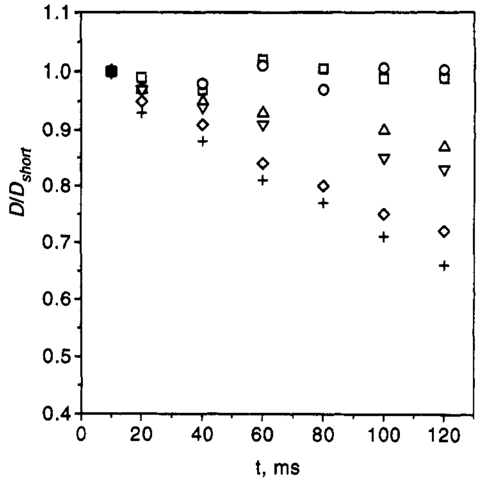

Figure 5. DMF diffusion coefficients as a function of time related to those measured at a *short* (t_d = 10 ms) time of diffusion within the DMF/CA solutions (γ = 1.00) for different polymer concentrations, c (mg/mL): 50 (□), 100 (○), 150 (△), 200 (▽), 250 (◇), and 400 (+).

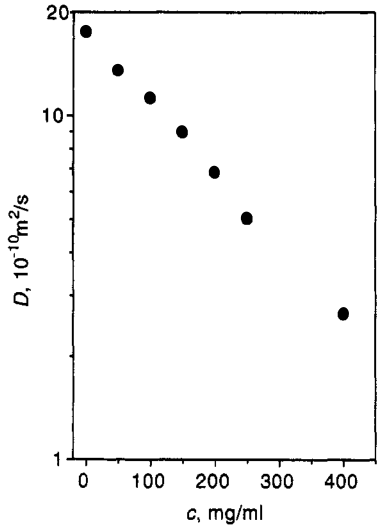

Figure 6. DMF diffusion coefficients as a function of polymer concentration in the solutions of CA with γ = 1.00 for t_d = 120 ms.

quantitative analysis of the data was complicated by the fact that the polymer component was unavoidable in the total proton signal.

The time dependence of D of DMSO and DMF molecules in CA gels indicates that the gels are not homogeneous within a space scale of several microns for the polymers with γ lower than 2.4. These polymers have a greater number of nonsubstituted OH groups and as a consequence a greater possibility for intermolecular aggregation. To explain the experimental D time dependence, we assumed that the spatial heterogeneity in the gels under investigation was caused by forming macromolecular aggregates when the polymer concentration increased and that the aggregates of greater dimensions are formed in the solutions of CA with lower γ. We assumed furthermore that the gels of CA consist of these clusters bound to each other, which might undergo a process of decomposition and further formation.

We have performed the measurements for DMSO and DMF because DMF is known to be a poor solvent for CA (the polymers with γ = 2.9 and 0.6 could not be dissolved in DMF). Since the polymer–polymer interaction is stronger in a weak solvent, one might expect that the clusters of greater dimensions would be formed in DMF and the time dependence of D of the solvent would be more apparent within the DMF/CA gels in comparison to that in DMSO/CA. However, as can be seen from Figures 2 and 3, the solvent $D(t)$ behavior within these two systems was very similar and only for gels with γ = 1.7 and 2.4 was the time dependence of D of DMF slightly more explicit. The effect of the gel matrix on a solvent's D is often characterized by determining the ratio of its diffusion coefficients in gel, D, and in a bulk solvent, D_0. The measured D_0 values for DMSO and DMF were 7 and 17.5 × 10^{-10} m^2/s, respectively, and we took the long-time diffusion coefficients (t_d = 120 ms) as D. The ratios D/D_0 (Figure 4) were very close for both solvents examined, being less for the gels with lower γ at fixed c = 400 mg/mL. The reduction of D with a decrease of γ occurs mainly due to strong hydrogen bonding of DMF and DMSO with the hydroxyl groups of the polymer. However, in our previous study on the CA/DMSO solutions,[14] it has been shown that even in the absence of hydrogen bonding with polymer the reduction of the diffusion coefficients of small molecules is greater in solutions of CA with a bigger amount of OH groups. This has been explained by the increased obstruction effect within these solutions due to the stronger inter- and intramacromolecular association. In our model that would correspond to the formation of "tight" clusters with smaller and fewer pores in the case of CA with a lower degree of OH substitution.

To test the assumption concerning the influence of the cluster formation on the character of the solvent diffusion, we studied $D(t)$ of DMF in solutions of CA with γ = 1 at different polymer concentrations. The obtained data are presented in Figure 5 as the ratios of the diffusion coefficients measured at the shortest t_d = 10 ms, D_{short}, and those measured at different t_d (the absolute values of D of DMF measured at t_d = 120 ms are shown in Figure 6 as a function of polymer concentration). It can be seen from Figure 5 that DMF diffusion coefficients were independent of time within the dilute polymer solutions, while the time dependence of D was observed for solutions with c starting from 150 mg/mL. In the framework of our interpretation, this means that the dimensions of clusters should be smaller than 1–2 μm when c is less than 150 mg/mL. The radii of the clusters of CA with γ = 0.6 and 2.4 in DMSO at c = 90 mg/mL obtained from the dynamic light scattering experiments were found to be about 256 and 179 nm, respectively, whereas the measured zero shear rate viscosity, η, of these solutions was 0.76 and 0.3 Pa s

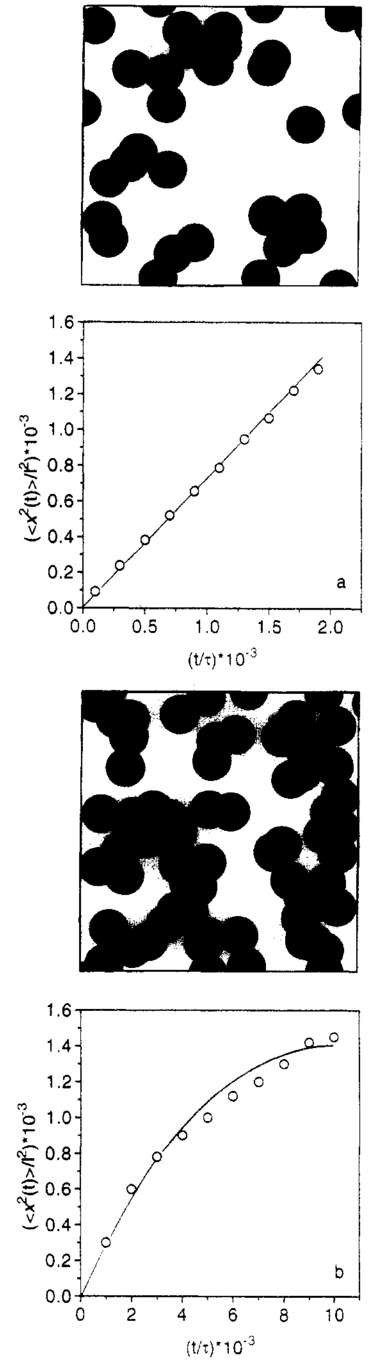

Figure 7. Results of msd computer calculation for particle random walk in a random inhomogeneous system, described in the text, for the different space occupied by the circles, ρ: ρ = 0.3 (a) and ρ = 0.7 (b).

with a higher η for γ = 0.6. These data are in agreement with our assumption about the cluster formation process in the solution under study.

The influence of polymer concentration on the nonlinearity of the time dependence of msd of solvent molecules has also been investigated by performing a computer simulation of particle random walk with periodic boundary conditions in a two-dimensional system of randomly fallen circles impermeable for the particle that was reflected at their surface. The circles that represent a polymer in our model could overlap and form different macroaggregates. For a fixed number of circles, we renewed their arrangement during the calculation and estimated the area occupied by the circles, ρ, that was used as a concentration parameter. The step length, l, was equal to 1/30 of the circle diameter. We calculated the particle msd as a function of time for different ρ values.

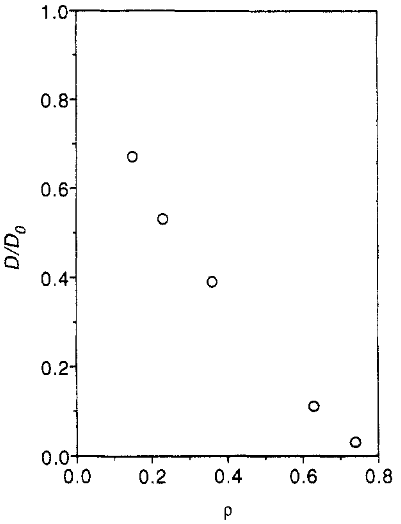

Figure 8. Calculated particle diffusion coefficients as a function of ρ. (D_0 corresponds to ρ = 0.)

Figure 7 sites an example of a calculation of msd along axis x depending on the time of motion for low (a) and high (b) concentrations of circles. The nonlinear nature of the curve is clearly apparent for higher concentration of "polymer", while particle msd remains linear for a lower one. The reduction of the slope of the curve in the latter case in comparison to free diffusion is due to the existence of circles in the "solution". The long time diffusion coefficients for the two curves a and b differ approximately by a factor of 4. $D(t)$ dependence estimated from the msd time dependence is very similar to the experimental ones. However, D determined from the computer calculation begins to depend on time at a much higher concentration of polymer than the experimental coefficients. The calculated asymptotic values of D (at $t \rightarrow \infty$) decrease more slowly as the concentration of circles increased (Figure 8) in comparison to the concentration dependence of DMF diffusion coefficients. The model of randomly fallen circles obviously oversimplifies the situation in real gel or solution (e.g., the complexation with polymer and diffusion inside the polymer has not been taken into account), but it describes qualitatively the experimental results.

Conclusions

The self-diffusion coefficients of solvent molecules within the CA gels and solutions in DMF and DMSO have been found to be dependent on time of diffusion measurement for the samples with a higher concentration of the polymer having a lower substitution degree. To interpret the experimental data, we assumed the existence of spatial heterogeneity within a space scale of several micrometers in the gels under investigation, which might be caused by intermolecular aggregation and formation of macromolecular clusters. The aggregates of greater dimensions appeared to be formed as the polymer concentration increased in the solutions of CA with a lower degree of OH substitution. The gels of these CA have been supposed to consist of the bound macromolecular clusters, which keep their spatial attributes to a large extent and do not form a homogeneous physical polymer network.

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