

MRPM11 – NMR Relaxation and Water Self-Diffusion Studies in Sodium Polyacrylate Solution and Gel

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Introduction

The polyelectrolyte gel and its associated gel-swelling phenomenon have been studied in polymer physics and biological science for a long time^{1,2}. However, there is still little known about how the mobility and state of the solvent are affected by the polymer network in polyelectrolyte system. In this work, the effect of polyelectrolyte polymer network (sodium polyacrylate) on solvent (water) will be studied systematically with a mobile NMR system. Both the self – diffusion coefficients and longitudinal relaxation rates of water were measured by NMR, with various polymer concentration in both solution and gel states. Different diffusion and relaxation physical models were compared and differences between solution and gel were presented finally.

Materials and Methods

Sodium polyacrylate solution were purchased from Sigma – Aldrich, with average molecular weight $M_w \sim 150,000$ and 35% w/w in water. It was then diluted to desired concentrations. Sodium polyacrylate gels were made by free – radical copolymerization of partially neutralized acrylic acid and N,N'-methylenebis(acrylamide) cross-linker in aqueous solution according to a procedure described by Sugatani et al. Monomers were partly neutralized by sodium hydroxide before polymerization and then diluted to desired concentrations. Potassium persulfate (0.5g/L) was added to initiate the polymerization reaction, and the solution was placed in the oven at 70 °C for gelation.

The NMR system used in this work is a mobile, single – sided NMR system (Profile NMR – MOUSE, ACT GmbH, Germany). Self-diffusion coefficients were measured by Hahn echoes ($90^\circ - \tau - 180^\circ - \tau - echo$) detected in the presence of a static and uniform magnetic field gradient. 8 b-values ($< 1200 \text{ s/mm}^2$) were used to get a diffusion decay curve, with 8 scans performed for each b-value and 1024 echoes added for each scan. Longitudinal relaxation times (T_1) were carried out by using a saturation recovery sequence (saturation – recover time Δ - detection), followed by a CPMG train to improve the sensitivity, similar to the methods above. 8 recovery times Δ were used to obtain a recover curve, and 8 scans for each recover time, with 1024 echoes added for each scan. Both the self-diffusion and relaxation measurements could be fitted by monoexponential functions well.

Results and Discussions

Three types of diffusion models were used to analyze the self-diffusion coefficients' results (Fig. 1a)). It included pure obstruction models, combined obstruction and hydration models, and free volume models. In pure obstruction models, Mackie–Meares model³, which assumes the geometry of polymer is rod – like, could fit the results in solution state very well within low polymer concentration, while Maxwell model⁴, which assumes both the polymer and solvent are spherical, obviously underestimated the obstruction effect of polymer in this system. This confirms the geometry of the sodium polyacrylate polymer in solution is more close to rod-like shape. The combined obstruction and hydration model – cell model⁵ – with only one fitting parameter failed in both solution and gel, which might be due to the wrongly spherical-geometry assumption or the too simple assumption of hydration effect in the model. However, a free volume model with a single fitting parameter, which was simplified from the complex free volume model under some assumptions⁶, could fit the diffusion results in polyacrylate solution in the whole polymer concentration range. The equation is⁶:

$$\frac{D}{D_0} = \exp\left(-A \frac{w_2}{1 + w_2}\right) \quad [1]$$

where A is a free parameter. Its failure in polyacrylate gel was due to that the gelation made the simplifying assumption didn't work any more. In the longitudinal relaxation rates' results (Fig. 1b)), a simple two – sites fast exchange model was used, which assumed two sites with constant

relaxation properties. Based on this model, the longitudinal relaxation rate should be a linear function of polymer concentration, which was observed in low polymer concentration within both gel and solution. A non-linear behavior was observed after a critical concentration, where the polymers begin to interact with each other and relaxation properties of the two sites will be changed. A higher self-diffusion coefficient and longer relaxation time were observed in gel than solution state with equivalent situation. Both imply that the polymer network has a smaller effect on bulk water in the gel state than in the solution state. This can be well explained by the formation of branched aggregates of polymer in the gel state⁷, which can reduce the effective interaction area between water and polymer and also reduce the obstruction effect by changing the polymer network geometry.

Conclusion

The self – diffusion coefficients and longitudinal relaxation rates of water dissolved in sodium polyacrylate solution and gel were measured using the NMR – MOUSE system. Different diffusion physical models were compared and a simple formula of free volume model was found to approximate the data in solution state well. A simple two – site fast exchange model could fit the relaxation results in low polymer concentration. In comparison between solution and gel states, the inhomogeneity of polymer network inside the gel was the main reason for the higher self – diffusion coefficient and longer relaxation time of water in gel.

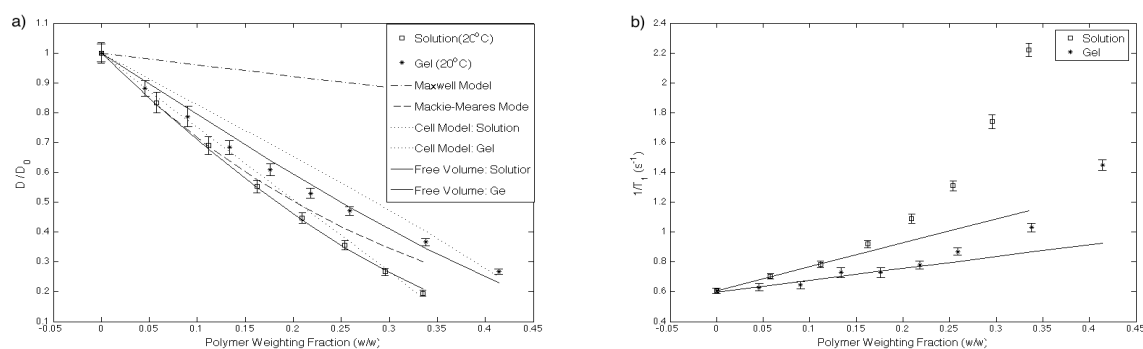


Fig. 1: a) Self-diffusion of water with different polymer weighting fractions, and comparison with different diffusion models; b) Spin-Lattice relaxation rate of water measurement with different polymer weighting fractions, and comparison with a simple physical model.

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