

# WETTING OF MINIGELS

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## Introduction

Polymer gels are cross-linked polymer networks that have the ability to change their volume by absorption of solvent and in response to external stimuli. Here, we show that the wetting kinetics of both the ionic and non-ionic minigels can be described with Tanaka's model. The diffusion coefficients for the minigels are of the same order of magnitude of those reported for macro and microgels and far from that of water self-diffusion. The presence of charge on the polymer network, makes its diffusion dependent on the ions present in the surrounding solvent.

## Experimental

### Systems

Non-ionic PNIPAM minigels are synthesized by inverse polymerization, following a modification of the procedure established by Dowding et al.[8]. The main monomer, cross-linker, and initiator are *N*-isopropylacrylamide (Aldrich, 5.0046 g), *N,N'*-methylenebisacrylamide (Fluka, 0.1548 g), and potassium persulfate (Fluka, 0.3523 g), respectively. The cross-linker concentration ends up being ~3 wt %. Once the particles are formed, the suspension is allowed to sediment and the surfactant removed by rinsing with pure *n*-heptane. This procedure was repeated five times. We then dilute the suspension with deionized water and placed it on a rotary-evaporator at 50 °C to remove the organic phase. The minigel particles in the aqueous phase are left behind. The final step is to eliminate any organic traces by rinsing several times with deionized water.

Ionic minigels were synthesised by polymerization of 3-ethyl-1-vinyl-1H-imidazol-3-ium bromide [1]. Cross-linked poly (3-ethyl-1-vinyl-1H-imidazol-3-ium bromide), [poly(ViEtIm<sup>+</sup>Br<sup>-</sup>)], minigels are prepared with water-in-oil (W/O) concentrated emulsion pathway. *N,N'*-methylene-bisacrylamide (BA) was added as cross-linking molecule. The emulsion was homogenized under magnetic stirring and purged with nitrogen gas to remove any residual oxygen. After 1 h of reaction at room temperature, the minigel particles were precipitated with acetone and next isolated by filtration and washed with distilled water. After solvent separation, the miniparticles were freeze-dried to remove residual solvent and water and stored at 4°C. The particles were re-dispersed in water, and dialyzed before use.

### Experimental Procedure

Particles swelling is tracked using a high-speed digital camera (RDT/16) connected to an optical microscope (Leica DMIRB). Digital video is recorded to 125 fps using standard lighting. Picture acquisition is calibrated with an 80 lines/mm diffraction grating (PHYWE 09827.00) and a 40x/0.55 objective. Calibration in horizontal and vertical directions, to account for anisotropy, is (0.15±0.01) μm/pixel. Particle perimeter is recorded during the swelling. The enclosed area is calculated and the particle size determined. Tanaka et al. mode for the swelling kinetics of a polymer gel network [2] is used in this work to determine de diffusion coefficient for the polymer network.

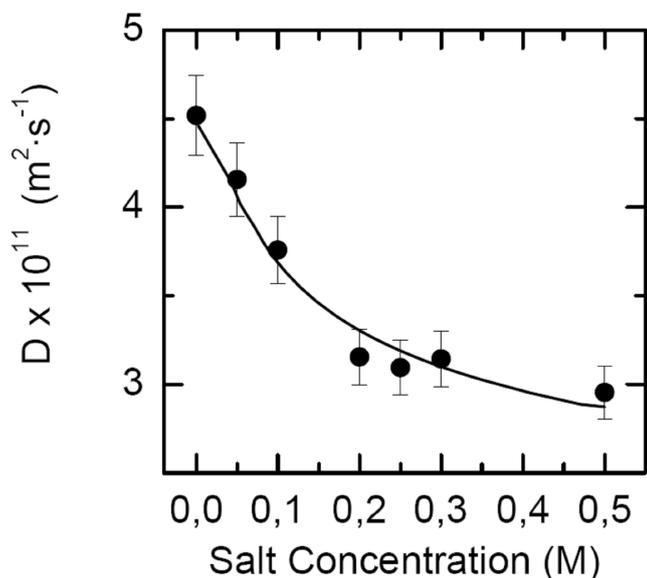
## Result and discussion

Using Tanaka's model the diffusion coefficients are calculated to be  $D_{\text{NON-IONIC}} = (6.0 \pm 0.2) 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , for the PNIPAM particles and  $D_{\text{IONIC}} = (3.7 \pm 0.2) 10^{-11} \text{ m}^2$  for completely charged system (See Table 1). These values are compared in **Table 1** to those corresponding to PNIPAM polymer networks into other size range. All values fall into the same order of magnitude, far from the solvent molecules self-diffusion. This fact indicates that the diffusion process is controlled by the polymer network, being independent of the size scale over a very broad range, from micro to macroscopic gels. It also suggests that the differences in the fabrication procedure do not change the overall picture.

Different Gels	D / 10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup>
Non-ionic Macrogel [7]	5.0 ± 0.3
Non-ionic Minigel	6.0 ± 0.2
Ionic Minigel	4.5*-2.9 ± 0.2
Non-ionic microgel [11]	4.2 ± 0.5
WATER Self-diffusion [12]	230

**Table 1.** Diffusion coefficients of different sized polymer networks. (\*) in the absence of salt.

An important difference between the two minigels reported in this paper is the charge beard by one of the system. One expects the presence of charge should modify the wetting kinetics since new forces define additional components for the osmotic pressure acting on the polymer mesh. In order to check this point, the wetting kinetics is monitored, tuning the amount of salt added to the solvent.



**Figure 3.** Dependence of the diffusion coefficient on the amount of salt.

**Figure 3** plots the network diffusion coefficient for different ion concentrations. For non-ionic particles, the diffusion is salt-independent, which is a clear signature of the absence of charge. A decreasing behavior is found for the ionic microgel. The diffusion of a polymer network is determined by the network elasticity (bulk and shear modulus,  $K$  and  $\mu$ , respectively) and the friction with the liquid. Forces due to internal stresses (produced by volume changes and shear deformations) are balanced by the friction exerted by the liquid on the network. The diffusion of the polymer network is finally expressed as  $D = \frac{(K + 4\mu/3)}{f}$ ,  $f$  being the friction coefficient.

Any change of the local viscosity is only possible through the characteristic time  $\tau$ , which is constant in the present work,  $\tau_{\text{ionic}} = (0.29 \pm 0.02)$  s, for all checked concentrations. This fact implies that the friction coefficient keep constant. For the ionic system, the observed decreasing diffusion coefficient should then be a consequence of a reduction of the network elasticity.

The influence of the ion nature was studied by inducing particle de-swelling in presence of electrolytes in the halogenide series: NaF, NaCl, NaBr, NaI. The final particle size depends on anion nature as well as the  $n$  value at which the plateau is reached. Both magnitudes quantify the solvency of the electrolyte. The de-swelling capacity evolves as the ion size increases ( $F^- < Cl^- < Br^- < I^-$ ) in opposite behaviour to the well-know Hofmeister series, H.S [3]. The last orders, for instance, the effectiveness of ions to precipitate proteins. H.S has been recently checked for neutral thermosensitive microgels based on poly (N-isopropylacrylamide) [4]. The authors found a clear correlation between the de-swelling capacity of the ions and their chaotropic (structure breaking) or

kosmotropic (structure making) nature. The halogenides follow strictly the H.S for neutral polymer network, just the opposite behaviour observed in this paper.

### Conclusion

We have shown that the wetting kinetics for both ionic and non-ionic minigels can be described with Tanaka's model. The diffusion coefficients obtained for the minigels are of the same order of magnitude of those reported for macro and microgels and far from that of water self-diffusion. The presence of charge makes its diffusion dependent on the amount of ions present in the surrounding solvent. Ionic particles show ion specificity. Deswelling capacity evolves as the ion size increases ( $F^- < Cl^- < Br^- < I^-$ ) in opposite behavior to the Hofmeister series. This finding is explained by the effect of the ions on the polymer-anion electrostatic interaction (counterion binding), which is ion-specific and is described by Desnoyer's model.

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