

Response to Osmotic Pressure versus Swelling Pressure: Comment on "Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy"

We appreciate the opportunity to respond to the comment of Dr Shuaifei Zhao¹ on our recent paper² describing the bifunctional responsive polymer hydrogels as draw agents for forward osmosis (FO) process. Zhao has argued that the process involving a polymer hydrogel draw agent should not be called a FO process because the swelling pressure of polymer hydrogel is different from osmotic pressure of a traditional draw solution.¹ In fact, in the FO (known as osmosis or direct osmosis) process, water transports across a semipermeable membrane from the side with higher water *chemical potential* to the other side with lower water *chemical potential*. Traditionally, the concentrated solution, termed as draw solution, osmotic agent, osmotic media, driving solution, or brine, and so on, is placed on the permeate side of the membrane to withdraw water from the feed in the FO process, and an osmotic pressure differential is commonly used to describe the driving force in such a process.³ From a thermodynamics perspective, our polymer hydrogel-driven process is essentially also a FO process. To discuss further, it is necessary to revisit the fundamentals of the swelling process and mechanisms of polymer hydrogels, which have been well documented in the literature.⁴

Thermodynamically, the polymer hydrogel swells in water due to lower chemical potential of water within hydrogel than that of surrounding water. The swelling pressure originates from polymer–water mixing, elastic reaction force of the network, and osmotic pressure of ionizable groups. Although the swollen hydrogel is an elastic rather than a viscous one, the swollen polymer hydrogel is in fact a *solution*.⁴ The polymer hydrogel network structure plays the multiple roles of solute, osmotic membrane, and pressure-generating device. In the case of the ionic hydrogel network, the swelling forces are greatly increased due to the localization of charges on the polymer chains,⁴ as would a polymer solution where ionic groups are dissolved into it. The structure of a swollen poly(sodium acrylate) hydrogel is schematically illustrated in Figure 1.

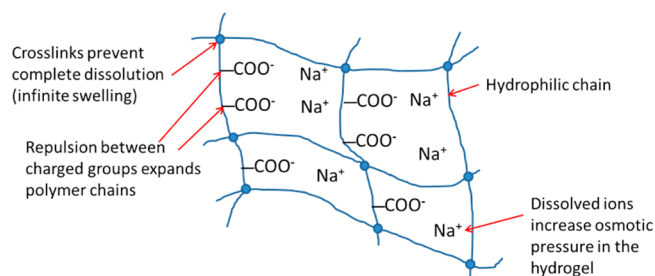


Figure 1. Schematic illustration of the structure of a swollen poly(sodium acrylate) hydrogel.

At the equilibrium of swelling, the total change in free energy reaches a minimum; this is similar to the system where the chemical potential of each mobile species becomes equal in the coexisting phases. For a nonionic hydrogel, the polymer–water mixing makes a negative contribution to the free energy, whereas the stretching of the polymer network makes a positive contribution. In the case of ionic polymer hydrogel, the dissociation of the counterions in water makes an additional negative contribution. In an osmotic swelling experiment, the measurable variables of an ionic polymer hydrogel involve derivatives of the free energy^{4,5}

$$\Pi_{\text{tot}} = \Pi_{\text{mix}} + \Pi_{\text{el}} + \Pi_{\text{ion}}$$

where Π_{tot} is the swelling pressure of the gel, Π_{mix} , Π_{el} , and Π_{ion} are the mixing, elastic, and ionic contributions, respectively.

From the above discussion, it is clear that although the swelling of polymer hydrogel is more complex than dissolution of solute in water, and their fundamental driving force can be described as a chemical potential differential; both polymer hydrogels and conventional liquid draw solution operate on the same principle in the FO process. In practice, dried polymer hydrogel powder is initially loaded into the membrane cell to start the process, which is similar to beverage powder used in the FO hydration bags.³ During the dewatering, the water is only partially recovered from the swollen hydrogels. In other words, the hydrogel draw agents remain hydrated in the process. Therefore, it is appropriate to classify our polymer hydrogel-driven membrane process as a FO process.

The search for suitable draw solution has been a main research focus in the development of commercially viable FO technology. We have recently demonstrated the use of stimuli-responsive polymer hydrogel as a new class of draw agent for FO process and investigated a range of parameters affecting the performance of the draw agent.^{6–12} Our work has extended the traditional draw solution to “solid” draw agent, which holds great potential for further development for commercial applications. Since our first paper on polymer hydrogel draw agents published in 2011, our work has been well received by the research community.^{13–18} We are pleased to see exciting development on hydrogel draw agents from other groups. For instance, Hu’s group demonstrated that quasicontinuous FO desalination process could be achieved by cyclic heating and cooling of thermally responsive semi-IPN hydrogel draw agent.¹⁹ In addition, more work is underway in our group to scale up the polymer hydrogel-driven FO process for wastewater treatment using industrial low-grade waste heat.

In conclusion, given the origins of swelling pressure, it is appropriate to term our polymer hydrogel-driven membrane

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process as a FO process. We welcome further discussions on this topic.

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Notes

The authors declare no competing financial interest.

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