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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"

Recently Razmjou et al. proposed a smart method of using bilayer polymer hydrogels as draw agents to absorb water from saline streams and using solar energy to dewater the hydrated hydrogels.1 The authors thought that the principle of absorbing water of the hydrogels was based on forward osmosis, that is, the hydrogel particles $(2-25 \mu m)$ provided the osmotic pressure. The authors may misunderstand the swelling pressure of hydrogels as the osmotic pressure. The following discussion aims to clarify two confused concepts (i.e., osmotic pressure and swelling pressure) and to differentiate the principles of forward osmosis and of hydrogel absorbing water for both readers and the authors. It is believed that the clarification is very necessary because a number of published papers²⁻⁷ are based on these misunderstood concepts.

■ FORWARD OSMOSIS AND OSMOTIC PRESSURE

Forward osmosis is an osmotic process in which water molecules diffuse across a semipermeable membrane from a solution with lower osmotic pressure to the other solution with higher osmotic pressure. 8,9 The driving force in forward osmosis is the osmotic pressure gradient across the membrane. The osmotic pressure of a solution is equivalent to the pressure that needs to be applied to prevent the passage of water through a semipermeable membrane and into a solution of greater concentration.

The osmotic pressure π of an ideal solution with low concentration can be approximated using the Morse equation $(eq 1)^{10}$ derived from the van't Hoff's formula

$$\pi = iMRT \tag{1}$$

where i is the dimensionless van't Hoff factor, M is the molarity of the solute, R is the gas constant, and T is the thermodynamic (absolute) temperature.

Osmotic pressure is a colligative property of a solution, dependent on the dissociation number of solute molecules only rather than on their nature.¹¹ Therefore, for a given mass of solute, larger dissociated molecule/ion size means lower resultant osmotic pressure. For dry hydrogel particles, they do not have osmotic pressure as they are not dissolved in a solution. However, dry hydrogel particles will become wet and expand significantly when contacting with sufficient moisture or water. Take an example, dry tissue (similar with hydrogels) has the ability to absorb water, but we can never say dry tissue has osmotic pressure.

In fact, the osmotic pressure of hydrogels (which is the most important factor determining the process performance) is experimentally measurable with an osmometer¹² if the gels do have osmotic pressure. However, such measurement was not done by the authors.

■ HYDROGELS AND SWELLING PRESSURE

Hydrogels (also called superabsorbent polymers) are highly hydrophilic networks of polymer chains, sometimes found as colloidal gels in which water is the dispersion medium.¹³ The water-absorbing properties of the networks result from the presence of chemical residues, such as hydroxylic (-OH), carboxylic (-COOH), amidic (-CONH-), primary amidic (-CONH₂), and sulfonic (-SO₂H), ¹⁴ rather than from the osmotic pressure of the hydrogels.

There is no specific definition for the swelling pressure of hydrogels in the literature. Analogy to the osmotic pressure, however, the swelling pressure of hydrogels could be regarded as the pressure that is required to prevent the swelling of the hydrogels. In hydrogel swelling, some swelling pressure relavent parameters like the swelling rate, swelling ratio, and swelling capacity are dependent on several physiochemical factors such as the gel size, network porosity, network structure, crosslinking conditions, and cross-linking degree of the hydrogel. ^{14,15} However, the osmotic pressure is determined by the number of solute molecules only. Compared with the osmotic driving force in forward osmosis, the driving force in hydrogel absorbing water (i.e., swelling) is more complex as it is associated with the elasticity force of the gel structure, the osmotic force of the ionic solution within the networks, and even the capillary force.¹⁴ Additionally, it is generally regarded that the sorption processes for polymer-solvent systems do not conform to the classical diffusion theory, 14,16 whereas forward osmosis does. ¹⁷ Therefore, the osmotic pressure of a solution is never equal to the swelling pressure of hydrogels.

CONCLUDING REMARKS

The osmotic pressure of a solution is essentially different from the swelling pressure of hydrogels. Hydrogels absorbing water via swelling and forward osmosis do not share the same process principle. Therefore, it is not reasonable to use "forward osmosis" in hydrogel absorbing water because their principles are essentially different.

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