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# Temperature Effect on Forward Osmosis

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## Abstract

Forward osmosis, or simply, osmosis, refers to a process by which a solvent moves across a semipermeable membrane due to the difference in the solute concentration established across the membrane. Because of its spontaneous nature, forward osmosis has received immense attention during the last few decades, particularly for its diverse applications, which include municipal wastewater treatment, seawater desalination, membrane bioreactor, potable water purification, food processing, drug delivery, energy generation, and so forth. Of many parameters that determine the performance of the forward osmosis process, the most fundamental factor that impacts performance is temperature. Considering the importance of the temperature on the forward osmosis process, there have been only a limited number of studies about the effect of temperature on the osmosis-driven process. In this chapter, we discuss the temperature effect on the forward osmosis process from two main aspects. First, we provide an extensive and in-depth survey on the currently available studies related to the anisothermal osmosis phenomena. Second, we then discuss a state-of-the-art theoretical framework that describes the anisothermal forward osmosis process that may shed light on achieving an enhanced performance via temperature control.

**Keywords:** forward osmosis, temperature, thermal effect, concentration polarization, water flux, solute flux, membrane scaling

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## 1. Introduction

Osmosis, one of the most fundamental transport processes responsible for homeostasis in living organisms, has a rich history of applications—ranging from food preservation to water treatment and drug delivery. Osmosis occurs when a solute concentration difference is established across a semipermeable membrane. Due to the chemical potential imbalance, the water molecules will spontaneously migrate across the membrane toward the higher solute concentration side. Such a process has been regarded as one of the most central mechanisms that dictates the

membrane-based water treatment technologies. The most widely utilized process, in our opinion, is reverse osmosis (RO) for solute removal, which requires an external hydraulic pressure to overcome the osmotic pressure difference across the membrane. In contrast to RO, the process that exploits the spontaneous transport of solvent molecules driven by the osmotic phenomenon is referred to as forward osmosis (FO) or direct osmosis (DO), which is, in principle, the same as the original osmosis.

FO was first conceptualized by Batchelder as a means for water treatment since the 1960s [1]. Since then, there has been a growing interest in applying FO to wastewater treatment technologies either as a stand-alone or in combination with other technologies such as membrane distillation, thermal distillation, or reverses osmosis [2]. Particularly, FO has been utilized in space stations for wastewater reclamation due to its excellent long-term stability and low energy consumption [3, 4]. Not limited to wastewater treatment, FO has also been explored extensively for many useful applications such as seawater desalination [5–7], portable hydration bags [8], food processing [9–11], pharmaceutical systems [12–14], and energy conversion [15, 16].

Unlike RO, FO is purely an osmosis-driven process, which is thermodynamically spontaneous. The osmotic pressure difference  $\Delta\pi$ , which is a driving force for the FO process, may be expressed using van't Hoff's law as

$$\Delta\pi = RT\Delta C \quad (1)$$

for weakly interacting molecules, where  $\Delta C$  is the solute concentration difference,  $R$  is the gas constant, and  $T$  is the temperature. From the equation, it can be noted that the temperature is one of the most critical factors determining the rate of osmosis. In addition, temperature further changes viscosity, diffusivity, and density, which are important parameters in momentum and energy transfer phenomena. Despite the importance of temperature on FO process and despite the fact that there exist a number of papers that address the temperature effect, the reported data are widely scattered and does not show an agreeable consensus. In this chapter, we aim to provide a holistic understanding of the temperature effect on an osmotic phenomenon. Our intention is not to give an exhaustive review of the FO process in detail but to focus on the temperature effect and hopefully to provide insight for better control over the osmotic phenomenon. Readers who wish to learn about the FO process more in detail may refer to the following review papers [2, 8, 17].

## 2. Operating principle

### 2.1. Mechanism

In the FO process, the solvent (water) transport is driven solely by osmotic pressure difference without the need of any external hydrostatic pressure, allowing for lower energy consumption compared to RO. To extract water from the feed solution, the osmotic pressure at the opposite side of the membrane must be higher, which requires a highly concentrated solution; this concentrated solution is typically referred to as the draw solution. Draw solutes need to be

inert and easily removable. A semipermeable membrane separates the feed solution and the concentrated draw solution where the chemical potential difference allows the water to flow through the membrane while leaving behind the solutes in the feed stream. Regions of high and low solute concentrations refer to those of low and high solvent chemical potentials, respectively. As the semipermeable membrane restricts the solute transport and maintains chemical potential differences of both solute and solvent, water migrates from its high solvent chemical-potential region (i.e., of low solute concentration) to low solvent chemical-potential region (i.e., of high solute concentration). Such a water transport leads to dilution of the draw solution where the diluted draw solution can be further recycled such that the initial solute concentration is recovered. Particularly for desalination applications, the solutes in the draw solution (osmotic agent or draw solutes) are chosen to be inert, nontoxic, and easily removed to obtain the desalinated water with ease. One example includes  $\text{NH}_4\text{CO}_2$ , which can be easily removed by decomposing at a moderately elevated temperature ( $\sim 60^\circ\text{C}$ ) followed by low-temperature distillation [18, 19]. Extra energy is, however, necessary to re-dissolve  $\text{NH}_4\text{CO}_2$  into the draw solution for a continuous FO operation.

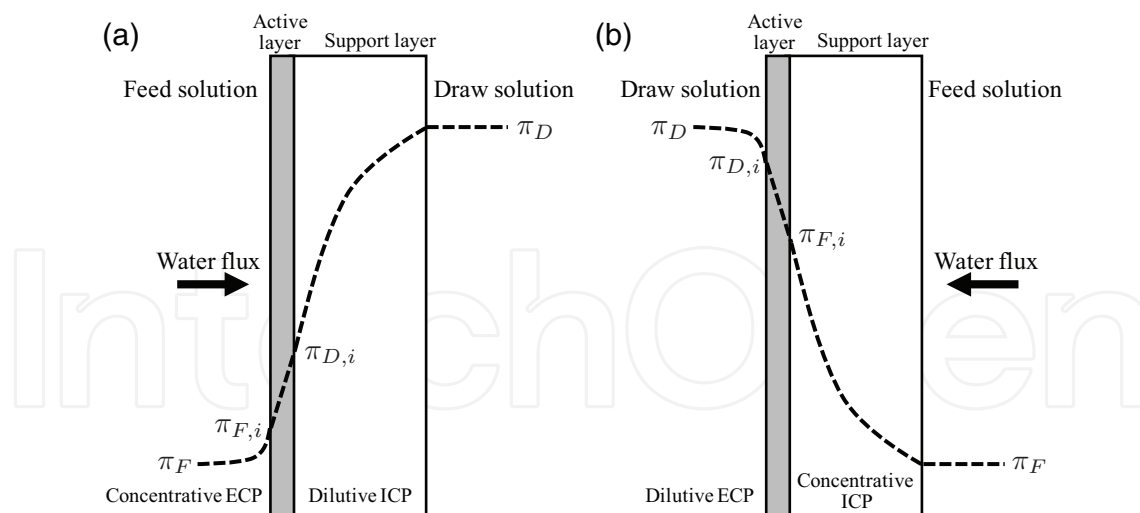
## 2.2. Concentration polarization

The water flux across the membrane results in concentration of the feed solution and dilution of the draw solution since the membrane mainly allows passage of water molecules. This phenomenon, referred to as concentration polarization (CP), has an adverse impact on the efficacy of the FO process since such an effect reduces the effective osmotic pressure difference across the membrane, thus hindering water transport.

CP is highly influenced by the morphology of the membranes. The membranes used in the FO process consist of a thin, dense layer that rejects the solutes (active layer) followed by a coarse, thick porous layer (support layer or porous substrate) to reinforce the mechanical stability against fluid pressure and shear. This configuration makes the membrane asymmetric in which the orientation of the membrane with respect to the direction of the water flux (i.e., from low to high osmotic pressure) leads to significantly different transport dynamics [20].

Typically in the FO process, the active layer is placed against the feed stream in order to minimize fouling since the support layer is more susceptible to colloidal fouling due to the large pores. This configuration is called FO mode, as shown in **Figure 1(a)**. However, the downside of placing it in this way is that there is a significant dilutive internal concentration polarization (ICP) in the thick porous substrate. This is because the support layer is in contact with the concentrated draw solution hindering the solute diffusion, which significantly reduces the water flux (**Figure 1(a)**).

In contrast, when the active layer is placed against the draw stream, one can expect a higher water flux since this configuration can avoid the dilutive ICP at the expense of accelerated membrane fouling. This configuration is called the pressure-retarded osmosis (PRO) mode, as shown in **Figure 1(b)**, typically realized in standard PRO systems. To avoid any confusion, we will refer to the membrane configuration in which the active layer is placed against the feed solution as the *FO mode*, whereas the opposite case is the *PRO mode* during FO processes.



**Figure 1.** Influence of CP on the osmotic pressure distribution in the FO process. The membrane is configured in (a) FO mode and (b) PRO mode.

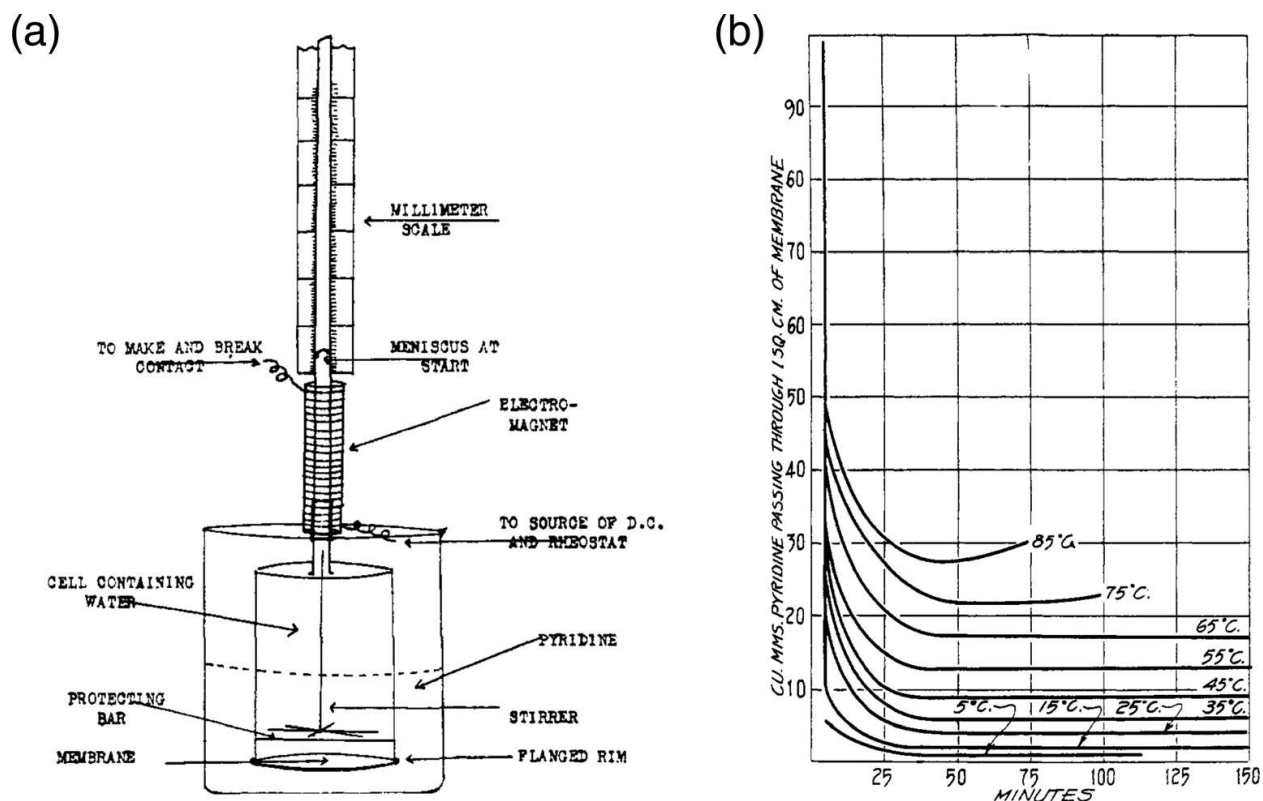
### 3. System temperature effect on FO

The first quantitative experiments on temperature-dependent osmosis go back almost a century ago [21]. Traxler demonstrated the osmosis of pyridine by using a thin rubber sheet as a semipermeable membrane within a uniform system temperature, ranging from 5 to 85°C (**Figure 2(a)**). He showed that as the temperature is increased, the transport of pyridine across the membrane is also increased (**Figure 2(b)**). In this chapter, such a uniform temperature will be referred to as ‘system temperature’ indicating the absence of local or transmembrane temperature gradient.

From the van’t Hoff equation, the osmotic pressure is directly proportional to the system temperature, which is an indispensable factor for the FO process. However, temperature not only influences the osmotic pressure but also impacts many other key properties that are important to the transport process such as viscosity, diffusivity, solubility, density, and so forth. Such a change in the properties not only influences the water flux but also alters the solute rejection/diffusion and membrane fouling. In this section, we provide a summary of how the system temperature influences the water transport, solute rejection, and membrane fouling. We note that the experimental studies that will be covered in the following sections employ a circulating crossflow type setup (in contrast to a dead-end type as seen in Traxler’s experiments in **Figure 2**).

#### 3.1. Water flux

The most direct consequence of raising the system temperature is the increased water flux across the membrane due to lowered water viscosity and increased water diffusivity, which effectively increases the water permeability across the membrane. Since the transport of water through the active layer of the membrane follows the solution-diffusion mechanism [22], it is



**Figure 2.** The first quantitative experiments reported on the effect of temperature on the osmosis phenomenon. (a) A schematic of the experimental setup that allows temperature control via a thermostat. (b) Transport of pyridine across a rubber membrane under various temperature conditions. Reprinted with permission from Ref. [21]. © 1928 American Chemical Society.

commonly believed (and also observed) that the diffusivity  $D$  exhibits an Arrhenius relation, that is,  $D \sim \exp(-s/T)$ , where  $s$  is an empirical constant related to the activation energy [23, 24]. However, we also note a counterexample where Petrotos et al. failed to show such a behavior [25].

On the basis of our survey, the available literature related to the temperature-dependent FO reported increased water flux with temperature. **Table 1** provides a summary of experimental conditions and resulting water flux from the available literature [23–31]. Here, we define a new quantity to indicate how much solvent flux increases with respect to the system temperature, as indicated in the last column of **Table 1**:

$$j_M = \frac{J_{w,M} - J_{w,0}}{T_M - T_0}, \quad (2)$$

where  $J_{w,M}$  and  $J_{w,0}$  are the water fluxes at a given maximum system temperature  $T_M$  and at base temperature  $T_0$ , respectively. The survey shows that raising the temperature does increase the water flux, but the extent of such an increase varies across the literature, especially depending on the membrane orientation. This observation implies that the CP phenomena are uniquely influenced by the temperature, leading to variations in the water flux.



| Reference | Feed solution<br>(concentration) | Draw solution<br>(concentration)        | Membrane <sup>1</sup> | Mode <sup>2</sup> | Temperature<br>(°C) | $J_{w,0}$<br>(LMH) | $j_M^3$<br>(LMH/°C) |
|-----------|----------------------------------|---|-----------------------|-------------------|---------------------|--------------------|---------------------|
| [25]      | Tomato juice (0.13 M)            | NaCl (3.9 M)                            | PA                    |                   | 26–58               | 1.5                | 0.030               |
| [26]      | NaCl (0–86 mM)                   | KCl (0.5–3 M)                           | CT                    | FO                | 25–45               | 19                 | 0.43                |
| [27]      | Deionized water                  | NaCl (0.5 M)                            | CT                    |                   | 20–40               | 5.5                | 0.14                |
|           |                                  |   | PA                    |                   |                     | 17                 | 0.49                |
| [23]      | Sucrose (0–1.65 M)               | NaCl (2–4 M)                            | CT                    |                   | 20–30               | 24                 | 0.91                |
|           | Sucrose (0–0.7 M)                | NaCl (4 M)                              | PA                    |                   |                     | 2.5                | 0.15                |
| [28]      | NaCl (0.1 M)                     | NaCl (1 M)                              | CT                    | PRO               | 20–40               | 11                 | 0.89                |
|           |                                  |   |                       | FO                |                     | 9.4                | 0.59                |
| [29]      | NaCl (0–1 M)                     | NaCl (1.5 M)                            | CT                    | PRO               | 20–40               | 43                 | 1.4                 |
|           |                                  |   |                       | FO                |                     | 18                 | 0.63                |
| [24]      | NaCl (60 mM)                     | Na <sub>2</sub> SO <sub>4</sub> (1.5 M) | CT                    |                   | 25–45               | 15                 | 0.35                |
| [30]      | NaCl (0.2–0.5 M)                 | NH <sub>4</sub> HCO <sub>3</sub> (3 M)  | CE                    | PRO               | 30–50               | 5.4                | 0.10                |
| [31]      | Deionized water                  | NaCl (1.2 M)                            | CT                    | FO                | 20–30               | 14                 | 0.61                |

<sup>1</sup>PA: polyamide; CT: cellulose triacetate; CE: cellulose ester  
<sup>2</sup>FO mode: active layer placed against feed solution; PRO mode: active layer placed against draw solution  
<sup>3</sup> $j_M = J_{w,M} - J_{w,0} / T_M - T_0$ ;  $J_{w,M}$ : water flux at maximum temperature  $T_M$ ;  $J_{w,0}$ : water flux at base temperature  $T_0$

**Table 1.** A summary of influence of temperature on the water flux.

McCutcheon and Elimelech were the first to study the influence of temperature on the CP phenomena [29]. Raising the temperature increases the water flux because of the decreased water viscosity in solutions (and/or solubility) and increased water solubility and diffusivity within the membrane. At the same time, however, the higher flux also increases both the ICP and ECP, which essentially limit the water flux as a feedback hindrance. Therefore, such a self-limiting behavior driven by two counteracting effects leads to the fact that the temperature has a “mod-est” effect on the water flux at high water flux conditions [29]. This self-hindering effect of the solvent flux is unavoidable in most membrane separation processes. It is similar to the fact that, in RO, applying high pressure initiates increasing permeate flux, which will eventually bring more solutes from the bulk phase to the membrane surface, enhancing the CP. Therefore, addi-tional gain of the RO permeate flux is not as much as anticipated when the pressure is increased.

The change in the temperature influences the CP phenomena in different ways depending on the orientation of the membrane. This is because the formation of the ICP, which is the most critical factor that limits the driving force, is dependent on the membrane configurations. In the PRO mode, the concentrative ICP is developed in the feed side (see **Figure 1(b)**). By reducing the ICP using deionized water as the feed, the water flux was shown to be highly dependent on the temperature, confirming the impact of ICP on the FO process [29].

In the presence of solutes in the feed side so that the ICP is present, however, the water flux was shown to be almost insensitive to the temperature, at least in the operating temperature range (20–40°C). This behavior is attributed to the coupled interaction between ICP and ECP.

Although the increased solute diffusion at higher temperature mitigates the concentrative ICP in the support layer so that the water flux can be increased, such an increased water flux carries more solutes from the feed bulk phase to the vicinity of the support layer surface and enhances the dilutive ECP, thereby reducing the osmotic driving force. Therefore, the two opposing effects on the water transport effectively limit the enhancement of the water flux such that the temperature has a marginal effect on the overall water flux. If both water and solute diffusivities increase in a similar behavior, the net diffusive transport must be more or less the same.

In the FO mode, however, the water flux was shown to be significantly influenced by the temperature. Overall, the water flux was observed to be lower than the PRO mode due to the presence of the dilutive ICP. This was proven mathematically using the method of proof by contradiction [32]. Such a low water flux effectively suppresses the extent of concentrative ECP in the feed side. Also, the influence of concentrative ECP on the water flux is less important than the dilutive ECP in the draw solution side because the initial solute concentration in the bulk phase is much lower at the feed solution than the draw solution. This implies that the ECP has a minor effect on the driving force in the FO mode. Therefore, when the membrane is placed in the FO mode, the water flux is significantly influenced by the temperature since the ICP is the only major factor that determines the driving force.

One assumption McCutcheon and Elimelech had made while analyzing their data were the insignificant solute diffusion across the membrane [29], which otherwise leads to further ICP. Obviously, commercially available membranes are known to permit diffusion of the solutes, which can impact the formation of the CP effect. Since the solute diffusion is also sensitive to the temperature, the transmembrane solute flux should also lead to a change in the water flux. We discuss the effect of temperature on the solute diffusion and rejection in the following section.

### 3.2. Diffusion and rejection of solutes

It is of general consensus that the transmembrane solute diffusion increases with temperature. A number of groups have recently investigated experimentally the temperature effect on the transmembrane solute diffusion and the solute rejection [26–28].

Xie et al. recognized that the effective size of the solute molecules was the most important parameter for the transmembrane solute diffusion [27], which was predicted theoretically using the integral equation theory [33]. Hydration of charged organic solutes results in an increase in the effective solute size, which directly influences the solute diffusion and rejection rate, as it was well understood that the rejection of the charged organic solutes would be much higher than the neutral organic solutes. In this regard, neutral solutes were more likely to diffuse across the pores than the charged solutes in both the cellulose triacetate membranes and polyamide membranes. This implies that increasing the temperature leads to higher solute diffusion due to the increased solute diffusivity. Moreover, increasing the temperature leads to faster dissolution of the solutes into the membrane such that even hydrophobic neutral solutes absorb into the membrane at an order of magnitude higher rate at elevated temperatures.

Notably, the ratio between the water flux  $J_w$  and the solute flux  $J_s$  was shown to be more or less constant regardless of the system temperature [27]. Such a constant ratio implies that the



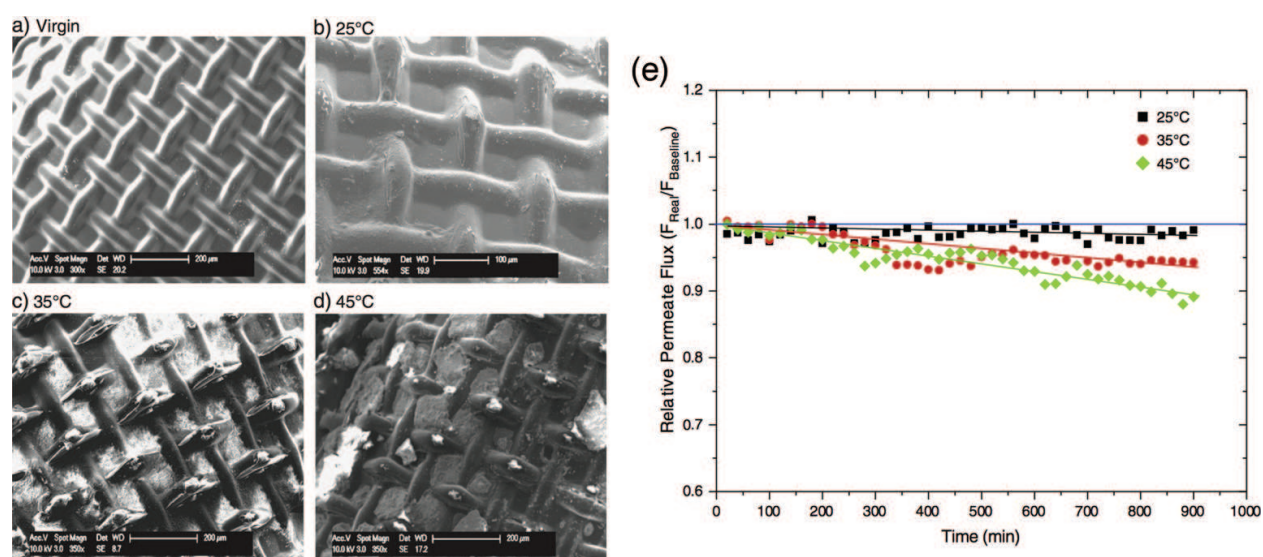
structural properties may not change, at least in the operating temperature range (20–40°C). In fact, although it is documented in the literature that the RO membrane properties such as pore sizes may change when the temperature is above 40°C [34], it was reported in various FO studies that the membrane structural properties do not change significantly below 45°C [26, 27]. However, it is more reasonable to say that the structural properties of FO membranes change with temperature in a way that the ratio between solvent and solute fluxes remain almost constant. In a solution-diffusion model, permeabilities of solvent and solutes,  $A$  and  $B$ , respectively, are believed to increase with membrane temperature. The permeate concentration is controlled by only their ratio,  $A/B$ . If  $A$  and  $B$  increase with  $T$  while  $A/B$  remains less sensitive to  $T$ , then the solute diffusion can be seen phenomenologically insensitive to temperature. This is because although higher  $T$  increases both the solute and solvent fluxes, it is only the ratio that influences the concentration of solutes passing through the membrane. This topic is discussed theoretically in detail in Section 5.

Meanwhile, You et al. showed that the transmembrane solute diffusion was also shown to be dependent on the membrane orientation regardless of the temperature in which the PRO mode was shown to exhibit higher solute flux across the membrane than the FO mode, which is similar to the behavior of the water flux [28].

### 3.3. Membrane scaling

Membrane scaling occurs when the solute concentration is high enough to initiate precipitation. This is directly related to solute rejection and the CP phenomena, implying that membrane scaling should also be temperature-dependent.

Zhao and Zou studied how the temperature influences the membrane scaling over time, which is important in long-term operations [24]. Due to the fast water flux at elevated temperature,



**Figure 3.** Temperature-dependent membrane fouling and associated water flux decline. (a–d) Scanning electron microscope images of the (a) virgin and (b–d) fouled membranes at various temperatures; (b) 25°C; (c) 35°C; (d) 45°C; and (e) water flux ratio over time at each temperatures. Reprinted with permission from Ref. [24]. © 2011 Elsevier.

increase in the final concentration of the feed solution (i.e., concentration after 28 hours of running) was accelerated by more than 100% when the temperature was raised from 25 to 45°C, which led to faster membrane scaling. Concentrative polarization is also enhanced when the water flux is increased, which results in an accelerated membrane scaling. This was confirmed by directly visualizing the fouled membrane by using a scanning electron microscope (**Figure 3(a)–(d)**) and also by measuring the decrease in flow rate over time (**Figure 3(e)**), showing faster decline of water flux over time at elevated temperatures due to the scaling. In addition to higher solute concentration near the membrane surface driven by the temperature-enhanced solvent flux, the changes in solubility limits for inorganic species may contribute to the accelerated fouling behavior.

#### 4. Transmembrane temperature gradient in FO

One step further, we can also consider a case where the temperature is unevenly distributed across the membrane. In such a case, the temperature gradient may allow independent control of transport on either side of the membrane. In practice, temperature gradients can occur frequently; temperature of the feed solution can increase due to the heat released from the hydraulic pumping or when the solution is pretreated. Likewise, the temperature of the draw solution may change due to the post-treatment process for recovery and recycling of draw solutes such as thermal and membrane distillation. Since heating only on one side of the solution requires lower energy than heating up the entire system, imposing a temperature gradient across the membrane may offer an energy-efficient control over the osmotic phenomena.

In the presence of a temperature gradient, van't Hoff's law (of Eq. (1)) cannot be used directly to calculate the osmotic pressure difference since it relies on the assumption of the constant system temperature. A full theory accounting for the temperature gradient in osmosis may result in highly nonlinear effects on the FO performance. Furthermore, the temperature gradient may provide an additional complexity to the coupled mass and heat transfer phenomena within the membrane. In this section, we provide a summary of how the temperature difference between the feed and the draw solution influences the FO performance, including the water transport and solute diffusion/rejection.

##### 4.1. Water flux

Although the temperature dependence on the water flux shows an agreeable consensus as shown in **Table 1**, the anisotropic temperature effect is shown to differ largely across various studies. When the temperature on either side of the solutions is increased, the water flux becomes higher than that at the base temperature, but lower than when the temperatures of both sides of the solutions are increased. It is, however, left unclear which side of the solution has more influence on the FO process when heated as this does not have an agreeable consensus. **Table 2** provides a summary of the effect of temperature difference on the FO process under various experimental parameters. For simplicity, we define

$$j_F = \frac{J_{w,MF} - J_{w,0}}{T_{MF} - T_0} \tag{3}$$

and

$$j_D = \frac{J_{w,MD} - J_{w,0}}{T_{MD} - T_0} \tag{4}$$

as included on the right-hand side of **Table 2**. Eqs. (3) and (4) refer to the water flux increase per temperature change when the *feed side* or the *draw side* is heated only, respectively. Phuntsho et al. calculated using a commercial software (OLI Stream Analyzer) where the osmotic pressure difference across the membrane can be higher when the draw side is heated in contrast to heating the feed side [26]. However, the temperature difference not only changes the osmotic pressure difference but also gives spatial nonlinearity to other important transport properties such as the solution viscosity as well as solvent/solute diffusivity in bulk phases and their solubilities in the membrane phase, which may impact the CP phenomena in various ways depending on the membrane orientation.

In general, regardless of either the feed or draw, raising the temperature on either side leads to increase in both the water flux and the solute flux. Xie et al. stated that raising the feed solution temperature leads to enhanced diffusivity of the water molecules, whereas raising the draw solution temperature leads to decreased draw solution viscosity and increased draw solute diffusivity, both of which lead to increased water flux and reverse solute flux [27]. However, the degree to which the water flux and solute flux are increased varies across the literature [10, 26–28, 31, 35, 36] (see **Table 2**).

| Reference | Feed solution            | Draw solution                            | Membrane | Mode | Temperature (°C) | $J_{w,0}$ (LMH) | $j_F^1$ (LMH/°C) | $j_D^2$ (LMH/°C) |
|-----------|--------------------------|--|----------|------|------------------|-----------------|------------------|------------------|
| [10]      | Pineapple juice (0.37 M) | Sucrose (40 wt%)+NaCl (12 wt%)           | CT       |      | 25–45            | 1.2             | 0.045            |                  |
| [26]      | NaCl (0–86 mM)           | KCl (0.5–3 M)                            | CT       | FO   | 25–45            | 19              | 0.048            | 0.12             |
| [27]      | Deionized water          | NaCl (0.5 M)                             | CT       |      | 20–40            | 5.5             | 0.045            | 0.065            |
|           |                          |  | PA       |      |                  | 17              | 0.125            | 0.175            |
| [35]      | NaCl (0–0.5 M)           | NH <sub>4</sub> HCO <sub>3</sub> (1–4 M) | CT       | PRO  | 25–45            | 2.5             |                  | 0.028            |
|           |                          |  |          | FO   |                  | 1.9             |                  | 0.018            |
| [28]      | NaCl (0.1 M)             | NaCl (1 M)                               | CT       | PRO  | 20–40            | 11              | 0.54             | 0.19             |
|           |                          |  |          | FO   |                  | 9.4             | 0.41             | 0.18             |
| [36]      | Anthocyanin (24 μM)      | NaCl (6 M)                               | CT       | PRO  | 25–40            | 4.9             | 0.013            |                  |
|           |                          |  |          | FO   |                  | 13              | 0.53             |                  |
| [31]      | Deionized water          | NaCl (1.2 M)                             | CT       | FO   | 20–30            | 14              | 0.22             | 0.54             |

<sup>1</sup> $j_F = J_{w,MF} - J_{w,0} / T_{MF} - T_0$ ; Feed side heated.  $J_{w,MF}$ : water flux at the maximum feed temperature  $T_{MF}$ .  
<sup>2</sup> $j_D = J_{w,MD} - J_{w,0} / T_{MD} - T_0$ ; Draw side heated.  $J_{w,MD}$ : water flux at the maximum draw temperature  $T_{MD}$ .

**Table 2.** A summary of influence of temperature difference on the water flux.

Phuntsho et al. showed that increasing the *draw solution* temperature resulted in more water flux compared to increasing the temperature of the feed solution [26]. Their membrane was oriented in the PRO mode where the active layer was facing the draw solution. They argued that increasing the draw temperature led to reduced solution viscosity and increased draw solute diffusivity. This change resulted in the reduction of dilutive ICP on the draw side, thereby increasing the water flux. Again, such a behavior is attributed to the fact that the dilutive ICP plays a more significant role than the concentrative ECP in determining the water flux [26]. Such a preferential water flux increase due to the increased draw temperature was also observed by Xie et al. [27] and Cath et al. [31].

You et al. showed, however, that regardless of the membrane orientation, the water flux increased more when the *feed solution* temperature is increased rather than the draw solution [28], which is in a disagreement with the observations made by Phuntsho et al. [26], Xie et al. [27], and Cath et al. [31]. You et al. argued that the water diffusion kinetics is more important than the thermodynamic driving force (i.e., osmotic pressure difference) of the solution in determining the water flux, thus the feed temperature governs the water flux rather than the draw solution temperature [28].

Interestingly, in Nayak and Rastogi's study [36], the water flux in the FO mode was shown to be higher than the water flux in the PRO mode particularly when the molecular size of the feed solute is large enough such that the external concentration polarization cannot be ignored. They also showed that this is indeed true for concentrating anthocyanin, which is a large sugar molecule. In their work, the water flux in the FO mode was measured to be 260% higher than that in the PRO mode.

#### 4.2. Solute diffusion/rejection

As mentioned in the preceding section, Xie et al. showed that the neutral solutes are more likely to diffuse through the membrane than the charged ones due to their smaller hydrodynamic size [27]. In this sense, transmembrane temperature differences barely influenced the solute rejection rate for the *charged* solutes, whereas the *neutral* solutes were significantly influenced by the temperature difference. It was shown that raising the draw temperature (from 20 to 40°C) led to more neutral solute rejection, even more compared to the isothermal condition at base temperature (20°C) [27]. The reason being is that raising the draw temperature leads to increased water flux, which contributes to the increased solute rejection. At the same time, keeping the feed temperature low reduces the deposition of the solutes on to the membrane, thus preventing the neutral feed solutes from dissolving into the membrane and diffusing across the membrane [27].

### 5. Theoretical perspectives

To the best of our knowledge, effects of temperature and its gradient on the osmosis phenomena and FO processes have been investigated only phenomenologically without fundamental understanding. The theoretical research is currently in a burgeoning state in explaining the transmembrane temperature gradient effect on the FO performance. In this section, we first briefly review the conventional FO theories [37, 38] based on the solution-diffusion model and

van't Hoff's law. Then, we revisit statistical mechanics to identify the baseline of the osmosis-diffusion theories, where the isothermal condition was first applied. We then develop a new, general theoretical framework on which FO processes can be better understood under the influence of the system temperature, temperature gradient, and chemical potentials.

### 5.1. Revisit to the solution-diffusion model

The solution-diffusion model is widely used to describe the FO process, which was originally developed by Lonsdale et al. to explain the RO phenomena using isothermal-isobaric ensemble [39]. In the model, the chemical potential of water is represented as a function of temperature, pressure, and solute concentration, i.e.  $\mu_w = \mu_w(T, P, C)$ , and its transmembrane gradient is

$$\Delta\mu_w = \int \left( \frac{\partial\mu_w}{\partial C} \right)_{T,P} dC + \int \left( \frac{\partial\mu_w}{\partial P} \right)_{T,C} dP, \quad (5)$$

where the integration is over the membrane region. From the basic thermodynamic relationship,

$$\int \left( \frac{\partial\mu_w}{\partial P} \right)_{T,C} = \bar{V}_w \quad (6)$$

is used where  $\bar{V}_w$  is the molar volume of water. In the isothermal-isobaric equilibrium ( $\Delta\mu_w = 0$ ), the applied pressure  $\Delta P$  is balanced with the transmembrane difference of the osmotic pressure, i.e.  $\Delta P = \Delta\pi$ . This condition gives

$$0 = \int \left( \frac{\partial\mu_w}{\partial C} \right)_{T,P} dC + \bar{V}_w \Delta\pi \quad (7)$$

and hence we derive  $\Delta\mu_w = \bar{V}_w(\Delta p - \Delta\pi)$ . It is assumed that the water transport within the membrane is phenomenologically Fickian, having the transmembrane chemical potential difference of water as a net driving force. The water flux is given as

$$J_w = \frac{D_w C_w}{RT} \frac{d\mu_w}{dx} \simeq \frac{D_w C_w}{RT} \frac{\Delta\mu_w}{\delta_m}, \quad (8)$$

which becomes

$$J_w = A(\Delta p - \Delta\pi), \quad (9)$$

where  $A (= D_w C_w / RT \delta_m)$  is the solvent permeability that can be obtained experimentally. The solute flux is similarly given as

$$J_s = -D_s \frac{dC'}{dx} \simeq D_s \frac{\Delta C'}{\delta_m} = D_s \left( \frac{\Delta C'}{\Delta C} \right) \frac{\Delta C}{\delta_m} = \frac{D_s K_m}{\delta_m} \Delta C = B \Delta C, \quad (10)$$



where  $\Delta C'$  and  $\Delta C$  are the concentration differences across the interior and exterior of the membrane, respectively, and  $K_m = \Delta C' / \Delta C$  is the partition coefficient, which is assumed to be constant, and  $B (= D_s K / \delta_m)$  is the solute permeability.

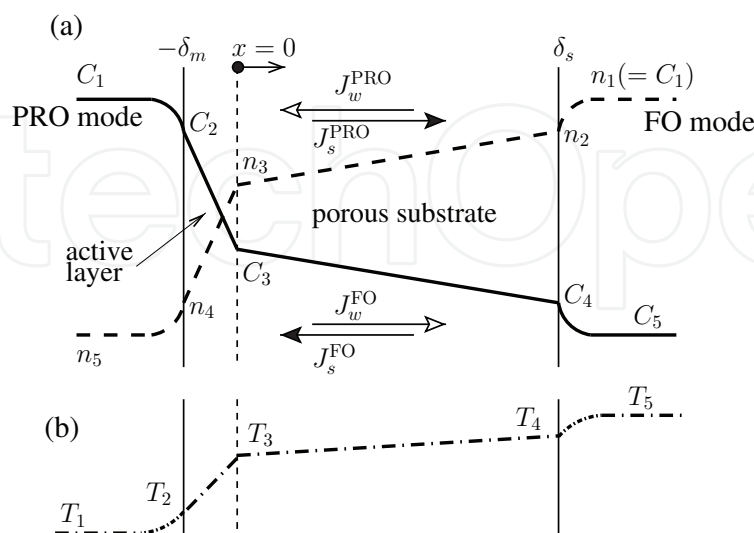
**Figure 4(a)** shows a schematic representing the PRO and FO modes altogether. Concentrations in the PRO and FO modes are denoted as  $C$  and  $n$ , respectively. In the PRO mode,  $C_1$  and  $C_5$  are the draw and feed concentrations, and  $C_2$ ,  $C_3$ , and  $C_4$  are concentrations at interfaces between the draw solution and the active layer, the active layer and the porous substrate, and the porous substrate and the feed solution, respectively. In the FO mode,  $n_1$  and  $n_5$  are the draw and feed concentrations, respectively, and similarly,  $n_2$ ,  $n_3$ , and  $n_4$  have the meanings corresponding to those in the PRO mode. To systematically compare the performances of the PRO and FO modes, we set  $n_1 = C_1$  and  $n_5 = C_5$ , which are the draw ( $C_d$ ) and feed ( $C_f$ ) concentrations, respectively. Solvent and solute fluxes in the PRO mode are denoted as  $J_w^{\text{PRO}}$  and  $J_s^{\text{PRO}}$ , and those of the FO mode are  $J_w^{\text{FO}}$  and  $J_s^{\text{FO}}$ , respectively. In each mode, solvent and solute fluxes are oriented in opposite directions, influencing each other's driving forces. The active layer and porous substrate have thicknesses of  $\delta_m$  and  $\delta_s$ , respectively, as located in regions of  $-\delta_m < x < 0$  and  $0 < x < \delta_s$ , respectively. Solute molecules migrate with molecular diffusivity  $D_0$  in the porous substrate that is characterized using its thickness  $\delta_s$ , porosity  $\varepsilon$ , and tortuosity  $\tau$ .

In the PRO mode, the solvent flux (in magnitude) is

$$J_w = A(\pi_2 - \pi_3) \quad (11)$$

where  $\pi_2$  and  $\pi_3$  are osmotic pressures at concentration  $C_2$  and  $C_3$ , respectively. In a steady state, the water flux  $J_w$  is constant in both the active and porous regions. The solute flux in the active layer is:

$$J_s = B(C_2 - C_3) \quad \text{for} \quad -\delta_m < x < 0 \quad (12)$$



**Figure 4.** A schematic representation of (a) concentration polarization across a skinned membrane during FO process in the PRO and FO modes, represented using the solid and dashed lines, respectively and (b) arbitrary temperature profile increasing from the active layer to the porous substrate.

and that in the porous substrate:

$$J_s = -\frac{\epsilon}{\tau} D \frac{dC}{dx} - J_w C \quad \text{for } 0 < x < \delta_s. \quad (13)$$

In a steady state,  $J_s$  of Eqs. (12) and (13) are equal to each other. Flux equations for the FO mode can be easily obtained by replacing subscript 2 by 4 in Eqs. (11) and (12) and replacing  $C$  by  $n$  in Eqs. (12), (13). Fluxes of the PRO and FO modes are calculated as

$$J_w^{\text{PRO}} \simeq \frac{1}{K} \ln \left[ \frac{B + A\pi_d - J_w^{\text{PRO}}}{B + A\pi_f} \right] \quad (14)$$

and

$$J_w^{\text{FO}} \simeq \frac{1}{K} \ln \left[ \frac{B + A\pi_d}{B + A\pi_f + J_w^{\text{FO}}} \right], \quad (15)$$

respectively, where  $\pi_d$  and  $\pi_f$  are the osmotic pressure of the draw and feed concentrations, respectively, and

$$K = \frac{\delta_s \tau}{D_0 \epsilon} = \frac{S}{D_0} \quad (16)$$

is interpreted as the characteristic mass transfer resistance, proposed by Lee et al. [37]. Following the convention of standard mass transfer theory,  $K^{-1}$  can be interpreted as the mass transfer coefficient of FO processes. In Eq. (16),  $S (= \delta_s \tau / \epsilon)$ , defined as the structural parameter having units in length, represents the actual path length of molecules passing through the tortuous porous substrate, which is by definition longer than the thickness  $\delta_s$ . For mathematical simplicity, one can write the flux equation for both modes:

$$J_w = \frac{1}{K} \ln \left[ \frac{B + A\pi_d - \varphi J_w}{B + A\pi_f + (1 - \varphi) J_w} \right] \quad (17)$$

where

$$\varphi = \begin{cases} 1 & \text{for PRO mode} \\ 0 & \text{for FO mode} \end{cases} \quad (18)$$

is an integer to toggle between the two modes. Any theoretical development can be initiated from Eq. (17) to consider universally both the FO and PRO modes, and then a proper value of  $\varphi$  can be chosen.

### 5.1.1. Underlying assumptions and approximations

In the theory, there are several key assumptions during derivations of Eqs. (14) and (15). These assumptions are summarized in the following for the PRO mode for simplicity, but conceptually are identical to those in the FO mode.

1. Mass transfer phenomena are described using the solution-diffusion model in which the solvent and solute transport are proportional to the transmembrane differences in the osmotic pressures and solute concentrations, respectively [39]. If one sees these combined phenomena as diffusion, the solvent transport can be treated as semibarometric diffusion. In other words, under the influence of pressure, the solute transport can be treated as Fickian diffusion, driven by the concentration gradient. In a universal view, the net driving forces of the solvent and solutes are their chemical potential differences.

2. In the flux equations,  $\pi_d$  and  $\pi_f$  are, respectively, overestimated and underestimated because their true values are those at the draw-membrane and feed-membrane interfaces, i.e.  $\pi_2$  and  $\pi_4$ , which are difficult to obtain. This approximation does not cause obvious errors if the flow velocities of the draw and feed solutions are fast enough to suppress formation of any significant external concentration polarizations. A necessary condition, which is less discussed in theories, is the high diffusivity or low molecular weight of solutes.

3. The osmotic pressure is presumed to be linear with the solute concentration  $C$ . In the PRO mode, one can indicate

$$\pi_2 - \pi_3 = \left( \frac{\pi_2 - \pi_3}{\pi_2 - \pi_4} \right) (\pi_2 - \pi_4) = \left( \frac{1 - C_3/C_2}{1 - C_4/C_2} \right) (\pi_2 - \pi_4) \quad (19)$$

using  $\pi_2 - \pi_k = \pi_2(1 - C_k/C_2)$  for  $k = 3, 4$ . Eq. (19) can be erroneous if the draw concentration is extraordinarily high or pair-wise interactions between solutes are very strong so that the weak solution approach fails. A study on nonlinearity of  $\pi$  with respect to  $C$  can be found elsewhere [37, 38].

4. Rigorously saying, mass transport phenomena are assumed to be in a steady state and equilibrium thermodynamics are used to explain the filtration phenomena. Although the FO phenomenon occurs in an open system, transient behavior is barely described in the literature.

5. In the porous substrate, the bulk porosity is assumed to be uniform, which implies isotropic pore spaces. Moreover, the interfacial porosity between the active and porous layers is assumed to be equal to the bulk porosity. An in-depth discussion on the interfacial porosity can be found elsewhere [40]. In the same vein, the tortuosity is a characteristic geometric constant of the substrate, which is hard to measure independently. More importantly, tortuosity is included in the definition of the structural parameter  $S$ , which is used to fit the experimental data to the flux equations.

6. The solute diffusivity  $D_0$  is assumed to be constant, that is, independent of the solute concentration such that the concentration profile is further implied to be linear within the porous substrate.

7. Finally, temperatures of the draw and the feed streams are assumed equal although hydraulic and thermal conditions of these two streams can be independently controlled. As a consequence, heat transfer across the membrane is barely discussed in the literature.

In practice, solvent and solute permeability  $A$  and  $B$  are measured experimentally in the RO mode using feed solution of zero and finite concentrations, respectively. The applied pressure is selected as a normal pressure to operate the RO, and the solute concentrations are usually in the range of that of a typical brackish water. Variations in  $A$  and  $B$  with  $C_d$  and  $C_f$  are

presumed to be negligible, similar to those of RO cases. In Eq. (17),  $J_w$  is directly related to the interfacial concentration, i.e.  $C_3$  and  $n_3$  in the PRO and FO modes, respectively, and therefore it can be predicted only if  $K$  is known. Mathematically, one FO flux equation has two unknowns, which are  $J_w$  and  $K$ . In most cases, the permeate flux  $J_w$  is measured experimentally and then used to back-calculate  $K$ . This experiment-based prediction often results in an imbalance of mass transfer [41, 42]. A recent study assumes that the interfacial porosity between the active and porous layers is different from the bulk porosity of the porous substrate, which successfully resolves the origin of the imbalance between theoretical and measured  $K$  values [40].

This chapter aims to explain how the temperature across the FO membrane, which consists of the active and porous layers, may affect the performance of the mass transfer at the level of statistical physics. The transmembrane temperature gradient prevents from using the abovementioned assumptions and approximations, which are widely used in the FO analysis. First, the SD model is purely based on isothermal-isobaric equilibrium in a closed system. Second, the external concentration polarizations in the draw and feed sides cannot be neglected at the same level because the temperature gradient causes a viscosity difference across the membrane. Third, the weighting factor connecting  $\pi_2 - \pi_3$  and  $\pi_2 - \pi_4$  cannot be represented only by concentrations but instead should include temperatures at the interfaces. Fourth, even if one can achieve a perfect solute rejection, i.e.  $B = 0$ , steady heat transfer across the membrane should be included since porous membrane is not a perfect thermal insulator. Fifth, the temperature gradient may change the (effective) properties of the active and porous layers such as  $A$ ,  $B$ ,  $\epsilon$ , and  $\tau$  in principle and the molecular diffusivity  $D_0 \rightarrow D(T)$ . Sixth, Fick's law should include additional thermal diffusion or temperature effects for determining the collective diffusion. Seventh, of great necessity is a novel, quantitative equation to calculate the osmotic pressure under the gradients of concentration as well as temperature, which generalizes van't Hoff's equation (1).

## 5.2. Heat transfer

**Figure 4(b)** shows an arbitrary temperature profile across the FO membrane, increasing from the active layer side to the porous layer side. In bulk phases of the active and porous sides, temperatures are maintained at  $T_1$  and  $T_4$ , respectively. For simplicity, we set  $T_1 < T_4$ . Stream temperature on the active side increases to  $T_2$ , and within the membrane, temperature elevates from  $T_2$  to  $T_3$ . Since the active layer is often made thin, a linear variation of temperature can be readily assumed. From the active-porous interface to the porous layer surface to the solution, the temperature increases from  $T_3$  to  $T_4$ . A similar external temperature polarization occurs in the PL-side bulk phase, generating the temperature change from  $T_4$  to  $T_5$ . The overall temperature profile is conceptually akin to the concentration profile in the FO mode. Having the same bulk temperatures, i.e.  $T_1$  and  $T_5$ , the flow direction can noticeably change values from  $T_2$  to  $T_4$ . For logical consistency, a steady state is assumed while investigating the heat transfer across the FO membrane in this chapter. Thus, heat fluxes of the four regions are

$$q_{BA} = h_{BA} (T_2 - T_1) \quad (20)$$

$$q_{AL} = h_{AL} (T_3 - T_2) \quad (21)$$

$$q_{PL} = h_{PL} (T_4 - T_3) \quad (22)$$

$$q_{BP} = h_{BP}(T_5 - T_4), \quad (23)$$

where subscripts BA and BP indicate bulk phases in the active and porous layer sides, respectively, and AL and PL mean the active layer and porous layer, respectively. The net temperature difference across the membrane is  $T_4 - T_2$ , which is to be approximated as  $T_5 - T_1$ . In the steady state, the heat flux  $q$  should be equal in each region, that is,  $q = q_{BA} = q_{AL} = q_{PL} = q_{BP}$ . Dividing each equation of (20)–(23) by the heat transfer coefficient  $h$ 's, one derives

$$q = h_{eq}(T_5 - T_1) \quad (24)$$

$$\frac{1}{h_{eq}} = \frac{1}{h_{BA}} + \frac{1}{h_{AL}} + \frac{1}{h_{PL}} + \frac{1}{h_{BP}}. \quad (25)$$

Note that Eq. (24) assumes that the heat transfer is solely based on thermal conduction without thermal convection, that is, transfer rate of heat by solvent flux. In the FO process with the transmembrane thermal gradient, Eqs. (21) and (22) should be revised as

$$q_{AL} = h_{AL}(T_3 - T_2) \pm H_w J_w \quad (26)$$

$$q_{PL} = h_{PL}(T_4 - T_3) \pm H_w J_w, \quad (27)$$

where  $H_w$  and  $J_w$  are the enthalpy and flux of the solvent, respectively, and the sign is plus when the concentration and temperature profiles both increase and decrease together, otherwise it is negative. For example, for the temperature profile shown in **Figure 4**, the FO concentration profile has the same trend to that of the temperature, and therefore signs in Eqs. (26) and (27) are positive. In this case, Eq. (25) needs to be modified to

$$\frac{1}{h_{eq}} = \frac{1}{h_{BA}} + \frac{1}{h'_{AL}} + \frac{1}{h'_{PL}} + \frac{1}{h_{BP}}, \quad (28)$$

where

$$h'_{AL} = h_{AL} \pm \frac{H_w J_w}{T_3 - T_2} \quad (29)$$

$$h'_{PL} = h_{PL} \pm \frac{H_w J_w}{T_4 - T_3} \quad (30)$$

This heat balance analysis is very similar to that of membrane distillation [43, 44], but the FO process does not have any solvent phase transition so that the latent heat is not considered.

### 5.3. Mass transfer mechanisms

#### 5.3.1. Anisothermal osmotic pressure

In statistical mechanics, Gibbs energy is the master function of the isothermal-isobaric ensemble. Consider a box in which two regions are separated by a semipermeable membrane. In



equilibrium, the maximum entropy condition requires that the chemical potential divided by the temperature should be constant, i.e.

$$\Delta\left(\frac{\mu(T, P, N)}{T}\right) = 0, \quad (31)$$

which converts to the constant chemical potential for the isothermal environment, i.e.  $\Delta\mu = 0$  for constant  $T$ . Note that in the conventional solution-diffusion model, the chemical potential of water  $\mu_w$  in the external phase is assumed as a function of solute concentration  $C$  and pressure  $P$ . From Eq. (31), van't Hoff's osmotic pressure difference is derived as

$$\Delta\pi = RT\Delta C, \quad (32)$$

which can perhaps be extended intuitively to  $\Delta\pi = R\Delta(CT)$  in the temperature gradient. Here we assume that the membrane properties do not change significantly with solute concentration  $C$  and local temperature  $T$ . In the presence of a concentration gradient only, van't Hoff's equation indicates that water (solvent) molecules tend to move from a lower solute concentration region to a higher solute concentration region. This is due to the water chemical potential being higher in the lower  $C$  region. Now we replace the concentration gradient by the temperature gradient. Diffusion of water molecules is purely based on their kinetic energy as proportional to  $T$  and the temperature gradient across the membrane, as shown in **Figure 4(a)**. For simplicity, we consider only the active layer of which  $A$  and  $B$  values are assumed to be insensitive to temperature. Therefore, similar to the direct contact membrane distillation, two solutions of high and low temperatures are in contact with the membrane surfaces. Since solutes are absent, the water motion is purely diffusive under the chemical potential gradient induced by the temperature gradient. Water molecules in the high temperature region move faster than those in the low temperature region. Therefore, water transfer must follow the direction of the temperature gradient. If one side of the membrane has a solution of both high temperature and concentration, then the net osmotic pressure must be less than that of the concentration gradient only, that is,

$$\Delta\pi = a\Delta C - b\Delta T \quad (33)$$

where  $a$  must be equal to  $RT$  and  $b$  is a positive constant. To the best of our knowledge,  $a(T) = RT$  has not been rigorously proven, and  $b(c)$  is so far unknown. The theoretical development of the anisothermal osmotic pressure,  $\pi = \pi(C, T)$ , as a natural extension from van't Hoff's equation is of urgent importance to the current literature in water transport theories, which are to be utilized not only in desalination and fresh water production but also in a broad applications of separation and filtration.

### 5.3.2. Anisothermal diffusion

Fick's law is a phenomenological equation based on experimental observations. The equation states that the diffusive flux  $J$  is proportional to the concentration gradient

$$\vec{J} = -D \vec{\nabla} C. \quad (34)$$

In the dilute limit, the diffusivity is independent of concentration  $C$ , i.e.  $D \neq D(C)$ , and if the solute molecules are Brownian,  $D$  is proportional to temperature  $T$ :  $D \propto T$ . If and only if the molecular motion is dragged by the viscous force, which is directly related to their relative velocity to the solvent (often stationary), then the drag force can be written as

$$\tilde{F}_{\text{drag}} = -\beta \vec{v}, \quad (35)$$

where  $\vec{v}$  is the molecular velocity relative to that of the solvent medium, and  $\beta$  is the drag coefficient independent of  $\vec{v}$ . The Brownian diffusivity is proven to be  $D = k_B T / \beta$ , where  $k_B$  is Boltzmann's constant. Stokes proved that  $\beta = 3\pi\eta_w d_p$  where  $\eta_w$  is the solvent viscosity and  $d_p$  is the particle (molecule) diameter.

In the presence of the spatial variation of  $T$ , Eq. (34) is generalized as [45]

$$\vec{J} = \frac{D}{T} \vec{\nabla} (CT). \quad (36)$$

Thus, substitution of the Stokes-Einstein diffusivity into Eq. (36) gives

$$\vec{J} = \frac{k_B}{\beta} \vec{\nabla} (CT) = \frac{1}{\beta} \vec{\nabla} (\pi), \quad (37)$$

which is valid if the solvent viscosity  $\eta_w$  is a weak function of  $T$  such as water. For a homogeneous system, the diffusive flux may in general be

$$\vec{J} = -\alpha \vec{\nabla} \mu - \beta \vec{\nabla} T, \quad (38)$$

where one can write the chemical potential gradient as

$$\vec{\nabla} \mu = \left( \frac{\partial \mu}{\partial C} \right)_{P,T} \vec{\nabla} C + \left( \frac{\partial \mu}{\partial T} \right)_{C,P} \vec{\nabla} T + \left( \frac{\partial \mu}{\partial P} \right)_{C,T} \vec{\nabla} P. \quad (39)$$

Substitution of Eq. (39) into (38) gives

$$\vec{J} = -D \left( \vec{\nabla} C + k_T \vec{\nabla} \ln T + k_P \vec{\nabla} \ln P \right), \quad (40)$$

which defines the thermal diffusion coefficient  $k_T D$ , where  $k_T$  is the thermal diffusion ratio, which is a dimensionless quantity. The coefficient  $k_P D$  is the barodiffusion coefficient. In the dilute limit,  $k_T$  vanishes as it is proportional to  $C$ . The barodiffusion is often negligible as the diffusion is characterized in a stationary fluid that will have finite velocity if the hydraulic pressure is applied.

### 5.3.3. Solute diffusivity matters

In the conventional isothermal theory of FO, one can write a conceptual relationship between the water flux and the transmembrane osmotic pressure difference as [33]

$$J_w \propto D \ln \Delta\pi, \quad (41)$$

which clearly indicates that  $J_w$  increases with both  $D$  and  $\Delta\pi$ , but  $\Delta\pi$  increases much slower than  $D$  due to the logarithmic dependence. To double the flux  $J_w$ , there are two mathematical choices:  $D \rightarrow 2D$  (linear) and  $\Delta\pi \rightarrow (\Delta\pi)^2$  (geometric in a specific unit, or  $\Delta C \rightarrow (\Delta C)^2$ ). The first way of increasing the solute diffusivity is related to finding or developing novel draw solutes, while the second option is practically challenging as it makes the draw recovery more energy consuming. Especially when selecting the draw solutes, their diffusivity is the most critical parameter in FO processes, as solutes of high diffusivity significantly decrease the ECP and ICP.

If we write intuitively the anisothermal osmotic pressure as

$$\Delta\pi = RT_m \Delta C - b \Delta T \quad (42)$$

across the membrane with  $\Delta T = T_1 - T_2$  and  $T_m = \frac{1}{2}(T_1 + T_2)$ , it would be interesting to know the particular transmembrane temperature difference that can nullify the net osmotic pressure gradient:

$$\Delta T = b^{-1} R \bar{T} \Delta C. \quad (43)$$

As both  $T_1$  and  $T_2$  increase while keeping  $\Delta T$  constant,  $\Delta\pi$  increases. Moreover, increased  $T_m$  may noticeably enhance the solvent as well as solute diffusion. This thought process strongly supports the experimental literature in FO research, equivocally showing that the solvent flux is proportional to the system temperature. Note that Eq. (41) includes the permeability coefficients of solvent ( $A$ ) and solute ( $B$ ). As we discussed in the previous section, we know

$$\frac{\partial A}{\partial T} \quad \text{and} \quad \frac{\partial B}{\partial T} \gtrsim 0 \quad (44)$$

so that both the solvent and solute fluxes increase with the mean temperature  $T_m$  of the membrane where  $\Delta T$  is maintained constant.

On the basis of our investigation, temperature effects on the osmotic phenomena are not as simple as expected from the linear van't Hoff equation, but highly correlated through the temperature-dependent material constants of solvent ( $\eta, A$ ), solutes ( $D, B$ ), and their strong linkage to the osmotic pressure:  $\pi \rightarrow \pi(C, T)$ .

## 6. Concluding remarks

This chapter provides a comprehensive review on the effect of temperature on the FO process. Although the motivation for studying the temperature effect comes from the fact that osmosis is a thermodynamically spontaneous process, changing the system temperature either locally or globally can offer more effective ways of engineering the FO process with lower energy consumption. However, as evidenced by the scattered data across the literature and a lack of theoretical descriptions, more robust and systematic studies are warranted for deeper understanding of the

phenomena. For example, most of the temperature-dependent FO studies relate the changes in the water and the solute flux to the change in the physical properties of the bulk solution only, neglecting any changes in the membrane properties such as water permeability  $A$ , solute permeability  $B$ , and mass transfer resistance  $K$ . Furthermore, a holistic theory accounting for the effect of transmembrane temperature gradient on the FO process is still missing, hence to be constructed in the near future.

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