

TECHNICAL PAPER

Scaling prediction for membrane distillation

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Abstract

Deposition of salts on the membrane, which is called scaling, decreases the distillate flux, and increases the energy consumption of membrane distillation. Therefore, knowing beforehand if scaling would occur is critical for the design of the process conditions. Here, the electrolyte non-random two liquid theory is discussed, and an example is given.

Introduction

Depositions of salts on the membrane, which is called scaling, can cause problems during operation of membrane distillation systems. Scaling can lead to a higher thermal energy consumption and to a lower amount of clean water production. Therefore, it is critical to be able to prevent scaling.

One way of preventing scaling is to use antiscalant, but this leads to an extra cost of purchasing the antiscalant and leads to more chemicals in the discharged water. The second way is to predict when scaling occurs, for which mathematical models can be employed. The mathematical model treated later uses the activity coefficient (γ), which is the deviation from the Raoult's law:

$$P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}$$

In an ideal system $\gamma = 1$. If the pressure is higher than the ideal pressure ($\gamma > 1$), there is a positive deviation from Raoult's law. This means that the molecules have weaker interactions and lower bond energies. In other words, 1-2 interactions are weaker than 1-1 or 2-2 interactions.

Scaling factor

In [1] the authors proposed a scaling factor which can be used to assess at which concentration scaling will occur. When the scaling factor is bigger than one, scaling will occur. Therefore, it is desirable for the scaling factor to be lower than one. The scaling factor can be determined by using the following equation:

$$SF_k = \frac{(x_M\gamma_M)^{v_+}(x_X\gamma_X)^{v_-}(x_{H_2O}\gamma_{H_2O})^{v_w}}{K_{sp,k}}$$

The solubility product constant of a dissociating salt ($M_v + X_{v^-} \leftrightarrow v + M^{z^+} + v_-X^{z^-}$) can be determined by:

$$\ln(K_{sp,k}) = -\frac{\Delta G_k^0(T_0)}{RT_0} + \frac{\Delta H_k^0(T_0)}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \frac{\Delta C_{p,k}^0(T_0)}{R}\left[\frac{T}{T_0} - 1 + \ln\left(\frac{T}{T_0}\right)\right]$$

The Gibbs free energy, change in enthalpy and heat capacity can be found in the supplementary data of [1].

Determination of activity factors

The electrolyte non-random two liquid theory (eNRTL) [3, 4] was used recently to identify the scaling factor of a salts in a MD process [1]. For the infinite dilution aqueous solution reference state, the following equation can be used to calculate the activity coefficient:

$$\ln(\gamma_i^*) = \ln(\gamma_{i_{lc}}^*) + \ln(\gamma_{i_{PHD}}^*)$$

The above equation can be used to determine the activity coefficients of the cation, anion, and molecular species. The activity coefficients are based on two terms, the first term is the effect of the local interactions between the various species, which is shown in Figure 1. The second term corresponds to the long-range interactions.

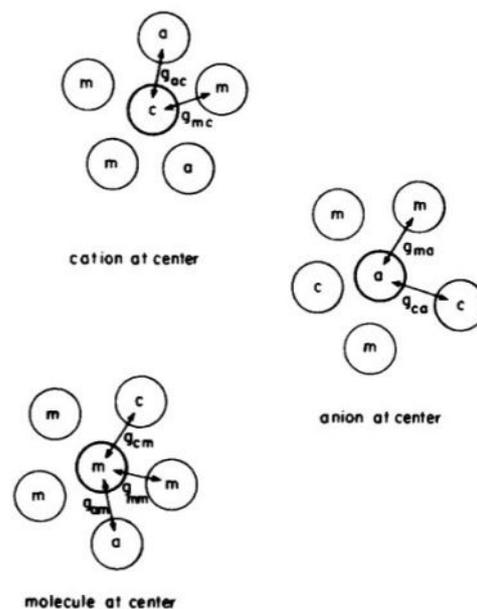


Figure 1 Types of local interactions of dissolved components. [2]

The local activity factor can be determined for each species as follows:

$$\frac{1}{z_c} \ln(\gamma_c^{lc, I_x}) = \sum_m \frac{X_m G_{cm}}{\sum_i X_i G_{im}} \left(\tau_{cm} - \frac{\sum_i X_i G_{im} \tau_{im}}{\sum_i X_i G_{im}} \right) + \frac{\sum_{i \neq c} X_i G_{ic} \tau_{ic}}{\sum_{i \neq c} X_i G_{ic}} + \sum_a \frac{X_a G_{ca}}{\sum_{i \neq a} X_i G_{ia}} \left(\tau_{ca} - \frac{\sum_{i \neq a} X_i G_{ia} \tau_{ia}}{\sum_{i \neq a} X_i G_{ia}} \right)$$

$$\frac{1}{z_a} \ln(\gamma_a^{lc, I_x}) = \sum_m \frac{X_m G_{am}}{\sum_i X_i G_{im}} \left(\tau_{am} - \frac{\sum_i X_i G_{im} \tau_{im}}{\sum_i X_i G_{im}} \right) + \frac{\sum_{i \neq a} X_i G_{ia} \tau_{ia}}{\sum_{i \neq a} X_i G_{ia}} + \sum_c \frac{X_c G_{ac}}{\sum_{i \neq c} X_i G_{ic}} \left(\tau_{ca} - \frac{\sum_{i \neq c} X_i G_{ic} \tau_{ic}}{\sum_{i \neq c} X_i G_{ic}} \right)$$

$$X_i = C_i \left(\frac{n_i}{n} \right)$$

G and τ are local binary quantities, C_i is the chare number for ionic species and one for molecular species. For the current reference state, the local contributions should be normalized. This can be done by using the following two equations:

$$\ln(\gamma_{c,lc}^*) = \ln(\gamma_c^{lc, I_x}) - z_c (G_{cw} \tau_{cw} + \tau_{wc})$$

$$\ln(\gamma_{a,lc}^*) = \ln(\gamma_a^{lc, I_x}) - z_a (G_{aw} \tau_{aw} + \tau_{wa})$$

G and τ can be calculated from the following equations:

$$G = \exp(-\alpha \tau)$$

$$G_{cm} = \sum_a Y_a G_{ca,m}$$

$$G_{am} = \sum_c Y_c G_{ca,m}$$

$$G_{mc} = \sum_a Y_a G_{ca,m}$$

$$G_{ma} = \sum_c Y_c G_{m,ca}$$

$$G_{ca} = \sum_{c'} Y_{c'} G_{ca,c',a}$$

$$G_{ac} = \sum_{a'} Y_{a'} G_{ac,a',c}$$

The non-randomness parameter, α , is 0.2. Y is the local charge composition factor of the cationic and ionic fractions.

The long-range contribution of the solvent, and cationic and ionic species can be calculated by the two following equations, respectively:

$$\ln(\gamma_{H_2O}^{PDH}) = \frac{2A_\phi I_x^{1.5}}{1 + \rho I_x^{0.5}}$$

$$\ln(\gamma_i^{PDH}) = -A_\phi \left\{ \frac{2z_i^2}{\rho} \ln(1 + \rho I_x^{0.5}) + \frac{z_i^2 I_x^{0.5} - 2I_x^{1.5}}{1 + \rho I_x^{0.5}} \right\}$$

The Debye-Hückel parameter, A_ϕ , can be calculated by using the empirical equation from [2]. The closest approach parameter, ρ , is equal to 14.9. I_x is the ionic strength.

$$A_\phi = -61.44534 \exp\left(\frac{T-273.15}{273.15}\right) + 2.864468 \exp\left(\frac{T-273.15}{273.15}\right)^2 + 183.5379 \ln\left(\frac{T}{273.15}\right) - 0.6820223(T-273.15) + 0.0007875695(T^2 - 273.15^2) + 58.95788\left(\frac{273.15}{T}\right)$$

Please refer to [3, 4] for more information about the eNRTL model.

Concentration polarization

At the membrane surface, water evaporates which results in a high concentration layer near the membrane surface. This is called concentration polarization and can be calculated the following equation [5]:

$$c_m = c_b \exp\left(\frac{J}{\rho K}\right)$$

Where K is the solute mass transfer coefficient, which can be calculated with the following equations [5]:

$$K = \frac{Sh \cdot D}{d_h}$$

$$Sh = 1.86 \left(ReSc \frac{d_h}{L} \right)^{0.33}$$

$$Sc = \frac{\mu}{\rho D}$$

Where D , L , d_h , are the diffusion coefficient of the solute, characteristic length, and hydraulic diameter, respectively.

Case study

In Table 1 the components and concentration of a fictitious water is shown.

Ion	Bulk concentration mg/L	Membrane surface concentration mg/L
Cl^-	3584	3674
SO_4^{2-}	4664	4782
N_a^+	2824	2895
M_g^{2+}	1152	1181
Ca^{2+}	3024	3100
S_r^{2+}	5	5.3
TDS	5.4	5.5

Table 1 Components and concentration of the case study

The results shown in Figure 1 indicate that there is risk of scaling of strontium sulphate, calcium sulphate. The temperature is of importance as the solubility product constant changes at higher temperatures. As the temperature is not the same over the membrane length, scaling will be worse at the high temperature sections. Therefore, at high scaling prone waters it might be beneficial to reduce the temperature of the process. By reducing the temperature there will be less distillate flux. This can be beneficial as this will also reduce concentration polarization.

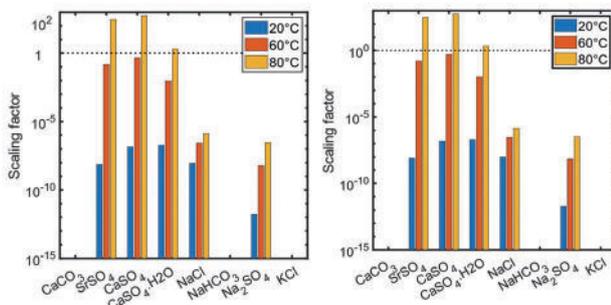


Figure 2 Scaling potential of the fictitious water at several temperatures, without concentration polarization shown on the left and with concentration polarization shown on the right

Fixed values for K and distillate flux of 0.2 and 5 l/m²/h were used here. The results shown in Figure 1 indicate that the effect of concentration polarization is low. The differences between the two are marginal. Therefore, concentration polarization can be omitted when calculating scaling factors. Furthermore, it can be stated that the composition of the water has the most influence on scaling.

Conclusion

By using the equations stated above, the scaling factor can be determined. This way, the process can be designed in such a way that scaling is limited or will not occur at all.

When the temperature of the brine is increased, the process is at higher risk of scaling. In this case study, strontium sulphate and calcium sulphate would form on the membrane surface and cause scaling. This would have an adverse effect on the performance of membrane distillation.

The effect of concentration polarization is low and can be omitted when calculating the scaling factor.

References

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