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A SIMPLE MODEL FOR PERVAPORATION DESIGN

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Membrane separation processes, from reverse osmosis to ultrafiltration to microfiltration, are gradually receiving more and more emphasis in undergraduate chemical engineering curricula. Of these processes, ultrafiltration tends to be the most amenable to the standard chemical engineering approach of theory development, mass and/or energy balancing, and subsequent problem solving, whether it be process design, process analysis, or process optimization.^[1]

Ultrafiltration is in many ways the perfect chemical engineering subject from a teaching perspective: the underlying theory – concentration polarization – is couched in the familiar language of mass transfer and it is not particularly complex; but the application of the theory to batch, fed-batch, and continuous systems provides many opportunities for problem solving and creative thinking. Furthermore, it turns out that the solution of ultrafiltration problems usually requires the student to apply his or her knowledge of numerical methods, whether this involves the numerical solution of ordinary differential equations, numerical integration, or the numerical solution of non-linear algebraic equations.

Reverse osmosis tends to be a little more challenging, requiring a deeper understanding of both multi-component solution thermodynamics and intra-membrane transport, and so the coverage of this process in undergraduate programs, and in unit operations textbooks, tends to be brief and a little superficial.

Like all solid-liquid separation processes, microfiltration, especially crossflow microfiltration, suffers from the problem that the underlying theory is far less rigorous than is the case with ultrafiltration. Consequently, coverage of this topic tends

to go little beyond the classic methods developed by Ruth when the theory of dead-end filtration was first formulated back in the 1940s.^[2]

Pervaporation is a less well-known membrane separation technique that is used mainly for the removal of small quantities of water from organic solvents. In pervaporation, hot liquid enters the module, which is operated in single-pass mode, and the solute transfers preferentially through the membrane. Transport through the membrane occurs in the vapor phase. While a large body of academic research exists into the precise mechanism of vapor transport through pervaporation membranes, less emphasis has been put on chemical engineering analyses to predict the performance of existing pervaporation modules, or to aid in the design of new ones. Nonetheless examples of pervaporation calculations are to be found in some well-known unit operations textbooks. In the third edition of his textbook, Wankat^[3] has employed mass and energy balances, and the assumption of perfect mixing,

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to conduct both feasibility and membrane area calculations. In contrast, Henley, et al.^[4] emphasize the calculation of component permeances from flux and activity coefficient data.

The purpose of this paper is to outline a simple design methodology for calculating the area of a single-stage, single-pass pervaporation system, a methodology that will be accessible to undergraduates. The approach we present requires no new knowledge of the precise mechanism of vapor transport in the membrane and employs standard mass and energy balances that will be very familiar to chemical engineering students in their junior and/or senior years.

MODEL DEVELOPMENT

The key assumptions in the proposed method are that the mass flux through the membrane is a linear function of the solute mass fraction in the liquid phase and that it exhibits an Arrhenius dependence on temperature. These properties of the pervaporation flux are commonly observed.^[5-8] Thus we propose the following expression for the flux:

$$J = xJ_0 e^{-E_j/RT} \quad (1)$$

where J is the flux, J_0 is the maximum possible flux (*i.e.*, the flux as $T \rightarrow \infty$), x is the local liquid composition (mass fraction), E_j is the activation energy of permeation, R is the ideal gas constant and T is the absolute temperature. Now let \dot{m} be the local liquid mass flowrate in the module. Then the differential mass balance for the liquid phase can be written

$$\frac{d\dot{m}}{dA} = -J \quad (2)$$

where dA is the differential area and J is the local flux. The total area of the membrane is given by

$$A = \int_{\dot{m}_r}^{\dot{m}_f} \frac{d\dot{m}}{J} \quad (3)$$

where \dot{m}_r denotes the mass flowrate of the retentate and \dot{m}_f is the mass flowrate of the feed. Therefore, using Eq. (1) we get

$$A = \int_{\dot{m}_r}^{\dot{m}_f} \frac{d\dot{m}}{xJ_0 e^{-E_j/RT}} \quad (4)$$

Now the solute balance can be written

$$\frac{d(x\dot{m})}{dA} = -Jy \quad (5)$$

where y represents the composition of the permeate. To keep things simple we assume that the permeate is pure solute, *i.e.*, $y = 1$.

Now using the product rule and combining Eqs. (2) and (5) gives

$$\frac{dx}{d\dot{m}} = \frac{1-x}{\dot{m}} \quad (6)$$

Separating variables gives

$$\int_z \frac{dx}{1-x} = \int_{\dot{m}_f}^{\dot{m}} \frac{d\dot{m}}{\dot{m}} \quad (7)$$

where z is the liquid feed composition. Integrating gives

$$x = 1 - (1-z) \frac{\dot{m}_f}{\dot{m}} \quad (8)$$

Now a heat balance for the system can be written

$$d(\dot{m}c_p T) = -Jh_v dA \quad (9)$$

where c_p is the specific heat capacity of the liquid and h_v is the specific enthalpy of the vapor.

Neglecting the effect of temperature and composition on c_p (for now) we can combine this expression with Eq. (2) to give

$$c_p T + \dot{m}c_p \frac{dT}{d\dot{m}} = h_v \quad (10)$$

Separating variables gives

$$\int_{T_f}^T \frac{c_p dT}{h_v - c_p T} = \int_{\dot{m}}^{\dot{m}_f} \frac{d\dot{m}}{\dot{m}} \quad (11)$$

where T_f is the feed temperature. Putting aside the temperature dependence of h_v (for now) we can integrate this expression to give

$$T = \frac{h_v}{c_p} - \left(\frac{h_v}{c_p} - T_f \right) \frac{\dot{m}_f}{\dot{m}} \quad (12)$$

The final expression for the membrane area then becomes

$$A = \int_{\dot{m}_r}^{\dot{m}_f} \frac{d\dot{m}}{xJ_0 \exp \left\{ -E_j / R \left(\frac{h_v}{c_p} - \left(\frac{h_v}{c_p} - T_f \right) \frac{\dot{m}_f}{\dot{m}} \right) \right\}} \quad (13)$$

Now defining $s = \dot{m} / \dot{m}_f$ and $p = \dot{m}_p / \dot{m}_f$, where \dot{m}_p is the permeate mass flowrate and p is the cut, we get the following expression for the dimensionless membrane area (\hat{A}):

$$\hat{A} = \frac{AJ_0}{\dot{m}_f} = \int_{1-p}^1 \frac{\exp \left(\frac{a}{b - (b-1)/s} \right)}{1 - (1-z)/s} ds \quad (14)$$

where

$$a = \frac{E_j}{RT_f} \quad (15)$$

and

$$b = \frac{h_v}{c_p T_f} \quad (16)$$

and where the physical properties are temperature- and composition-averaged values.

BOX 1 Example Problem

Problem Statement

A 0.1 mass fraction water-in-ethanol solution is to undergo pervaporation. The feed is heated to 370K and p is 0.03. The activation energy for pervaporation is 30,000 J/mol. If J_0 is 3.0×10^6 kg/m²h, calculate the membrane area required per unit mass flowrate of feed, *i.e.*, A/\dot{m}_f .

You may assume that the specific heat capacities are related to temperature by an equation of the form^[9]

$$c_p = A + BT + CT^2 + DT^3$$

The constants for water and ethanol are given below, where c_p is in J/kgK and T is in K.

	A	B	C	D
Water	5109.8	-2.218	-0.01171	2.97×10^{-5}
Ethanol	1288.1	7.892	-0.02640	3.91×10^{-5}

You may also assume that the specific heat capacity of the solution at any given composition is a weighted average of the pure component values.

The specific enthalpy of water vapor can be computed using the following expression:

$$h_v = 724.3T^{0.221}$$

where T is in K and h_v is in kJ/kg

Solution

With $p = 0.03$, $z = 0.1$, and $y = 1$, a component balance on the water gives $x_r = 0.072$. Now, to calculate the value of T_r , we follow the procedure shown below:

- Calculate the average specific heat capacity as

$$c_{pav} = c_{pw} \left(\frac{0.1 + 0.072}{2} \right) + c_{pe} \left(\frac{0.9 + 0.928}{2} \right)$$

where the pure component specific heats are evaluated at T_r .

- Calculate h_v at T_r
- Calculate T_r using Eq. (12)
- Re-calculate the physical properties using the average temperatures and compositions in the module
- Re-calculate T_r using Eq. (12)
- It is unlikely that further iterations will be required and, in fact, there is very little loss in accuracy if the physical properties are simply computed at the feed temperature and the iterative procedure omitted altogether.

In this case, we converge to $T_r = 350.7$ K giving $c_{pav} = 2676$ J/kgK and $h_v = 2660$ kJ/kg. With these values, we find $a = 9.752$ and $b = 2.687$. Thus the integral to be computed can be written

$$\frac{AJ_0}{\dot{m}_f} = \int_{0.97}^{1.0} \frac{e^{\frac{9.752}{2.687x} - 1.867/s}}{1 - 0.9/s} ds$$

We chose to use WolframAlpha to evaluate the integral. Thus we enter:

Simpsons Method $\exp(9.752/(2.687-1.687/x))/(1-0.9/x)$ from 0.97 to 1.0

Thus we get

$$\frac{A}{\dot{m}_f} = \frac{8048}{3.0 \times 10^6} = 0.003 \frac{\text{m}^2}{\text{kg/h}}$$

An alternative and approximate approach to doing the area calculation, one that avoids the numerical integration step, is to write

$$A = \frac{\dot{m}_p}{J_{av}} = \frac{p}{J_{av} / J_0} \quad (17)$$

where J_{av} is the average flux in the module.

Expanding on similar work in our laboratory in which we examined pervaporation design in systems with composition-independent flux,^[5] we have conducted a large number of membrane area and average flux calculations for both water-ethanol and water-IPA systems where the flux is described by Eq. (1). In our calculations, values of p up to 0.05 were chosen, giving values of x_r/z between 0.175 and 0.9. For water-IPA, the water mass fraction ranged from 0.01 to 0.16 while for water-ethanol it ranged from 0.01 to 0.1. Feed temperatures ranged from 350K – 395K. E_j values ranged between 15,000 J/mol and 63,000 J/mol. For both systems, we found that the average flux can be computed to within an accuracy of 8% by writing

$$J_{av} = \sqrt{J_r J_f} \quad (18)$$

where J_r is the flux evaluated at the retentate temperature. Figures 1 and 2 illustrate the accuracy of the geometric mean approximation for both systems.

Use of the geometric mean approximation, which is analogous to Cheryan's arithmetic mean approximation used in batch ultrafiltration,^[10] simplifies the calculation outlined in the above example and can be used if the instructor wishes to avoid the numerical integration step. For the data used in

the example problem above, the geometric mean approach yields a value for AJ_0 / \dot{m}_f of 7950 which is within 2% of the exact answer.

Finally, an alternative approach to solving the pervaporation design problem is to approach it as one requiring the solution of a system of ordinary differential equations. It would be a useful exercise for the students to show that the model can be expressed in dimensionless form as shown in Box 2. This model can be solved using the student's preferred ODE solver, and the advantage of this approach is that the temperature and composition dependence of the specific heat and vapor enthalpy terms can be incorporated directly into the model without approximation.

Box 2 ODE model of pervaporation

$$\begin{aligned} \frac{d\hat{m}}{d\hat{A}} &= -x e^{-a/\hat{T}} \text{ with } \hat{m} = 1 @ \hat{A} = 0 \\ \frac{d\hat{T}}{d\hat{A}} &= -\frac{1}{\hat{m}} (b - \hat{T}) x e^{-a/\hat{T}} \text{ with } \hat{T} = 1 @ \hat{A} = 0 \\ x &= 1 - 1(1 - z) / \hat{m} \\ \hat{m} &= \frac{\dot{m}}{\dot{m}_f}, \hat{T} = \frac{T}{T_f}, \hat{A} = \frac{AJ_0}{\dot{m}_f} \\ a &= \frac{E_j}{RT_f}, b = \frac{h_v}{c_p T_f} \end{aligned}$$

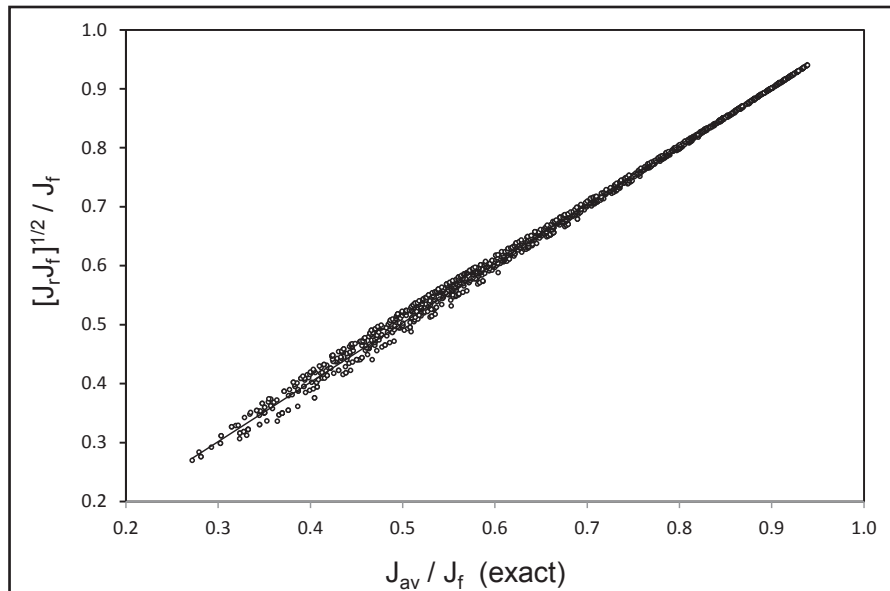


Figure 1. Approximate value of J_{av} / J_f versus exact value for dehydration of IPA-water solutions

CONCLUSIONS

In this paper we have outlined a simple approach to pervaporation design that should not overly stretch junior- and senior-level undergraduates. Although we have assumed a linear relationship between flux and composition, other composition dependencies are possible. For example, there is evidence to suggest that while the flux is a linear function of composition at low compositions, it tends to become independent of flux above a critical composition.^[5]

Thus, there is plenty of scope for the student to extend this work by using different expressions for the flux. The key point is that the engineering student does not have to get bogged down in issues related to the precise mechanism of solute transport through the membrane; all that is required is that they have an accurate empirical expression for the flux.

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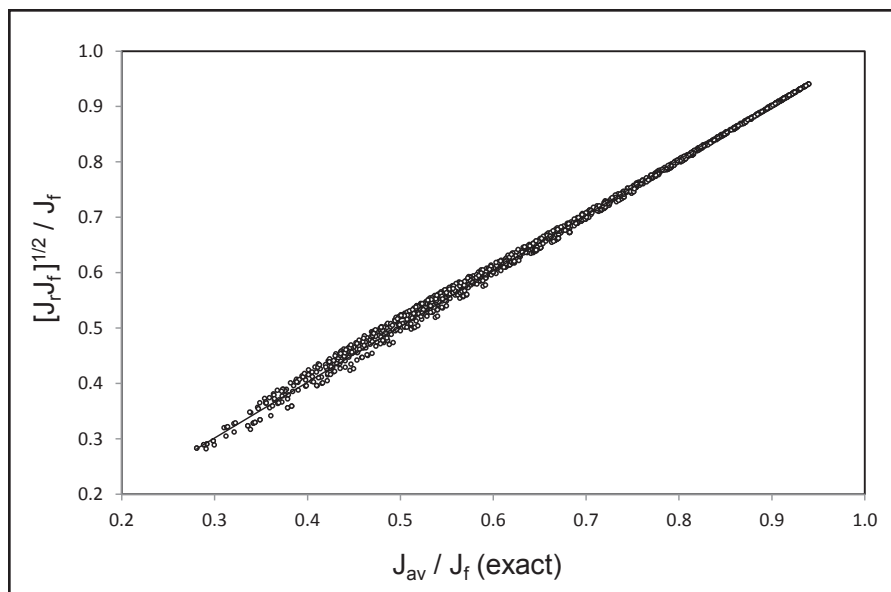


Figure 2. Approximate value of J_{av} / J_f versus exact value for dehydration of ethanol-water solutions.