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A thermodynamic approach to calculating the operating osmotic pressure of pressure-driven membrane separation absorption cycles

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Abstract

Membrane separation of absorption solutions has potential application in refrigeration technology. Operating osmotic pressure is a basic parameter governing the design and evaluation of a membrane separation absorption system. This study presents a thermodynamic approach to calculating the osmotic pressure of an absorption solution using its density and vapour pressure. A correlation between osmotic pressure, density and vapour pressure has been deduced and a calculation example is given. Furthermore, combination of this correlation with the Clausius–Clapeyron equation has produced a simple and interesting result. For a membrane separation absorption cycle, the operating osmotic pressure required is related to the specific latent heat of refrigerant, operating temperatures and density of absorption solution.

Keywords: Operating osmotic pressure; Membrane separation; Absorption cycle

1. Introduction

Membrane separation is a basic process used in chemical engineering. In comparison with distillation, membrane separation requires the input of a small amount of mechanical work instead of a large amount of heat and has been used extensively in desalination of seawater and treatment of wastewater [1,2]. Use of membrane separation in absorption refrigeration systems has also attracted interest in the field of refrigeration [3,4]. Pressure-driven membrane separation absorption cycles may be a potential alternative to conventional vapour compression cycles which suffer the environmental limitations on CFCs. Environmentally-benign absorption solutions (e.g., $\mathrm{LiBr/H_2O}$) may be employed in this cycle. Operating osmotic pressure is a basic parameter governing the design and evaluation of a membrane separation absorption cycle. Theoretically, the osmotic pressure Π may be calculated by [5,6]:

$$\Pi = -\bar{\rho}^{\mathrm{rf}} \cdot RT \ln(\gamma \cdot x) \tag{1}$$

where $\bar{\rho}^{\mathrm{rf}}$ is the average density of solvent (or refrigerant), R is the gas constant of solvent, and γ and x are the activity coefficient and mole fraction of solvent, respectively.

This equation is usually used to determine the activity of the solvent in a solution from the experimental osmotic pressure. It is worth to notice that the calculated activity should be for the solution at the pressure of $P + \Pi$, but the effect of pressure on the activity is usually neglected for a smaller osmotic pressure. When Eq. (1) is employed to calculate the osmotic pressure, the activity or activity coefficient must be known. However, it is not easy to determine the activity coefficient of a pressurized solution. Some approximations have been made. For a very dilute solution, the activity coefficient may be assumed to be unity. Eq. (1) then becomes:

$$\Pi = -\bar{\rho}^{\mathrm{rf}} \cdot RT \ln(x) \tag{2}$$

For a general dilute solution, if the effect of pressure on the activity of solvent is neglected, the activity of solvent in a pressurised solution may be replaced by that at its saturation pressure. This leads to:

$$\Pi = -\bar{\rho}^{\mathrm{rf}} \cdot RT \ln \frac{P(T, x)}{P_s(T)} \tag{3}$$

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Nomenclature

Π	osmotic pressure	Pa
ρ	density	$\mathrm{kg \cdot m^{-3}}$
$\bar{\rho}$	average density	$\mathrm{kg \cdot m^{-3}}$
R	gas constant	$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$
T	temperature	K
x	mole fraction	$\mathrm{mol \cdot mol^{-1}}$
γ	activity coefficient	
P	pressure	Pa
P_s	saturated pressure of a pure refrigerant	Pa
w	work	$\mathrm{J \cdot kg^{-1}}$
f	circulation ratio	
v	specific volume	$\mathrm{m^3 \cdot kg^{-1}}$
$\bar{v}$	average specific volume	$\mathrm{m^3 \cdot kg^{-1}}$
δ	relative error	
T_a	end absorption temperature	K
ΔT	absorption temperature glide	K
T_e	evaporating temperature	K
ΔL	specific latent heat of evaporation	$\mathrm{J \cdot kg^{-1}}$

Superscripts

wk	weak solution deficient in absorbent
st	strong solution rich in absorbent
rf	refrigerant
mb	membrane separation
cp	compression-aided distillation

where $P(T,x)$ is the solvent partial pressure in a solution and $P_s(T)$ is the saturated pressure of a pure solvent at the same temperature as solution.

If the above approximate equations are used to calculate the osmotic pressure of an absorption solution, a considerable error would be introduced due to a larger deviation from the above assumptions. Absorption solution has much higher concentration and therefore it has larger osmotic pressure. The effect of pressure on the activity must be considered. However, it is not easy to determine the activity of refrigerants in a pressurized absorption solution. This study aims to determine a new thermodynamic approach to calculating the osmotic pressure of an absorption solution. There is no need to know the activity of refrigerants in absorption solutions at high pressure. A correlation of the osmotic pressure, density of solution and refrigerant vapour pressure will be formulated.

2. Principle

Pressure-driven membrane separation of an absorption solution is shown schematically in Fig. 1. The weak solution is isothermally pumped to a pressure so that the pressure difference between both sides of membrane could exceed the osmotic pressure of the strong solution. When the refrigerant permeates the membrane, the weak solution is concentrated. The strong solution is then expanded isothermally through a turbine, the work output of which is recovered to the pump. The heat released from the pump may be provided to the turbine. It is assumed that the compression and expansion processes are isothermal and friction-free and the pressures of the feed solution and discharge solution are same. Therefore, the minimum mechanical work required may be given by:

$$w^{\mathrm{mb}} = f \cdot \bar{v}^{\mathrm{wk}} \cdot \Pi - (f-1) \cdot \bar{v}^{\mathrm{st}} \cdot \Pi \tag{4}$$

where f is the ratio of the mass flow rate of the weak solution to the mass flow rate of the refrigerant and $\bar{v}$ is the average specific volume of a solution.

In Eq. (4), osmotic pressure Π corresponds to the strong solution and is greater than that of the weak solution. The strong solution is therefore in permeation equilibrium whereas the weak solution is not. The osmotic pressure of the weak solution is less than the given operating pressure difference. This means that membrane separation process is not reversible for a given range of operating concentration. However, when the range of concentration is very small, the irreversibility across the membrane may be neglected. Eq. (4) then becomes:

$$w^{\mathrm{mb}} = \bar{v} \cdot \Pi \tag{5}$$

Alternatively, an absorption solution may be separated by compression-aided distillation, as shown in Fig. 2. Before entering the generator, the weak solution expands to its saturation pressure by passing through a turbine. The refrigerant vapour from the generator is isothermally compressed to the saturated pressure at the temperature of solution and then condenses to a liquid. The heat released from the compressor and condenser may be provided to the generator. The strong solution and refrigerant liquid produced are both compressed to the pressure of the weak solution. Similarly, it is assumed that all the processes are isothermal and friction-free and the pressures of the feed

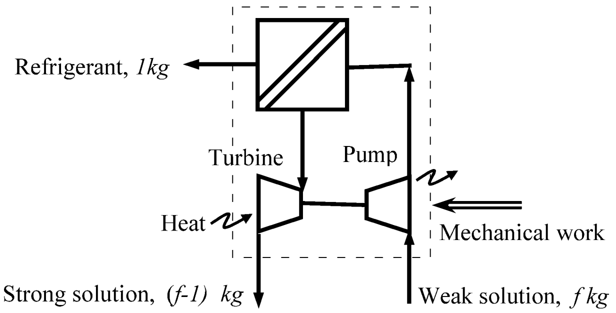


Fig. 1. Membrane separation of a solution.

solution and discharge solutions are same. The minimum mechanical work required is therefore:

$$w^{\mathrm{cp}} = \int v^{\mathrm{rf}}\,\mathrm{d}P + (f-1)\cdot \bar{v}^{\mathrm{st}}\cdot\left(P^{\mathrm{wk}} - P_s^{\mathrm{st}}\right) + \bar{v}^{\mathrm{rf}}\cdot\left(P^{\mathrm{wk}} - P_s\right) - f\cdot \bar{v}^{\mathrm{wk}}\cdot\left(P^{\mathrm{wk}} - P_s^{\mathrm{wk}}\right) \tag{6}$$

Compared with the compression work of vapour, the sum of compression and expansion work of solution is very small, and the last three items in Eq. (6) may be neglected. If the refrigerant vapour is assumed to be ideal, for a very small range of concentration Eq. (6) becomes:

$$w^{\mathrm{cp}} = \int v^{\mathrm{rf}}\,\mathrm{d}P = -RT\ln\frac{P(T,x)}{P_s(T)} \tag{7}$$

Because the state parameters of the feed and product solutions are assumed to be the same in both processes, the total changes in the Gibbs free energy and enthalpies of solutions are same. The two processes are equivalent from the viewpoint of thermodynamics. The minimum mechanical work required for both processes should be same and equal the change in the Gibbs free energy of solutions; the heat effects should be also same. Substitution of Eq. (7) into Eq. (5) therefore yields:

$$\Pi = -\bar{\rho}\cdot RT\ln\frac{P(T,x)}{P_s(T)} \tag{8}$$

Eq. (8) correlates the osmotic pressure, density, temperature and vapour pressure of solution. It may be used to calculate the osmotic pressure from the refrigerant vapour pressure of absorption solutions. If the density of solution at a certain pressure is used to replace the average value in Eq. (8), the relative error in calculating the osmotic pressure will be $(\bar{\rho}-\rho)/\bar{\rho}$.

Compared with Eq. (8), the relative error caused by using Eq. (3) is:

$$\delta = \frac{\bar{\rho}-\bar{\rho}^{\mathrm{rf}}}{\bar{\rho}} \tag{9}$$

which is dependent on the concentration. For 40–65% concentration of $\mathrm{LiBr/H_2O}$, the relative error could be 30–50%. Obviously, the relative error for a salt solution is larger than a liquid–liquid mixture due to a larger density difference between solvent and solution.

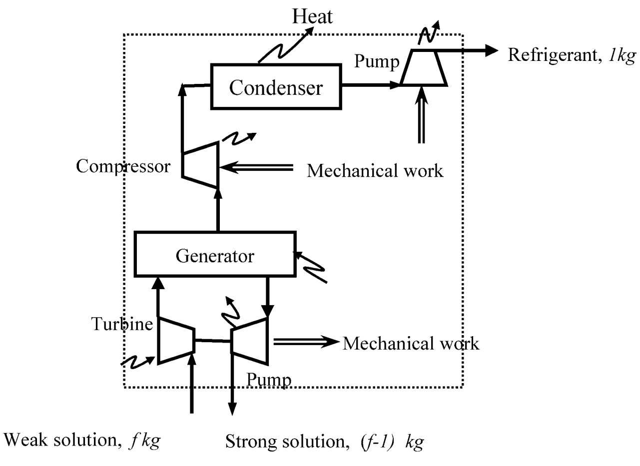
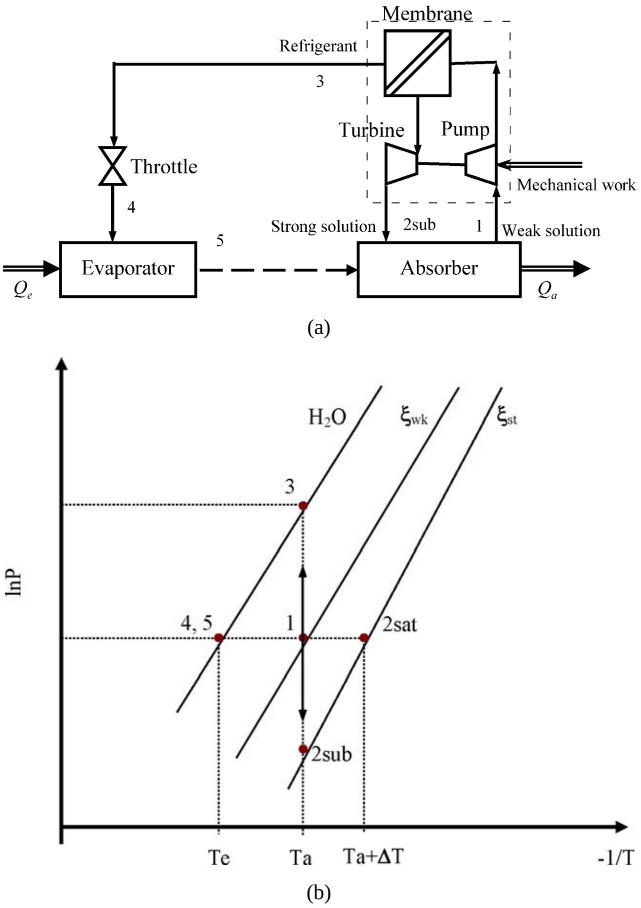


Fig. 2. Compression-aided separation of a solution.

3. Membrane separation absorption cycle

A schematic view of a membrane separation absorption cycle is shown in Fig. 3. The weak solution 1 is pumped to a pressure so that membrane permeation may take place. The refrigerant permeate 3 is expanded to state 4 by passing through a valve before the evaporator; while the concentrated solution is expanded to state 2sub by passing through a turbine. The weak solution, concentrated solution and refrigerant may be at the same temperature, for example, end absorption temperature T_a. The strong solution at state 2sub is subcooled and may be marked in Fig. 3(b) according to its temperature and concentration. The solution at 2sub will change to its saturated state 2sat as soon as it enters the absorber and absorption takes place. On absorbing the vapour 5, the strong solution 2sat becomes the weak solution 1. For a small temperature range, the effect of temperature on the activity may be neglected. Assuming that the vapour pressure in the absorber equals that in the evaporator, we have:



(a)

(b)

Fig. 3. View of a membrane separation absorption system.

$$\frac{P(T,x)}{P_s(T)} = \frac{P(T_a,x)}{P_s(T_a)} = \frac{P(T_a+\Delta T,x)}{P_s(T_a+\Delta T)} = \frac{P_s(T_e)}{P_s(T_a+\Delta T)} \tag{10}$$

where T_e is the evaporation temperature, T_a is the end absorption temperature and ΔT is the absorption temperature glide which is the difference between the start and end absorption temperatures.

Substituting Eq. (10) into Eq. (8) may yield:

$$\Pi = -\bar{\rho} \cdot RT \ln \frac{P_s(T_e)}{P_s(T_a+\Delta T)} \tag{11a}$$

Assuming that the separation temperature, T, equals the end absorption temperature, T_a, we obtain:

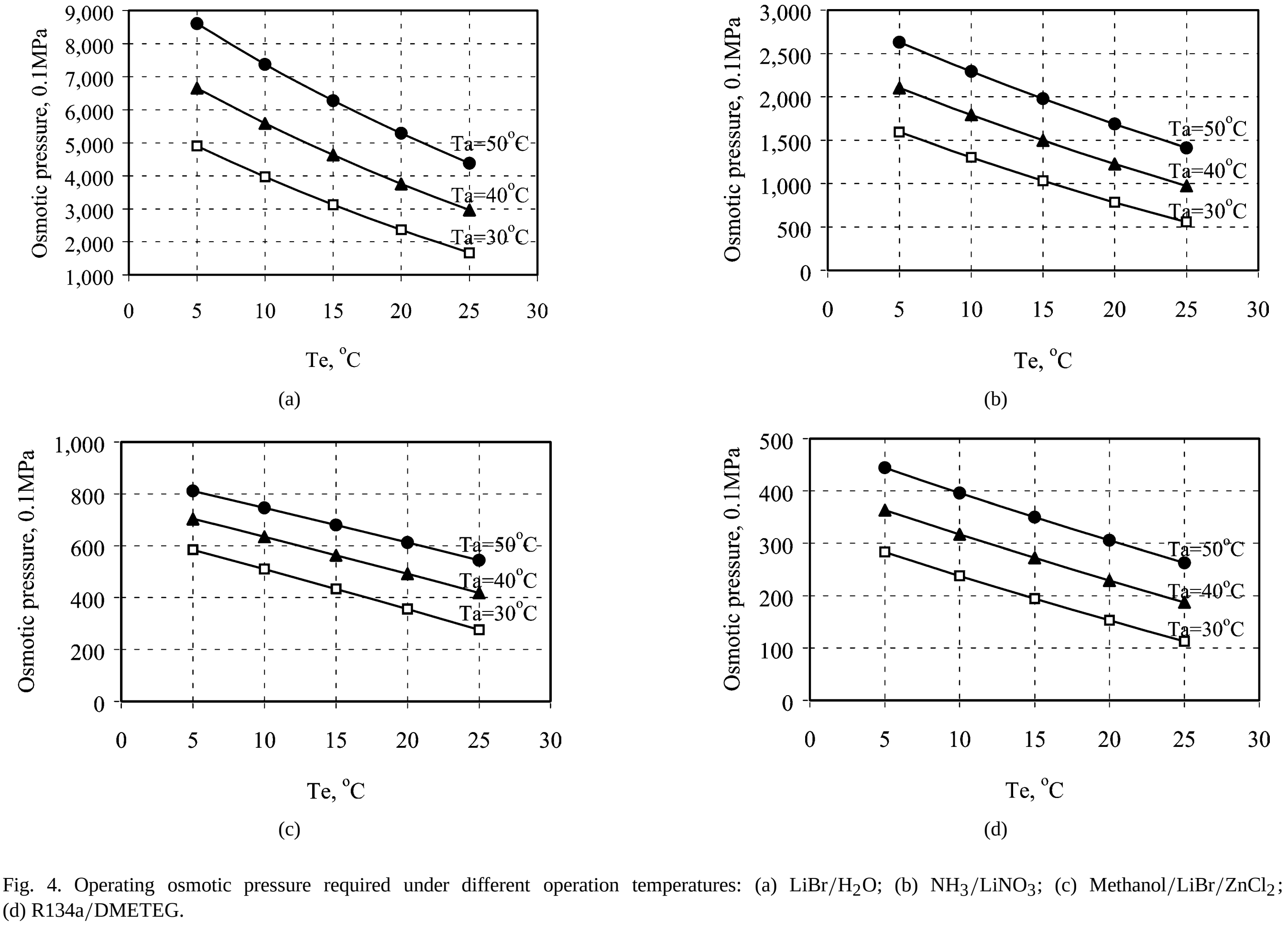
$$\Pi = -\bar{\rho} \cdot RT_a \ln \frac{P_s(T_e)}{P_s(T_a+\Delta T)} \tag{11}$$

Eq. (11) gives the operating osmotic pressure required for given operating temperatures in a membrane separation absorption cycle. It can be seen that the operating osmotic pressure depends on the properties of the refrigerant, operation temperature and density of absorption solution. For calculation purposes, the density at absorption pressure would need to be used to replace the average density, due to the difficulty of determining the pressure dependence of density. This would cause a relative error of $(\bar{\rho} - \rho)/\bar{\rho}$. Fig. 4 gives the operating osmotic pressure required for several absorption solutions. For usual operating temperatures, for example, $T_e = 5\,^\circ\mathrm{C}$, $T_a = 40\,^\circ\mathrm{C}$ and $\Delta T = 10\,^\circ\mathrm{C}$, the operating osmotic pressure could be up to 6000 bars for $\mathrm{LiBr/H_2O}$. This operating osmotic pressure is well beyond the operating range of any commercially available membrane, even exceeding the strength limitations of most materials. It is therefore essential to reduce the required operating osmotic pressure in order to apply the membrane separation absorption cycle. As indicated in Fig. 4, the required operating osmotic pressure may be lower for other absorption solutions. For example, for $\mathrm{NH_3/LiNO_3}$ [7], the operating osmotic pressure required is about 2000 bars; for $\mathrm{methanol/LiBr/ZnCl_2}$ [8], about 700 bars and for R134a/DMETEG [9], about 300–400 bars. The calculations show that the required operating osmotic pressure depends mainly on the properties of the refrigerant for a given operation temperature. This may be further illustrated as follows.

Use of the Clausius–Clapeyron equation gives:

$$\ln \frac{P_s(T_e)}{P_s(T_a+\Delta T)} = -\frac{\Delta L}{R}\left(\frac{1}{T_e} - \frac{1}{T_a+\Delta T}\right) \tag{12}$$

Substituting Eq. (12) into Eqs. (11a) and (11), respectively, yields:



(a)

(b)

(c)

(d)

Fig. 4. Operating osmotic pressure required under different operation temperatures: (a) $\mathrm{LiBr/H_2O}$; (b) $\mathrm{NH_3/LiNO_3}$; (c) $\mathrm{Methanol/LiBr/ZnCl_2}$; (d) R134a/DMETEG.

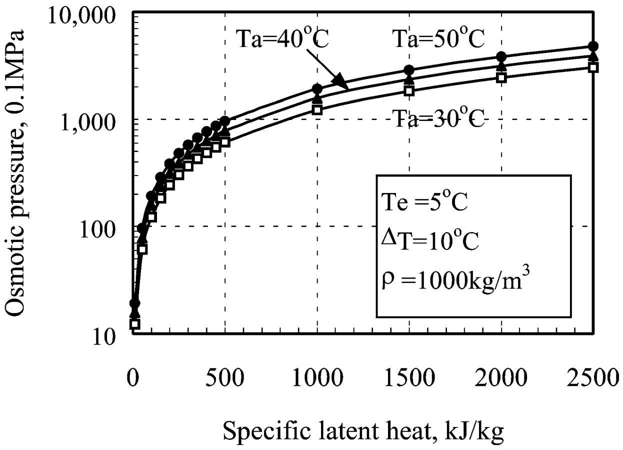


Fig. 5. Operating osmotic pressure required against specific latent heat.

$$\Pi = \Delta L \cdot \bar{\rho} \cdot T \cdot \left(\frac{1}{T_e} - \frac{1}{T_a + \Delta T}\right) \tag{13a}$$

$$\Pi = \Delta L \cdot \bar{\rho} \cdot \left(\frac{T_a}{T_e} - \frac{T_a}{T_a + \Delta T}\right) \tag{13}$$

where ΔL is the specific latent heat of evaporation of refrigerant.

Considering a limited change in density, Eq. (13) shows that the operating osmotic pressure required depends mainly on the specific latent heat of evaporation of refrigerant for a given operation temperature. A small specific latent heat would lead to a small operating osmotic pressure. This case may be related to a refrigerant with a low boiling point and a large molecular weight, for example, hydrocarbons and HFCs. Therefore, from the viewpoint of practicable operating osmotic pressure, it would be better to use a HFC-based absorption solution than a water-based solution in a pressure-driven membrane separation absorption cycle. Fig. 5 shows the effect of the latent heat on the operating osmotic pressure. For 2500 $\text{kJ}\cdot\text{kg}^{-1}$ of latent heat (e.g., water), the operating osmotic pressure required is up to a few thousands bars; For 200–250 $\text{kJ}\cdot\text{kg}^{-1}$ of latent heat (e.g., hydrocarbons and HFCs), the operating osmotic pressure required is in the range of 300–400 bars. If an operating osmotic pressure below 100 bars is required, the specific latent heat should be less than 100 $\text{kJ}\cdot\text{kg}^{-1}$.

4. Conclusions

A new thermodynamic approach for calculating the osmotic pressure of absorption solutions has been presented. This has led to the derivation of an equation correlating the osmotic pressure, density and vapour pressure of a solution. It is of particular use for the calculation of the osmotic pressure of an absorption solution from its refrigerant vapour pressure. For pressure-driven membrane separation absorption cycles, combination of this correlation with the Clausius–Clapeyron equation has allowed the required operating osmotic pressure to be related to the specific latent heat of evaporation of the refrigerant for specified operating temperatures and density of solution. This would be useful for the evaluation of the feasibility of employing a membrane separation in absorption systems.

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