Solutions for R&D to Design

Effect of Pressure on Distillation Separation Operation

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Introduction

Generally, it is known that, for distillation, separation tends to be enhanced by lower pressures.

For two components, the ease of distillation separation can be judged from the value of the relative volatility (α).

Here, we will take typical substances as examples and examine the effect of pressure changes on their relative volatilities.

Ideal Solution System

The relative volatility (α) is a ratio of vapor-liquid equilibrium ratios and can be expressed by the following equation:

$$\alpha = \frac{K_1}{K_2} \qquad K_1 = \frac{y_1}{x_1}, K_2 = \frac{y_2}{x_2}$$

In the case of an ideal solution system , using Raoult’s law, the relative volatility can be expressed as a ratio of vapor pressures.

$$\left.\begin{aligned} Py_1 &= x_1 P_1^o \\ Py_2 &= x_2 P_2^o \end{aligned}\right\} \text{Raoult's law}$$

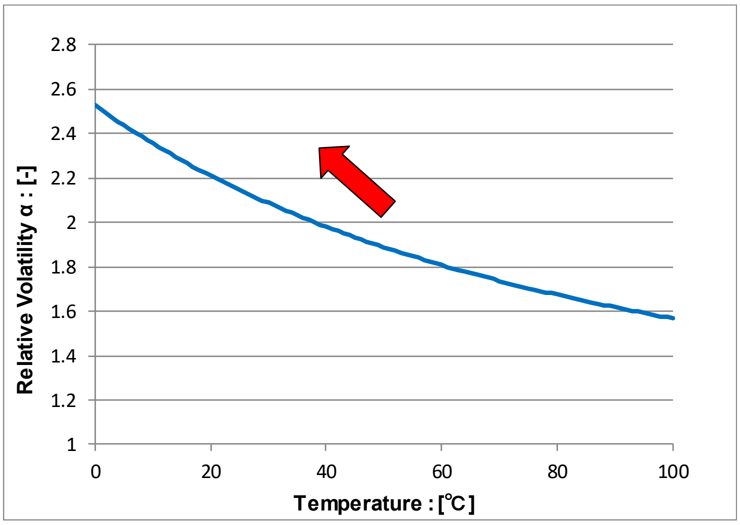
$$\boxed{\alpha = \frac{K_1}{K_2} = \frac{P_1^o}{P_2^o}}$$

$$K_1 = \frac{y_1}{x_1} = \frac{P_1^o}{P}$$

$$K_2 = \frac{y_2}{x_2} = \frac{P_2^o}{P}$$

Methanol-Ethanol System

As an example of an ideal solution system , let’s consider a methanol-ethanol binary system. α is calculated by obtaining vapor pressures from the Antoine constants in the table below.



$$\ln(P_i{}^0[Pa]) = A - \frac{B}{C + T[K]}$$

	A	B	C
Methanol	23.4803	3626.55	-34.29
Ethanol	23.8047	3803.98	-41.68

As the temperature (saturated pressure) decreases, the value of α increases.

From this, it can be seen that the lower the operation pressure, the easier the separation.

Next, we will examine the reasons for which separation becomes easier.

Antoine Constants: “Kagaku Kougaku Binran revised 7th ed.” (in Japanese) (P12-13)

Clausius-Clapeyron Equation

Clausius-Clapeyron equation (*) is a formula that is the theoretical basis of the Antoine equation. A linear relationship can be obtained by plotting the logarithm of the vapor pressure ln(P0) versus the inverse of the absolute temperature 1/T. At this time, <u>the slope of the straight line is obtained by dividing the latent heat of vaporization by the gas constant.</u>

$$\frac{dP}{dT} = \frac{P\Delta H_v}{RT^2}$$

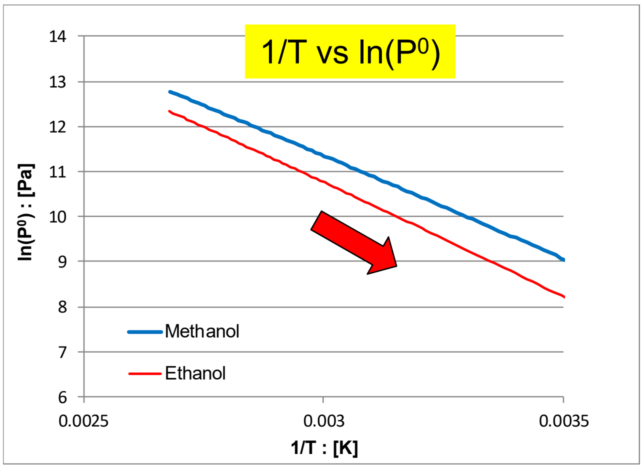
$$\frac{dP}{P} = \frac{\Delta H_v}{R}\frac{dT}{T^2}$$

$$\int \frac{dP}{P} = \frac{\Delta H_v}{R}\int \frac{dT}{T^2}$$

$$\ln(P) = -\frac{\Delta H_v}{R}\frac{1}{T} + const$$

$$\boxed{\therefore \ln(P) = const - \frac{\Delta H_v}{R}\frac{1}{T}}$$

Note: For the derivation of the equations, refer to "On the B Value of the Antoine Equation" (Tips #0811).



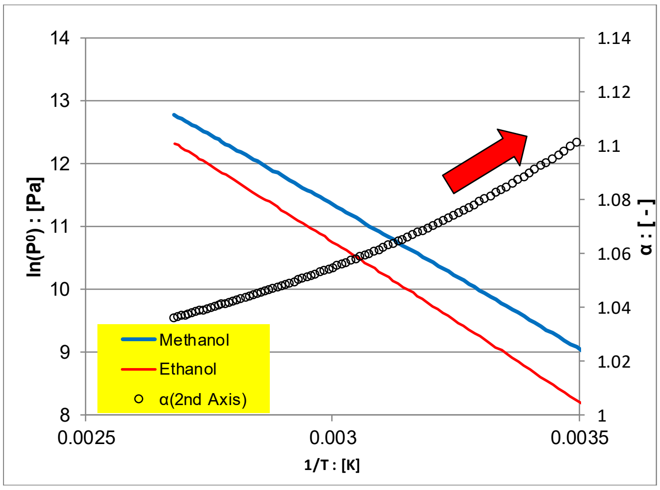
When plotting the vapor pressure of the two methanol/ethanol components against 1/T, the difference in vapor pressure widens as the temperature (saturation pressure) decreases.

Relationship between Vapor Pressure and Latent Heat of Vaporization

In general, the latent heat of vaporization increases in proportion to the boiling point (Hildebrand rule). In the case of methanol and ethanol, ethanol has a higher boiling (a larger molecular weight) and its latent heat of vaporization is larger. Therefore, if ln(P0) is plotted against 1/T, the gradient is larger for ethanol which has a larger latent heat of vaporization.

$$\ln(P) = const - \frac{\Delta H_v}{R}\frac{1}{T}$$

	Latent Heat of Vaporization @ Normal Boiling Point (kcal/mol)
Methanol	8.3932
Ethanol	9.2994



A system showing ideality contains substances of homologous series having close molecular sizes. For homologous substances, the latent heat of vaporization is almost proportional to the difference in boiling points (molecular weights). For this reason, it can be seen that for an ideal system composition, α increases (separation becomes easier) as pressure decreases.

Latent heat of vaporization: "DIPPR Databank"

Non-Ideal Solution System (*)

For a non-ideal solution system, the relative volatility (α) can be expressed using vapor pressures and activity coefficients (γ).

$$\boxed{\alpha = \frac{K_1}{K_2} = \frac{\gamma_1 P_1^o}{\gamma_2 P_2^o}}$$

$$\left.\begin{aligned} Py_1 &= \gamma_1 x_1 P_1^o \\ Py_2 &= \gamma_2 x_2 P_2^o \end{aligned}\right\} \text{Modified Raoult's Law}$$

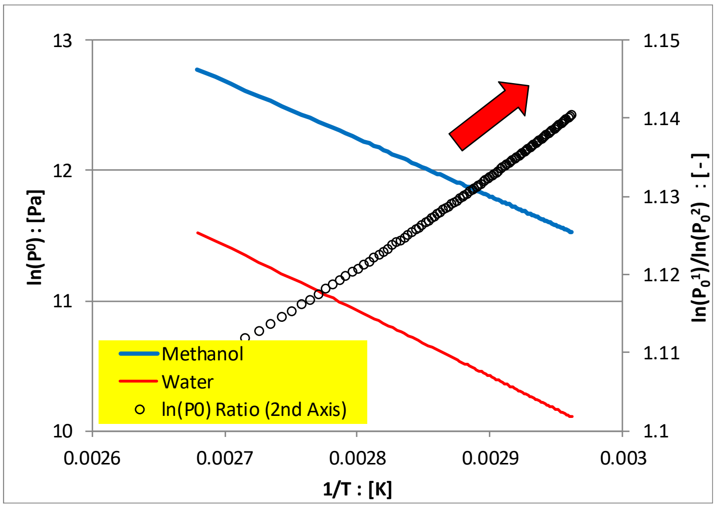
$$K_1 = \frac{y_1}{x_1} = \frac{\gamma_1 P_1^o}{P}$$

$$K_2 = \frac{y_2}{x_2} = \frac{\gamma_2 P_2^o}{P}$$

Note: For simplification, it is assumed that the non-ideality of the vapor phase can be ignored.

Methanol-Water System (Vapor Pressure Ratio)

As an example of a non-ideal system, consider a methanol- water binary system. Regarding the latent heat of vaporization, since methanol < water, the vapor pressure ratio increases as pressure (temperature) decreases.

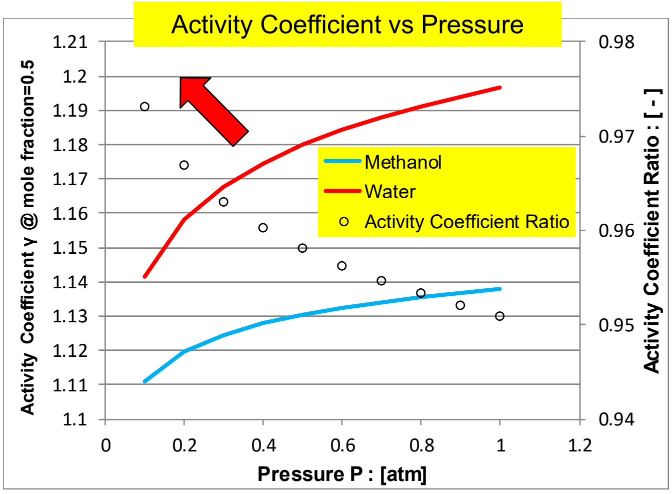


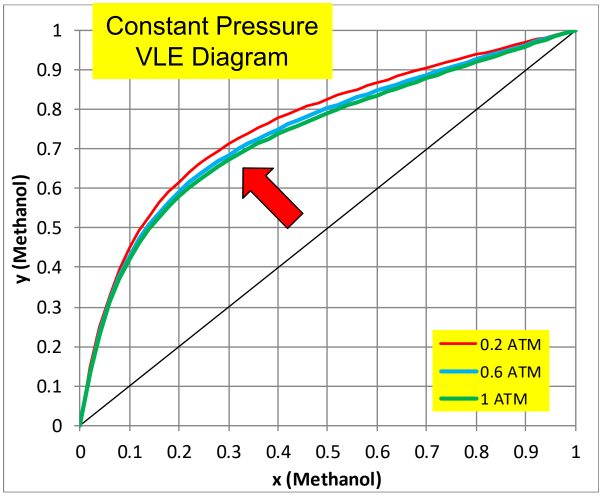
	Latent Heat of Vaporization @ Normal Boiling Point (kcal/mol)
Methanol	8.3932
Water	9.7479

Latent heat of vaporization: "DIPPR Databank"

Methanol-Water System (Activity Coefficient Ratio)

Considering a constant pressure vapor-liquid equilibrium, the activity coefficient ratio (*) is verified for an equimolar liquid phase composition (mole fraction = 0.5) by reducing the pressure starting from the atmospheric pressure (left figure). The lower the pressure, the larger the activity coefficient ratio becomes. From this, it can be seen that the relative volatility increases as pressure decreases thus making separation easier (right figure).





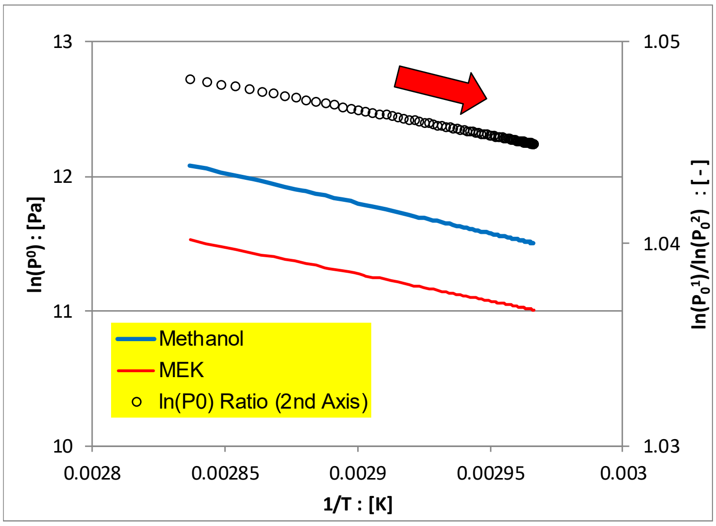
Next, let us consider a system in which the relationship between the boiling points and the latent heats of vaporization is inversed.

Activity coefficient equation: Wilson Equation

Wilson parameters are fitted from VLE data

Methanol-MEK(Methyl-Ethyl-Ketone) System

In a homologous system, the boiling point is proportional to the latent heat of vaporization, but in a heterogeneous system the situation may differ due to the influence of hydrogen bonds and other factors. For instance, consider a methanol / MEK binary system. Methanol is the low boiling point component, but has a greater latent heat of vaporization than MEK. For this reason, the vapor pressure ratio decreases with decreasing pressure (temperature).



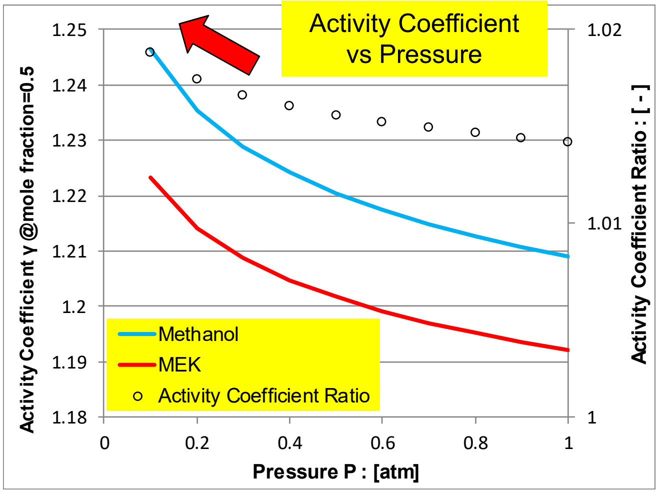
	Latent Heat of Vaporization @ Normal Boiling Point (kcal/mol)	Normal Boiling Point (˚C)
Methanol	8.3932	64.7
MEK	7.5364	79.6

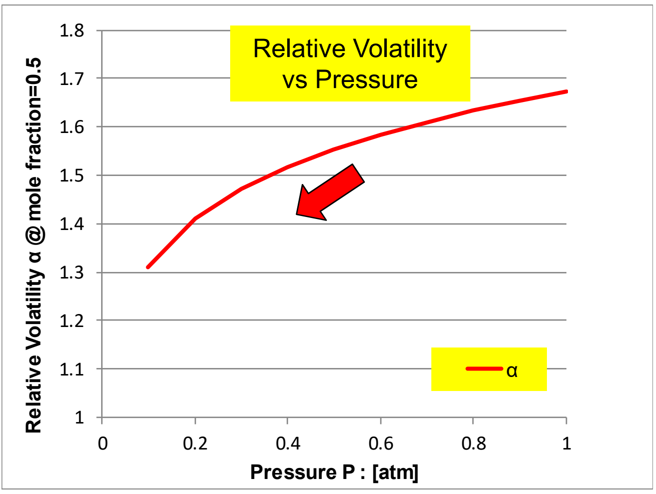
Latent heat of vaporization: "DIPPR Databank"

Methanol-MEK System (Activity Coefficient Ratio)

As in the methanol/water system, considering a constant pressure vapor-liquid equilibrium, the activity coefficient ratio (*) is verified by reducing the pressure starting from the atmospheric pressure (left figure).

The activity coefficient ratio is increased due to pressure decrease, but the vapor pressure ratio shows the opposite trend. As a result, it can be seen that, unlike the other system, the relative volatility decreases as pressure decreases (right figure).



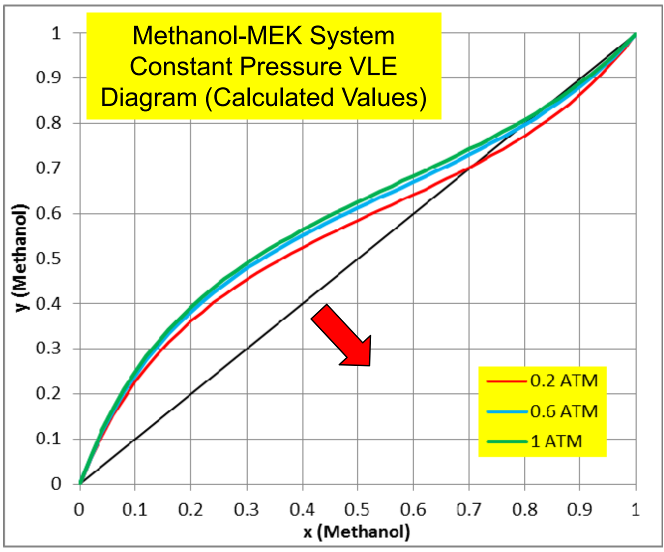


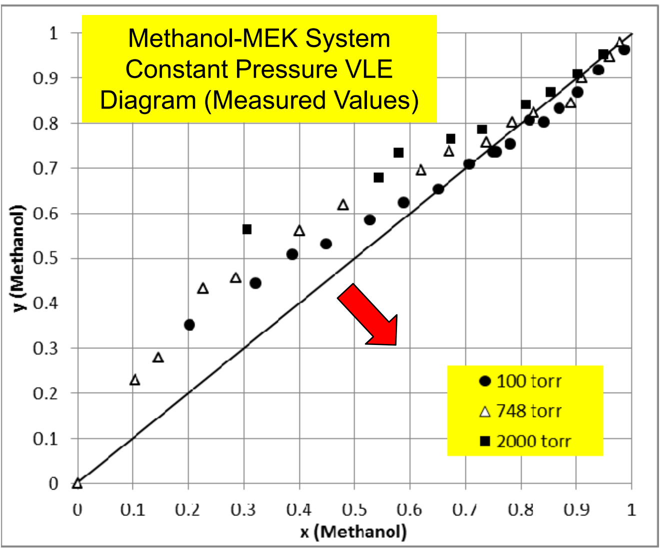
Activity coefficient equation: Wilson Equation

Wilson parameters are fitted from VLE data

Methanol-MEK System (VLE)

The methanol-MEK binary system has a minimum azeotrope, thus it cannot be separated into pure substances by a simple distillation operation. However, it can be seen that the higher the pressure, the better the distillation separation operation will work.

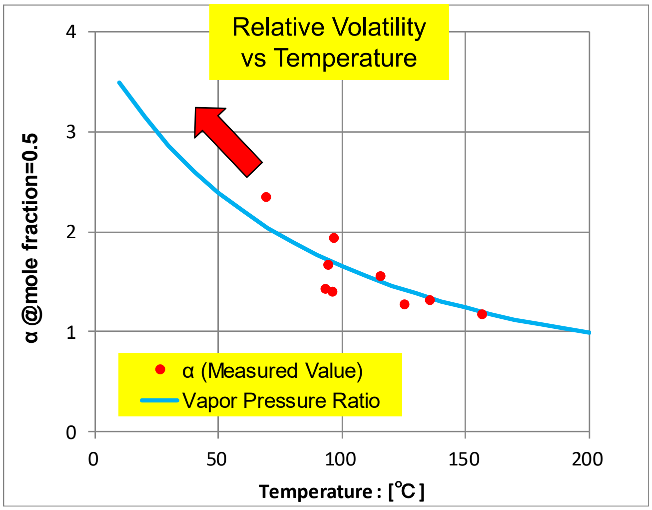


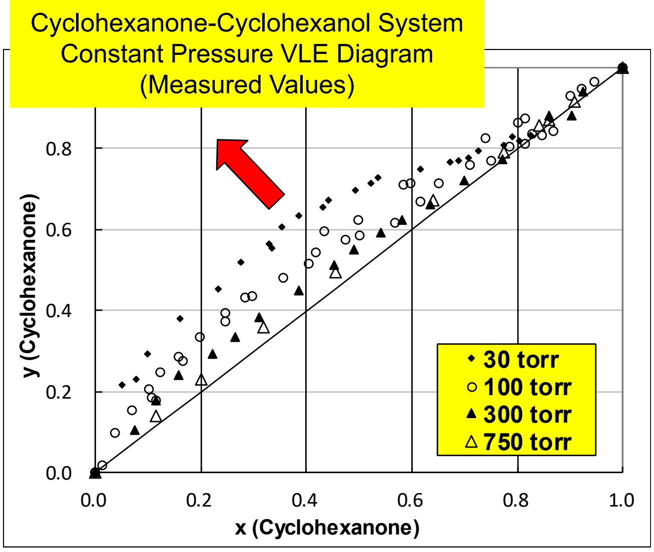


VLE data : Dechema Chemistry Data Series

Industrial Case Study
(Cyclohexanone-Cyclohexanol System)

Typical production methods of caprolactam include the phenol method and method of direct oxidation of cyclohexane. In these processes, cyclohexanone obtained by the oxidation of cyclohexane or cyclohexanol is separated by distillation and used as a raw material for caprolactam production. At this time, since the cyclohexanone / cyclohexanol system has a low relative volatility, a very large number of stages is required for distillation separation at atmospheric pressure. This is why vacuum distillation has been adopted industrially. Sulzer also introduced an example where a packed tower is used to suppress the pressure loss in the column.





Conclusion

- In an ideal solution system, the latent heats of vaporization are proportional to the differences in boiling points (molecular weights). For this reason, in an ideal system, the relative volatility always increases as pressure decreases, making distillation separation easier.
- On the other hand, in the case of a non-ideal solution system, it is not possible to determine as a rule whether distillation separation will be enhanced by decreasing pressure.
- Generally, if there is a proportional relationship between the latent heat of vaporization and the boiling point difference, the relative volatility will tend to increase by decreasing the pressure of the system. However, specific verifications are required for systems with a large change ratio of activity coefficients.