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# On the Responses of Azeotropes to Pressure Variations

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## **Abstract**

Systems with azeotropes cannot be separated by simple distillation since the vapor and liquid compositions are the same. Variation of the applied pressure can shift the azeotropic composition out of the range of purification of a single column or may allow pressure swing operation of two columns. Because of the sensitivity of column size to accurate estimates of the relative volatility, it is important to use reliable phase equilibrium thermodynamics when exploring the possibility of varying pressure to avoid an azeotrope. Based on an analysis of the pressure sensitivity of azeotropic compositions, we show examples of the impact of different modeling strategies for binary and multicomponent mixtures.

## **Keywords**

Azeotropy, distillation, pressure sensitivity.

## **1. Introduction**

Distillation has been the separation method of choice for systems that have coexisting vapor and liquid within the allowable temperature range, because of its simplicity of equipment, robustness of operation, and ease of maintenance. The process is viable as long as the phases have different compositions at equilibrium. Many combinations of substances will form azeotropes in which the vapor and liquid have the same composition, a phenomenon that has been known for at least one and a half centuries [i]. There are two fundamental approaches to eliminating azeotropes: One is to add another component, in extractive and azeotropic distillation, to shift the separability of the components to obtain one stream of desired composition followed by removal and recycle of the added component in another column also producing the other desired product. This can be very effective, but requires addition and separation of a solvent that can have undesirable contamination and cost effects. An alternative is to change the pressure of the distillation column either to conditions for which there is no azeotrope over the range of compositions, or to use two columns at different pressures (pressure swing) where azeotropes of different compositions from the columns are recycled while they also produce streams of the desired products. However, there are limits to the effectiveness of pressure variations because the effect on composition may not be large enough to achieve the desired effect. Important elements of decisions about conceptual process design are commonly based on estimates of properties from thermodynamic models. With azeotropes there is high sensitivity of equipment size and operating costs to the separability of components. Here we analyze and show examples of the responses of azeotrope composition and temperature to variations of pressure that should provide reliable screening about the feasibility of using this approach for overcoming azeotropes. In particular, we address the impact of models and parameter regressions on pressure sensitivity of homogeneous azeotropes of binary and multicomponent mixtures.

## 2. Results and discussion

### 2.1 Theory

The thermodynamics of phase equilibrium shows that for  $P$  phases to exist in a system of  $C$  components with only PV work, the number of independent intensive variables,  $F$ , is given by the Gibbs Phase Rule

$$F = C - P + 2 - S \quad (2.1)$$

Here  $S$  is the number of special constraints on the system. For an azeotrope, the value of  $S$  is  $C - 1$  for equality of vapor and liquid mole fractions of each of the components. Thus, setting the pressure for an azeotrope sets all phase mole fractions and the temperature, a total of  $C$  variables. To find the values of these variables,  $C$  phase equilibrium relations are solved. Commonly these set the fugacity of a component,  $i$ , in the vapor equal to its fugacity in the liquid. Equation (2.2) shows the general form for a system below the critical temperatures of the pure components using the Lewis/Randall standard state:

$$f_i^V(T, P, [y]) = f_i^L(T, P, [x])$$

$$y_i \varphi_i(T, P, [y]) P = x_i \gamma_i(T, [x]) \varphi_i^S(T) P_i^S(T) \exp \left[ \int_{P_i^S}^P \frac{\bar{V}_i(T, p, [x])}{RT} dp \right] \quad (2.2)$$

Here,  $\varphi_i$  is the vapor fugacity coefficient, a function of system temperature, pressure and vapor composition, and is obtained with a selected equation of state model. Also,  $\gamma_i$  is the liquid activity coefficient, a function of system temperature and liquid composition, and is obtained from a selected excess Gibbs energy model. Further,  $\varphi_i^S P_i^S$  is the product of the fugacity coefficient and pressure of the pure saturated vapor, functions only of system temperature. Finally,  $\bar{V}_i(T, p, [x])$  is the partial molar volume of the component in the liquid [iii]. In the treatment below, we assume the pressure is low enough that the fugacity coefficients effectively cancel and the exponential term is unity. Then for an azeotrope at mole fraction,  $z$

$$P = \gamma_i(T, [z]) P_i^S(T) \quad (2.3)$$

The analysis of Rowlinson and Swinton [ii] for the pressure derivatives of temperature and composition, directly shows the pressure sensitivity of the temperature and the azeotropic composition,  $z_1$ , in a binary mixture:

$$\frac{dT}{dP} = \frac{\sum_{j=1}^2 z_j \Delta \bar{V}_j}{\sum_{j=1}^2 z_j \Delta \bar{S}_j}, \quad \frac{dz_1}{dP} = \frac{\Delta \bar{V}_1 \Delta \bar{S}_2 - \Delta \bar{V}_2 \Delta \bar{S}_1}{(\partial^2 \Delta g / \partial z_1^2) \sum_{j=1}^2 z_j \Delta \bar{S}_j} \quad (2.4)$$

Here,  $\Delta$  denotes the property difference between the vapor and the liquid phases. Note that the properties in Eq. (2.4) are derivatives of the property models. For the 10 systems we have examined here, the range of  $dz_1/dP$  is from -0.08 to 0.2. Consistent with the approximations of Eq. (2.3), the pressure derivative of the composition can also be expressed

$$\frac{dz_1}{dP} = -\frac{1}{P} \frac{1}{\text{Det}(\mathbf{J}_p)} \left[ \left( \overline{H}_1^E - \overline{H}_2^E \right) + \left( \Delta h_1^{lv} - \Delta h_2^{lv} \right) \right] \quad (2.5)$$

$$\text{Det}(\mathbf{J}_p) = \frac{1}{1-z_1} \left. \frac{\partial \ln \gamma_1}{\partial z_1} \right|_T \times \left[ z_1 \overline{H}_1^E + (1-z_1) \overline{H}_2^E + z_1 \Delta h_1^{lv} + (1-z_1) \Delta h_2^{lv} \right]$$

This is the binary result of a general multicomponent mathematical development. The ternary azeotrope relation for the same approximations is

$$\frac{dz_1}{dP} = \frac{1}{P \cdot \text{det}(\mathbf{J}_p)} \left\{ \begin{aligned} & \left[ \left( \overline{H}_1^E - \overline{H}_2^E \right) + \left( \Delta h_1^{lv} - \Delta h_2^{lv} \right) \right] \left. \frac{\partial \ln \gamma_3}{\partial z_2} \right|_{T, z_1} + \left[ \left( \overline{H}_2^E - \overline{H}_3^E \right) + \left( \Delta h_2^{lv} - \Delta h_3^{lv} \right) \right] \left. \frac{\partial \ln \gamma_1}{\partial z_2} \right|_{T, z_1} \\ & + \left[ \left( \overline{H}_3^E - \overline{H}_1^E \right) + \left( \Delta h_3^{lv} - \Delta h_1^{lv} \right) \right] \left. \frac{\partial \ln \gamma_2}{\partial z_2} \right|_{T, z_1} \end{aligned} \right\} \quad (2.6)$$

Here

$$\text{Det}(\mathbf{J}_p) = \frac{1}{z_3} \left[ \begin{array}{cc} \left. \frac{\partial \ln \gamma_1}{\partial z_1} \right|_{T, z_2} & \left. \frac{\partial \ln \gamma_2}{\partial z_2} \right|_{T, z_1} \\ - \left. \frac{\partial \ln \gamma_1}{\partial z_2} \right|_{T, z_1} & \left. \frac{\partial \ln \gamma_2}{\partial z_1} \right|_{T, z_2} \end{array} \right] \quad (2.7)$$

$$\times \left[ z_1 \left( \overline{H}_1^E + \Delta h_1^{lv} \right) + z_2 \left( \overline{H}_2^E + \Delta h_2^{lv} \right) + z_3 \left( \overline{H}_3^E + \Delta h_3^{lv} \right) \right]$$

Thus, for both binary and multicomponent systems, the principal effect on pressure sensitivity of the azeotropic composition is a difference of non-ideality terms plus a difference of pure component enthalpies of vaporization. Enthalpies of vaporization are much greater than the non-ideality terms, but often similar in magnitude. For example, Trouton's rule gives a universal value at the normal boiling point,  $T_b$ , of  $\Delta h^{lv} / RT_b = 10$ . Table 1 shows some substances without hydrogen bonding within the range from 10.2 to 10.6; those with hydrogen bonding range from 12.5 to 13.2. Out of the 220 substances tabulated by Poling et al. [iii], boiling between 300 and 460 K, less than ¼ deviate from the average over 10%. Table 1 also shows the liquid molar volumes and Antoine vapor pressure model parameters used in calculations below. As we will show, the term for the non-ideality difference can be greater than the term for the pure component difference in Eqs. (2.5) and (2.6). Thus, the reliability of computed pressure sensitivity may in some cases be determined by the reliability of the temperature dependence of the selected excess Gibbs energy model.

## 2.2 Method of analysis

To illustrate the effects of different systems and excess Gibbs energy models, we choose binary systems for which ternary azeotrope pressure data exist. We show that there can be an impact of non-ideality from fitting the model parameters to only vapor-liquid equilibrium data or to a combination of VLE data for activity coefficients and heats of mixing data for  $h^E$  as well as when the parameters are considered temperature independent as well as linearly dependent. An indication of the non-ideality term will be the excess Gibbs energy at equimolar composition, while an indication of the pure component vaporization enthalpy difference is found from the last column of Table 1. We also compare the resulting pressure dependencies with results from smoothing the azeotrope composition variation with pressure with polynomial fitting of azeotropic data [iv] directly.

Substance	$V, \text{m}^3 \text{kmol}^{-1}$	$T_b, \text{K}$	$A^*$	$B^*$	$C^*$	$\Delta h^{\text{lv}}, \text{kJ mol}^{-1}$	$\Delta h^{\text{lv}}/RT_b$
acetone	0.0738	329.22	4.42448	1312.253	-32.445	29.1	10.6
chloroform	0.0805	334.33	4.56992	1486.455	-8.612	29.2	10.5
n-hexane	0.131	341.88	4.00266	1171.530	-48.784	28.9	10.2
methanol	0.0406	337.69	5.20409	1581.341	-33.500	35.2	12.5
ethanol	0.0586	351.80	5.24677	1598.673	-46.424	38.6	13.2
water	0.0181	373.15	4.65430	1435.264	-64.848	40.7	13.1

\*A,B,C: Antoine Constants for the form:  $\log_{10}(P^{\text{S}}) = A - (B / (T + C))$ ;  $P^{\text{S}}$ , bar;  $T$ , K

## 2.3 Results

### 2.3.1 Binary Systems

The Wilson model parameters have been fitted to VLE data only and VLE plus heats of mixing data [v] for several binary systems.

$$\ln \gamma_i = 1 - \ln e_i - \sum_k \Lambda_{ki} \frac{x_k}{e_k}, \quad e_i = \sum_k x_k \Lambda_{ik}, \quad \Lambda_{mn} = \frac{V_n}{V_m} e^{-\frac{A_{mn} + B_{mn}(T - T_0)}{T}} \quad (2.8)$$

Here  $T_0 = 273.15 \text{ K}$  [vi]. We have used the liquid volumes and Antoine constants in Table 1. We have treated ternary systems with the NRTL model, in addition (see below). Table 2 lists the excess Gibbs energy at midpoint composition, to indicate the non-ideality of the system, and the derivative,  $dz_1/dP$ , evaluated at 1 atmosphere for ethanol(1)/water(2) from the Wilson model with constant (all  $B_{ij} = 0$ ) and linearly dependent parameters ( $B_{ij} \neq 0$ ). Also given is a ‘‘Smoothed’’ result from differentiation of a function which described well, measured  $(z_1, P)$  data [iv]. Scatter in the data limits the number of reliable significant figures, but the signs and orders of magnitude should be reliable. Because the  $\Delta h^{\text{lv}}/RT_b$  values are very similar for water and ethanol, the pure component terms are comparable to the non-ideality terms. Depending upon the data included, we find pressure sensitivities can even differ in sign, so temperature dependence of the parameters makes significant difference. Consistent with this, Gmehling and Kolbe [vii] concluded that the Wilson model (only fitted to VLE data) produces erroneous pressure dependence of the azeotropic composition for this system. Addition of heats of mixing improves the predicted pressure sensitivity, however.

Data Included	$A_{12}$	$A_{21}$	$B_{12}$	$B_{21}$	$g^{\text{E}}/RT (x_1 = 0.5)$	$dz_1/dP (\text{bar}^{-1})$
VLE [viii]	289.6	471.9	0	0	0.32 (352.5 K)	0.04
VLE [viii]+ $h^{\text{E}}$ [v]	-7.33	424.7	3.0	0.76	0.32 (352.5 K)	-0.01
Smoothed [iv]:						-0.03

Data Included	$A_{12}$	$A_{21}$	$B_{12}$	$B_{21}$	$g^{\text{E}}/RT (x_1 = 0.5)$	$dz_1/dP (\text{bar}^{-1})$
VLE [ix]	-164.0	763.2	0	0	0.24 (335 K)	-0.08
VLE [ix]+ $h^{\text{E}}$ [x]	-206.5	964.4	0.94	-4.2	0.24 (335 K)	-0.08
Smoothed [iv]:						-0.05

Table 3 shows results for chloroform(1)/ethanol(2) with VLE and VLE plus  $h^{\text{E}}$  data fitted to the Wilson model. In Table 3, however, the same pressure sensitivity is

found regardless of the data and temperature dependence of the parameters because the pure component difference term is much larger than the non-ideality difference. Table 4 shows results resembling the ethanol/water system for chloroform(1)/n-hexane(2). Meanwhile, Table 5 shows that although n-hexane/ethanol is much more non-ideal than chloroform/ethanol, the pure component vaporization enthalpies differ substantially, and so their azeotropic pressure sensitivities are independent of liquid non-ideality. In a similar fashion NRTL ( $\alpha = 0.3$  in all cases) parameters have been determined from regressing binary data for the three pairs of the and acetone(1)/chloroform(2)/n-hexane(3) systems [xi], using VLE with and without  $h^E$  data. For brevity we do not give the equation and parameters; they can be obtained from the authors upon request. Table 6 gives the pressure sensitivities. The pressure sensitivities chloroform/hexane are very similar, but not exactly the same as those from the Wilson model given in Tables 4-5.

Data Included	$A_{12}$	$A_{21}$	$B_{12}$	$B_{21}$	$g^E/RT (x_1 = 0.5)$	$dz_1/dP (bar^{-1})$
VLE [xii]	112.9	66.8	0	0	0.10 (334.5 K)	0.001
VLE [xii] + $h^E$ [xiii]	116.6	77.5	0.40	-0.86	0.10 (334.6 K)	0.01
					Smoothed [iv]:	0.03

Data Included	$A_{12}$	$A_{21}$	$B_{12}$	$B_{21}$	$g^E/RT (x_1 = 0.5)$	$dz_1/dP (bar^{-1})$
VLE [xiv]	149.4	1082.1	0	0	0.53 (332.0 K)	-0.08
VLE [xiv] + $h^E$ [xv]	181.9	1140.2	-0.41	-1.3	0.53 (332.0 K)	-0.08
					Smoothed [iv]:	-0.07

	Acetone	Chloroform	n-hexane
Acetone		-0.07(-0.03)*	0.006(0.01)*
Chloroform	-0.04(-0.03) <sup>+</sup>		-0.01(0.03)*
n-hexane	0.018(0.01) <sup>+</sup>	0.012(0.03) <sup>+</sup>	

\*Temperature independent parameters (all  $B_{ij} = 0$ ) (Smoothed Value [iv])

<sup>+</sup>Linearly dependent on  $T (B_{ij} \neq 0)$  (Smoothed Value [iv])

### 2.3.2 Ternary Systems

We now examine ternary systems composed of the substances considered above: ethanol(1)/chloroform(2)/n-hexane(3) [iv] {System I}, and acetone(1)/chloroform(2)/n-hexane(3) [iv] {System II}. We want to test whether the binary parameters can describe the ternary azeotrope compositions and their variation with pressure as well as whether the apparent pattern of sensitivity to the parameter dependence on temperature and data regressed would be maintained. Table 7 shows the variations for System I where there are 3 data points over the pressure range from 0.53 to 1.01 bar, while Table 8 shows results for System II where there are 6 data for pressures from 0.27 to 1.01 bar. First it can be seen that the calculated azeotrope compositions are close to experiment for System I and for System II (though less), with little difference between the parameter sets. Second, both constant and linearly dependent parameters describe the azeotrope composition dependence on pressure of System I, as well as for its binaries. The linearly dependent parameter set describes the pressure sensitivity of System II somewhat better. This is consistent



with the pattern described above for binaries because the components of System II all have similar  $\Delta h^v$  values whereas those of System I are significantly different.

Parameters	Ethanol (1)		Chloroform (2)	
	$z_1$	$dz_1/dP$	$z_2$	$dz_2/dP$
Constant	0.42 (0.44)	-0.2 (-0.2)	0.370 (0.358)	0.066 (0.08)
Linear in $T$	0.42 (0.44)	-0.2 (-0.2)	0.367 (0.358)	0.068 (0.08)

Parameters	Acetone (1)		Chloroform (2)	
	$z_1$	$dz_1/dP$	$z_2$	$dz_2/dP$
Constant	0.0358(0.065)	-0.014 (-0.01)	0.695 (0.60)	0.054(0.1)
Linear in $T$	0.0347(0.065)	-0.003 (-0.01)	0.688 (0.60)	0.066(0.1)

### 3. Conclusions

In determining the variation of azeotropic composition with pressure, we have shown that if enthalpies of vaporization of the components forming a binary or ternary azeotrope are similar, e.g., all hydrogen-bonding, care must be taken in regressing the parameters of the applied excess Gibbs energy model since the calculated pressure sensitivity of these cases depends on the accuracy of predicting the temperature dependence of activity coefficients. In particular, heat of mixing data should be included and temperature-dependent parameters should be used in these cases. However, if one or more of the components in a binary or ternary azeotropic system have significantly different enthalpy of vaporization, e.g., nonpolar with hydrogen bonding, the sensitivity of the estimate to the  $g^E$  model is much less, and prediction of composition dependence is adequate, regardless of the  $g^E$  model and parameterization. Though the testing of these conclusions as presented here is limited, we believe they are correct for all systems.

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