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Responses of azeotropes and relative volatilities to pressure variations

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ABSTRACT

Mixtures with azeotropes cannot be separated by simple distillation since the vapor and liquid compositions are the same. One option to overcome this limitation is to vary the applied pressure to shift the azeotropic composition out of the range of a single column or use pressure-swing operation of two columns. Because operating costs are highly sensitive to the pressure dependence of azeotropic compositions, reliable and accurate phase equilibrium thermodynamic property information is needed to computationally explore pressure variation for such processes. An analysis of property modeling has been done for the pressure sensitivity of azeotropic composition, and examples are given of modeling strategies for binary and ternary mixtures. A quantitative criterion for the need to consider nonideality effects in both modeling and parameter regression has been established, based on similarity of mixture excess enthalpies and pure component enthalpies of vaporization.

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1. Introduction

Many combinations of fluid substances form azeotropes in which the vapor and liquid have the same composition at equilibrium, a phenomenon that has been known for at least one and a half centuries (Lewis, 1928). Extensive experimental data collections exist (Gmehling et al., 1994), and new measurements of azeotropic data continue to appear (Ortega and Susial, 1991; Galvan et al., 1994; Susial et al., 2010). Phase diagrams of azeotropes are found in many texts (Rowlinson and Swinton, 1982), with an emphasis on ternary mixtures in more recent papers (Hilmen et al., 2002; Kiva et al., 2003). Options for separations of azeotropic mixtures are also widely available (Seader and Henley, 1998).

1.1. Azeotropy and relative volatilities in separations

Distillation has long 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 over the whole column, which is assured when there is no azeotrope condition for any equilibrium composition at the column pressure. There are several approaches for separating azeotropic mixtures by distillation (Knapp and Doherty, 1992). One involves adding another component, as in extractive and azeotropic distillation and salting by shifting the separability of the components. In such cases, additional separation must be done to remove the added component for recycling. This can be very effective, but requires addition and separation of a solvent, perhaps leading to undesirable contamination and excessive costs. An alternative is to change the pressure, either to conditions for which there is no azeotrope over the range of compositions of a single column, or to use two columns at different pressures (pressure-swing) where the product streams are desired compositions and azeotropes of different compositions that are recycled. Fig. 1 shows one

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Nomenclature

A	Porter equation parameter in Eq. (3.2)
a, b, c	Antoine equation coefficients (singly subscripted) in Table 2
A, B	Wilson/NRTL parameters (doubly subscripted) in Eq. (2.10)
B, D, F	streams in Fig. 1 (singly subscripted)
C	number of components
C_{ij}	matrix of cofactors (C^T represents the matrix transpose).
Det	determinant
e	sum in the Wilson equation in Eq. (2.10)
F	feed stream in Fig. 1
f	fugacity
g	Gibbs free energy
h	enthalpy
J	Jacobian matrix and its elements
K	K-factor as in Eq. (2.16)
M_{ij}	matrix of minors
N	number of special constraints on the system
P	pressure
R	universal gas constant
s	entropy
T	temperature (Kelvin)
v	volume (singly subscripted)
x_i	(liquid) mole fraction, species i
y_i	(vapor) mole fraction, species i
z	composition (azeotropic)

Greek letters

α	NRTL parameter or relative volatility (doubly subscripted)
Γ	degrees of freedom (Phase rule) in (2.1)
π	number of phases
γ_i	activity coefficient, species i
φ_i	fugacity coefficient, species i
Λ_{nj}	Wilson equation matrix in Eq. (2.10)

Subscripts

b	boiling point
i	component i

Sub/Superscripts

E	excess
S	saturation
L	liquid phase
V	vapor phase
-	(overbar) partial molar property

Abbreviations

AAPE	Average Absolute Percent Error
NRTL	Non-Random Two Liquid
VLE	Vapor-Liquid Equilibrium
LLE	Liquid-Liquid Equilibrium
VLE	Vapor-Liquid-Liquid Equilibrium

configuration of pressure-swing distillation where the overhead streams are sent to the other column and the bottoms are the purified products. Column 1 (C1) may operate at a low pressure, while column 2 (C2) may be at a higher pressure, but the reverse situation can also occur.

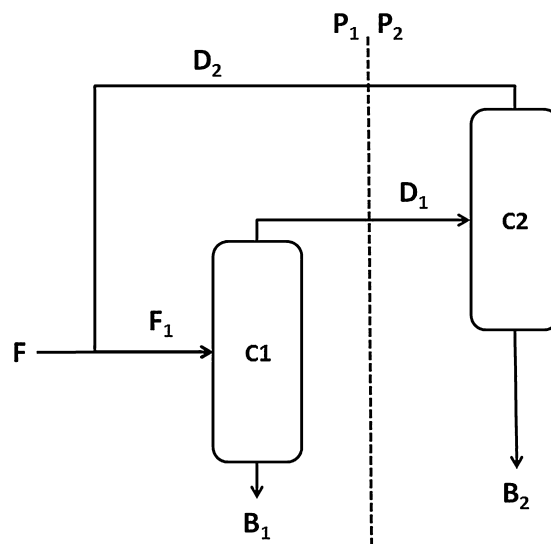


Fig. 1 – Example pressure swing distillation flowsheet. P_1 and P_2 are column pressures on either side of the dashed line. Columns are denoted C1 and C2, respectively. F, F_1 , D_1 , D_2 , B_1 and B_2 denote streams.

However, there are limits to the effectiveness of pressure variations because the pressure effect on composition may not be large enough to achieve the desired effect, including causing the recycle streams D_1 and D_2 in Fig. 1 to become very large. Li et al. (2007) discuss both a design structure and a criterion for the feasibility of pressure-swing distillation. These must be based on estimates of properties from accurate thermodynamic models because of sensitivity of the results to small errors and limited data. Here we analyze and show examples of azeotrope composition and temperature responses to variations of pressure. They elucidate some unrealized, but important, features of thermodynamic analyses of pressure-swing distillation systems.

In particular, we address how different models and parameter regressions affect pressure responses of binary and ternary mixture azeotropes, especially through the relative volatility. In addition to conceptual design considerations, the results of this work connect to control strategy selection (Li et al., 2006; Mauricio-Iglesias et al., 2014). In most distillation columns pressure at the top of the column is controlled. This choice makes sense since controlled and manipulated variables should be closely situated to minimize dynamic effects. However, Li et al. (2006) indicate that controlling the bottom pressure could be preferable when the relative volatility decreases with pressure. If the top pressure is controlled, together with the top and bottom concentration, a disturbance decreasing the top or bottom purity will typically be rejected by increasing the internal flow via greater reflux. This action will increase pressure drops across the trays and the average pressure in the column will increase. This would be preferable if the relative volatility increases with pressure. On the other hand, if the bottom pressure is controlled and kept constant, an increase of the pressure drop across the trays would lead to a decrease of average pressure, which is preferable if the relative volatility decreases with pressure. The effect is more pronounced in case of high purity operations. Thus, distillation control systems can be determined by the sign on the pressure variation of the relative volatility.

Here we analyze model predictions of the pressure dependence of azeotropic compositions and relative volatilities.

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