# Modeling of Phase and Chemical Equilibrium on the Quaternary System Acetic Acid, n-Butanol, Water and n-Butylacetate

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# Modeling of Phase and Chemical Equilibrium on the Quaternary System Acetic Acid, n-Butanol, Water and n-Butylacetate[*]

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### Abstract

The correlation of the data for phase and chemical equilibrium in acetic acid-n-butanol-water-n-butylacetate is presented. The azeotropic properties, the topological structure and the existence of a reactive azeotrope are discussed. The data are correlated by Hayden-O'Connell second virial coefficients and NRTL. Chemical equilibrium constant has a strong influence on the reactive azeotrope.

**KEYWORDS:** phase equilibrium, chemical equilibrium, esterification, reactive distillation

## 1. INTRODUCTION

Reactive distillation has received increasing attention in the last decade. The combination of certain types of reactions and separation in a process unit brings important advantages such as overcoming azeotropes, increasing reaction yield, and reducing energy and capital costs. The most important among those reactions are those whose maximum conversion is limited by chemical equilibrium. The esterification reaction of n-butylacetate is an example of such reactions. Modeling of reactive distillation for a reliable process engineering design is quite complex, as it involves multicomponent phase equilibria and chemical reaction. Thus, in order to achieve the process simulation required for design, experimental data and thermodynamic modeling of the reactive vapor - liquid equilibrium of the quaternary acetic acid (1), n-butanol (2), water (3), n-butylacetate (4) are necessary.

The synthesis of n-butylacetate through esterification has been studied for several years (Leyes and Othmer, 1945, Al-Saadi and Jeffreys, 1981a, 1981b, 1981c, Löning et al., 2000, Grob and Hasse, 2005, Venimadhavan et al., 1999, Gumus and Ciric, 1997, Zhicai et al., 1998, Hanika et al., 1999, Smejkal and Šoóš, 2002, Steinigeweg and Gmehling, 2002, Gangadwala et al., 2003, Gangadwala et al., 2004, Singh et al., 2005, Liu et al., 2005). Some articles investigated the kinetics (Leyes and Othmer, Al-Saadi and Jeffreys, 1981b, Steinigeweg and Gmehling, Gangadwala et al., 2003) and others covered the phase and chemical equilibria (Al-Saadi and Jeffreys, 1981a, Löning et al., Grob and Hasse, Campanella and Mandagarán, 2003). In recent years several articles studied batch production (Venimadhavan et al.), continuous design (Gumus and Ciric, Zhicai et al., Gangadwala et al., 2004), computer simulation (Hanika et al., Smejkal and Šoóš), pilot plant experiments (Steinigeweg and Gmehling), catalytic distillation (Gangadwala et al., 2003, Singh et al.) and hybrid processes (Liu et al.).

To correlate the vapor - liquid equilibrium in mixtures containing an associating component like acetic acid the Hayden-O'Connell (1975) second virial coefficients in combination with liquid activity coefficient models is usually applied (Mandagarán and Campanella, 2006). In this study the NRTL model (Renon and Prausnitz, 1975) was used in combination with the Hayden-O'Connell second virial coefficient model for predicting the phase equilibrium behavior of the quaternary system containing acetic acid, n-butanol, water and n-butylacetate. The main objective of this work is to check the existence of a reactive azeotrope. In this article we introduce the conditions for the existence of reactive azeotropes in the mixture and study the formation of such azeotropes with different activity coefficient parameters and chemical equilibrium constants.

## 2. PHASE EQUILIBRIA WITH CHEMICAL EQUILIBRIUM

The temperature, pressure, and composition of liquid and vapor in equilibrium are calculated by simultaneous solution of the equations describing phase and chemical equilibrium. For a vapor phase (superscript V) and a liquid phase (superscript L), at the same temperature and pressure, the equilibrium relationship for component i is expressed in terms of fugacity, $f_i$ :

$$f_i^V = f_i^L \qquad\qquad i = 1,2,3,4 \qquad\qquad (1)$$

Using the fugacity coefficient, $\Phi_i$ , and the activity coefficient, $\gamma_i$ , eq. 1 can be rewritten as :

$$\Phi_i \, y_i \, P = \gamma_i \, x_i \, f_i^0 \qquad\qquad i = 1,2,3,4 \qquad\qquad (2)$$

where $f_i^0$ is the standard state fugacity.

In the case of liquid phase in equilibrium with other liquid phase, eqs. 1 and 2 take the following form:

$$f_i^{L'} = f_i^{L''} \qquad\qquad i = 1,2,3,4 \qquad\qquad (3)$$

and

$$\gamma_i' \, x_i' = \gamma_i'' \, x_i'' \qquad\qquad i = 1,2,3,4 \qquad\qquad (4)$$

And when two liquid phases are in equilibrium with a vapor phase, eq. 1 is:

$$f_i^{L'} = f_i^{L''} = f_i^V \qquad\qquad i = 1,2,3,4 \qquad\qquad (5)$$

The equilibrium constant for the esterification reaction in the liquid phase is defined by:

$$K_a = \prod_i (x_i \, \gamma_i)^{\nu_i} = \prod_i x_i^{\nu_i} \prod_i \gamma_i^{\nu_i} = K_x \, K_\gamma \qquad i = 1,2,3,4 \qquad\qquad (6)$$

with

$$K_a = \exp(-\Delta G^0 / RT) \qquad\qquad (7)$$

where

$$\Delta G^0 = \sum_i \nu_i \, G_i^0 \qquad\qquad i = 1,2,3,4 \qquad\qquad (8)$$

Ung and Doherty (1995) introduced a set of transformed composition variables $(X_i, Y_i)$. The transformed compositions represent the overall compositions of the independent components in each phase (liquid and vapor) and account for the total amount of these chemical species present in any chemical combination, whether it is in the form of a product or of a reactant. This coordinate system captures a special projection of the phase diagram along lines of constant overall composition of the independent components. The transformed compositions have the properties that they sum to unity, and have the same dimensionality as the number of composition degrees of freedom in an isobaric (or isothermal) reactive system. For a quaternary system with one reaction, the system is two-dimensional, there are three transformed compositions that sum to unity and only two of them are independent variables. The conditions for reactive azeotropy take the same functional form in terms of transformed compositions as the conditions for azeotropy for nonreactive mixtures in terms of mole fractions. Then, for a single chemical reaction in a four component system, we can define three transformed compositions in each phase:

$$X_i = (\nu_k\, x_i - \nu_i\, x_k) / (\nu_k - \nu_T\, x_k) \qquad\qquad i = 1,2,3,\text{or } 4 \quad i \neq k \qquad (9)$$

$$Y_i = (\nu_k\, y_i - \nu_i\, y_k) / (\nu_k - \nu_T\, y_k) \qquad\qquad i = 1,2,3,\text{or } 4 \quad i \neq k \qquad (10)$$

with

$$\nu_T = \textstyle\sum_i \nu_i \qquad (11)$$

The subscript k represents a reference component, corresponding to n-butylacetate in the present work. As seen from eqs. 9 and 10 transformed compositions could be negative or larger than one. However, they sum to unity. For the quaternary acetic acid (1), n-butanol (2), water (3), n-butylacetate (4) system the transformed composition variables taking n-butylacetate as the reference component and using eq. 9 are:

$$X_1 = x_1 + x_4 \qquad (12)$$

$$X_2 = x_2 + x_4 \qquad (13)$$

$$X_3 = x_3 - x_4 \qquad (14)$$

The same relations are obtained for the vapor phase using eq. 10. Two summations rules for these new composition variable should be satisfied:

$$X_1 + X_2 + X_3 = 1 \tag{15}$$

$$Y_1 + Y_2 + Y_3 = 1 \tag{16}$$

By using the transformed composition variables the condition for a reactive azeotrope can be expressed as:

$$X_i = Y_i \tag{17}$$

In the case of an heterogeneous reactive azeotrope the conditions are (Okasinski and Doherty, 2000):

$$Y_i = \alpha \, [(\nu_k - \nu_T \, x'_k) / (\nu_k - \nu_T \, x^T_k)] \, X'_i + (1 - \alpha) \, [(\nu_k - \nu_T \, x''_k) / (\nu_k - \nu_T \, x^T_k)] \, X''_i = X^T_i$$

$$i = 1,2,3, \text{or } 4 \quad i \neq k \tag{18}$$

where

$$\alpha = (L' / L^T), \quad (1 - \alpha) = (L'' / L^T), \quad L^T = L' + L'',$$

$$x^T_i = \alpha \, x'_i + (1 - \alpha) \, x''_i \tag{19}$$

The fugacity coefficients and the standard state fugacities as well as the necessary parameters and constants (vapor pressures, for example) needed to solve both phase and chemical equilibrium equations were calculated with the Virial equation of state and the Poynting correction using HYSYS (Hyprotech software) and DISTIL (AEA software). To calculate activity coefficients we used NRTL (Renon and Prausnitz).

## 3. RESULTS AND DISCUSSION

Calculations done to correlate the quaternary reactive phase equilibrium involved binary parameter estimation. As already mentioned we did calculations with DISTIL and HYSYS. The nonreactive azeotropes, phase equilibria, residue curve map and binary parameter were calculated with DISTIL. The reactive azeotrope was calculated with HYSYS, the azeotrope was found optimizing a reactive separator tank by changing its feed as it is shown in Appendix A. Reactive distillation lines were calculated using programs writing in the Macro Language Editor of HYSYS. For all of the reactive phase equilibrium calculations, we used the transformed coordinates of eqs. 9 and 10 to represent mixture compositions. The stability scheme used to test stability is that proposed by Michelsen (1982).

Table 1 lists the NRTL binary parameters and the sources of data used to find the parameters. The table also shows normal boiling points, vapor pressure information and virial association parameters for the acetic acid-n-butanol-water-n-butylacetate system. Different initial guesses were tried and a unique set parameter was found.

To obtain the binary parameters the program minimize the objective function:

$$Minimize\ f = \sum_{i=1}^{No\ of\ Po\text{int}\ s} \sigma_i^{\text{mod}\,el} \left( g_i^{\text{mod}\,el}(\bar{x}) - g_i^{\exp\,erimental} \right)$$

where

$g_i$ = the value of the property for the point *i* predicted by the model and actual measured

$\bar{x}$ = the vector of parameters which can be manipulated in the thermodynamic model (usually the $a_{ij}$ for an activity model)

$\sigma_i$ = a weight for a specific point used to distort the data fit in a convenient way

The algorithm used in regression module is the Powell optimization method (Press et al., 1986). For VLE data, the property minimized was the *components' activity coefficient*. It combines the lumping of the error in the liquid phase with a fairly rapid convergence rate. For LLE data, the property minimized was the *separation factor*, that is the quotient between the component molar fraction in the organic rich phase and the component molar fraction in the water rich phase.

In Figures 1, 2, 3 and 4 calculations from the model are compared to VLE data. Figures show that the model is able to correlate well vapor-liquid equilibrium for the four binary systems, including predicting very well the azeotropic behavior of the n-butanol-n-butylacetate and acetic acid-n-butanol systems, as shown in Table 2.

Table 2 displays experimental and calculated azeotropic point comparison. In Figures 5 and 6 calculations from the model are compared to LLE data. Figure 5 shows experimental results and correlation for ternary LLE in the system acetic acid-water-n-butylacetate. The model represents phase envelope and tie lines very well in spite that calculation was done using binary NRTL parameters obtained from VLE data. Figure 6 shows experimental results and correlation for ternary LLE in the system acetic acid-water-n-butanol. The model representation is, in this case, reasonable. NRTL model predictions were also checked against quaternary LLE data, and predictions were only fair. The absolute mean deviation

$(AMD = \dfrac{1}{N} \sum\limits_{i=1}^{N} \left| x_i^{\exp} - x_i^{cal} \right|)$ between the experimental and calculated LLE composition is 1.71 %. Ruiz et al. (1984) report 0.15 % using a different set of parameters.

**Table 1**. Thermodynamic data for the n-butyl acetate system at 101.3 kPa.
Binary parameters from DISTIL

| Component | acetic acid | n-butanol | water | n-butylacetate |
|---|---|---|---|---|
| Normal boiling point /ºC | 117.95 | 117.75 | 100.00 | 126.15 |
| Vapor pressure coefficient [a] | | | | |
| A | 61.3409 | 108.826 | 65.9278 | 103.79 |
| B | -6768.88 | -10069.5 | -7227.53 | -8763.56 |
| C | 0 | 0 | 0 | 0 |
| D | -6.72663 | -13.2566 | -7.17695 | -13.1176 |
| E | 4.84 E-6 | 4.38 E-06 | 4.03E-6 | 8.44 E-06 |
| F | 2 | 2 | 2 | 2 |
| NRTL parameter [a] ($a_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
| i = acetic acid | 0 | 529.722 | 842.608 | 602.592 |
| i = n-butanol | -485.544 [b] | 0 | 2794.666 | 177.124 |
| i = water | -219.724 [c] | 570.1362 [e] | 0 | 859.5686 |
| i = n-butylacetate | -13.813 [d] | 210.456 [f] | 3822.76 [g] | 0 |
| NRTL parameter [a] ($\alpha_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
| i = acetic acid | 0 | 0.304 | 0.300 | 0.300 |
| i = n-butanol | 0.304 | 0 | 0.470 | 0.301 |
| i = water | 0.300 | 0.470 | 0 | 0.292 |
| i = n-butylacetate | 0.300 | 0.301 | 0.292 | 0 |
| Virial coefficient [a] ($\eta_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
| i = acetic acid | 4.5000 | 2.5000 | 2.5000 | 2.0000 |
| i = n-butanol | 2.5000 | 2.2000 | 1.5500 | 1.3000 |
| i = water | 2.5000 | 1.5500 | 1.7000 | 1.3000 |
| i = n-butylacetate | 2.0000 | 1.3000 | 1.3000 | 0.5299 |

a)see Appendix A, $b_{ij} = 0$ for all; b)Rius et al. (1959); c)Sebastiani and Lacquanity (1967); d)Andreeva et al. (1976); e)Boublik (1960); f)Brunjes and Furnas (1935); g)Schuberth (1958).
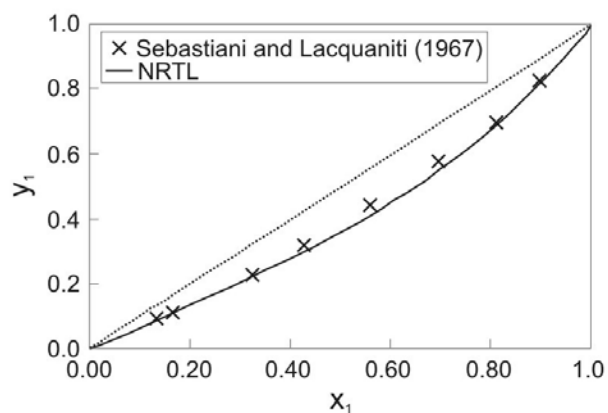
**Fig. 1**. Binary xy diagram in the system acetic acid (1) - water (2) at 101.3 kPa. Binary parameters from Table 1. Experimental data from Sebastiani and Laquaniti.
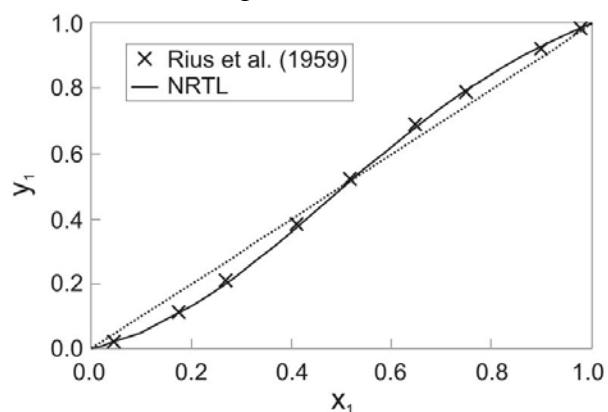


**Fig. 2**. Binary xy diagram in the system acetic acid (1) - n-butanol (2) at 94.1 kPa. Binary parameters from Table 1. Experimental data from Rius et al..
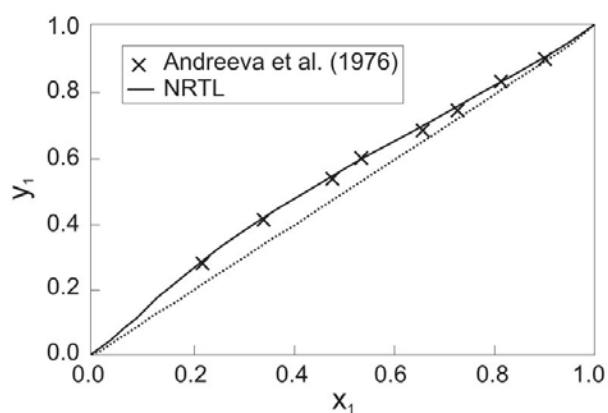


**Fig. 3.** Binary xy diagram in the system acetic acid (1) - n-butylacetate (2) at 101.3 kPa. Binary parameters from Table 1. Experimental data from Andreeva et al.
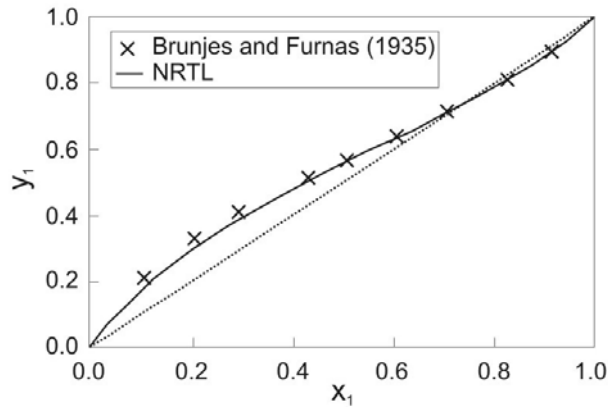
**Fig. 4**. Binary xy diagram in the system n-butanol (1)-n-butylacetate (2) at 101.3 kPa. Binary parameters from Table 1. Experimental data from Brunjes and Furnas.

**Table 2**. Experimental and calculated azeotropic points at 101.3 kPa with data from Table 1

| Azeotrope | Experimental [a] | | Calculated | |
| --- | --- | --- | --- | --- |
| | Range T / °C (type [b]) | Range $x_1, x_2$ | T / °C (type [b]) | $x_1, x_2, x_3$ |
| BuOH(1) - W(2) | 92.25-93.10 (het.) | 0.2360-0.2928 | 93.08 (het.) | 0.2282 |
| W(1) - BA(2) | 90.20-91.04 (het.) | 0.7010-0.7220 | 90.83 (het.) | 0.7144 |
| BuOH(1) - BA(2) | 116.35-117.60 (hom.) | 0.7290-0.7900 | 116.95 (hom.) | 0.7435 |
| AA(1) - BuOH(2) | 122.6 (hom.) | 0.4040 | 123.34 (hom.) | 0.5205 |
| BuOH(1) - W(2) - BA(3) | 89.40-90.60 (het.) | 0.0726-0.1347 0.7034-0.7545 | 90.32 (het.) | 0.0940 0.6986 |
| AA(1) - BuOH(2) - BA(3) | 121.30 [c] (hom.) | 0.4600 0.2000 | 121.32 (hom.) | 0.4205 0.2242 |

a)From Gmehling et al. (1994); b)het. = heterogeneous; hom. = homogeneous; c)From Karpilovski (1997).

Assuming atmospheric pressure as the operating pressure of reactive distillation columns the nonreactive system has four pure components, one minimum-boiling homogeneous binary azeotrope (BuOH - BA), two minimum-boiling heterogeneous binary azeotropes (W - BuOH) and (W - BA), one maximum-boiling homogeneous binary azeotrope (AA - BuOH), one intermediate

-boiling homogeneous ternary azeotrope (BuOH - AA - BA) and one minimum-boiling heterogeneous ternary azeotrope (W - BuOH - BA). All these azeotropic points are presented in Table 2 where experimental and NRTL prediction are compared. The azeotropic points are also marked in Figure 7. The plot shows a few residue curves to indicate the existence of two distillation regions. In one of them, residue curves start at the heterogeneous BuOH - W - BA ternary azeotrope and end at the AA - BuOH binary azeotrope. In the other region, residue curves start at the same ternary azeotrope and end at the pure n-butylacetate.

The chemical equilibrium constant varies over a range of values, 10 to 60, as determined experimentally by several authors. Table 3 summarizes those data. For calculations involving the reactive systems we have used values of chemical equilibrium constants given by the equation of Grob and Hasse.

As calculation shows that the reactive azeotrope is heterogeneous a different set of NRTL binary parameters were determined to better correlate the LLE. The binary parameters $b_{ij}$ and $b_{ji}$ of n-butanol - water and n-butylacetate - water were fitted to the binary LLE. Then the binary parameter $\alpha_{ij}$ ($= \alpha_{ji}$) of n-butanol - water was fitted to LLE data of the ternary acetic acid-n-butanol- water. Figure 6 displays difference between parameters. The new set of NRTL binary parameters that is shown in Table 4 correlate the LLE better with an small loss of accuracy in the representation of VLE.
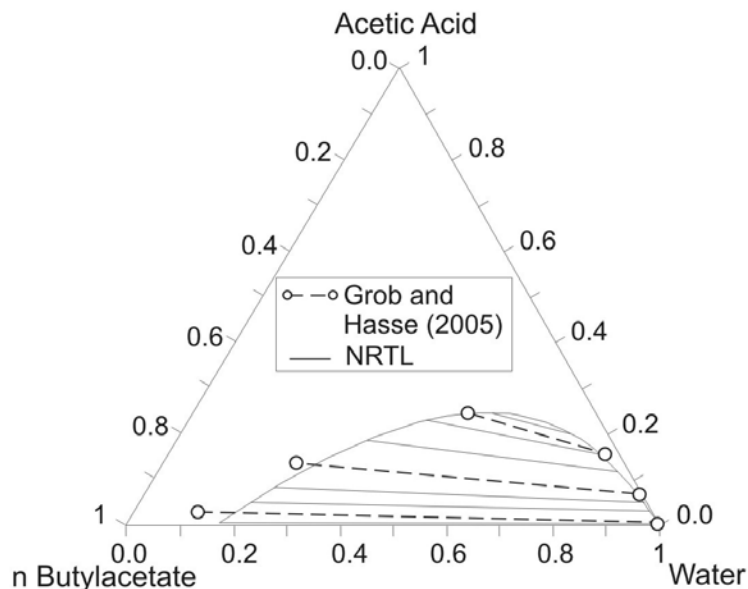


**Fig. 5**. Liquid-liquid equilibria in the system acetic acid (1) - water (2) - n-butylacetate (3) at 80 ºC and 101.3 kPa. Binary parameters from Table 1. Experimental data from Grob and Hasse.
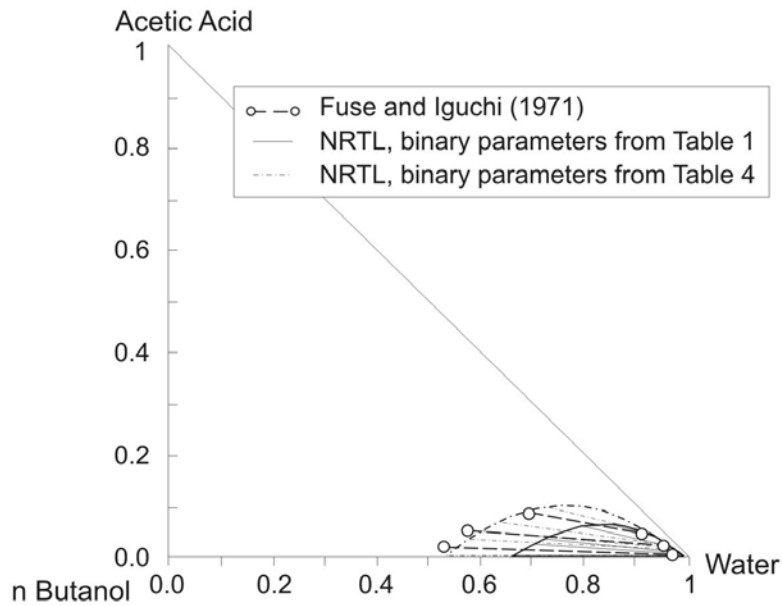
**Fig. 6**. Liquid-liquid equilibria in the system acetic acid (1) - water (2) - n-butanol (3) at 25 ºC and 101.3 kPa. Binary parameters from Tables 1 and 4. Experimental data from Fuse and Iguchi.
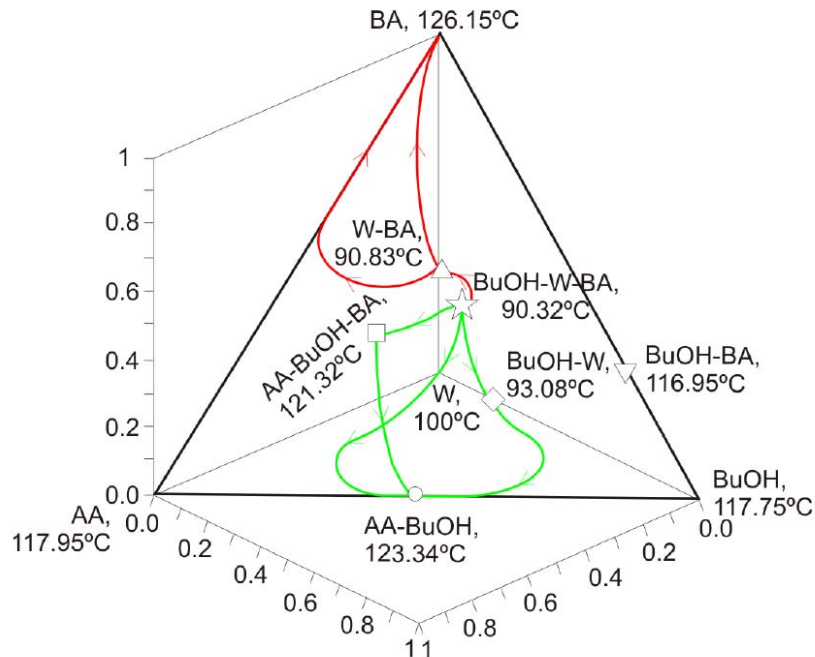


**Fig. 7**. Residue curve map for the n-butyl system at 101.3 kPa. AA: acetic acid, BuOH: n-butanol, BA: n-butylacetate, W: water. Binary parameters from Table 1.

**Table 3**. Chemical equilibrium constant ($K_a$) from literature at 101.3 kPa

| $K_a$ (Range) | T (Range)/$^o$C | Equation | Reference |
|---|---|---|---|
| 12.57 (11.3-15.1) | (100.-120.) | - | Venimadhavan et al. |
| 22.28 | 70. | | |
| 18.81 | 92. | $K_a = \exp(0.2294+962.25/T(K))$ | Löning et al. |
| 12.90 | 153. | | |
| 4.27 | 75. | - | Smejkal and Šoóš |
| (24.-60.) | (80.-120.) | - | Grob and Hasse |
| 32.44 | 70. | | |
| 31.87 | 80. | | |
| 28.02 | 92. | $K_a = 2.841 \exp(835.7/T(K))$ | Grob and Hasse |
| 27.99 | 100. | | |
| 24.92 | 120. | | |
| 20.19 | 153. | | |

**Table 4.** Binary parameters from liquid-liquid equilibria at 101.3 kPa

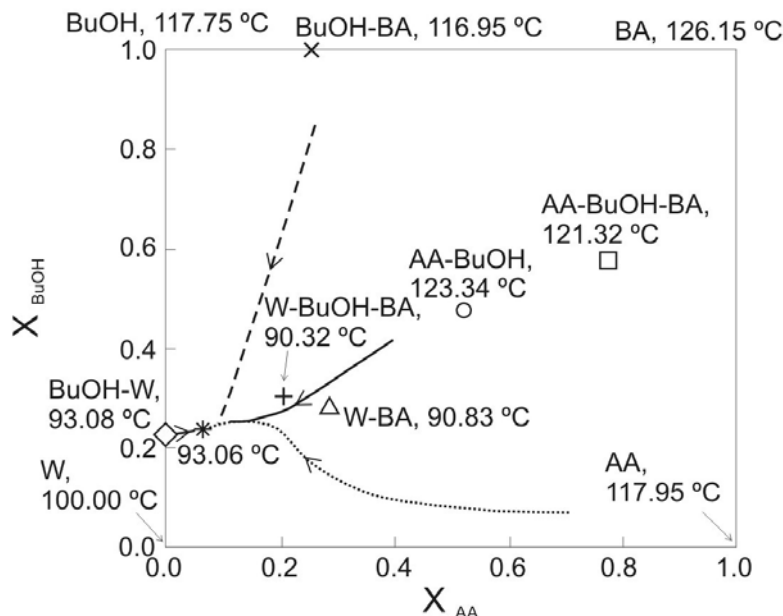| NRTL parameter [a] ($a_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
|---|---|---|---|---|
| i = acetic acid | 0 | 529.722 | 842.608 | 602.592 |
| i = n-butanol | -485.544 | 0 | 2794.666 | 177.124 |
| i = water | -219.724 | 570.1362 | 0 | 859.5686 |
| i = n-butylacetate | -13.813 | 210.456 | 3822.76 | 0 |
| NRTL parameter [a] ($b_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
| i = acetic acid | 0 | 0 | 0 | 0 |
| i = n-butanol | 0 | 0 | -0.49266 | 0 |
| i = water | 0 | -1.32322 | 0 | 0.37071 |
| i = n-butylacetate | 0 | 0 | -1.48552 | 0 |
| NRTL parameter [a] ($\alpha_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
| i = acetic acid | 0 | 0.304 | 0.300 | 0.300 |
| i = n-butanol | 0.304 | 0 | 0.38 | 0.301 |
| i = water | 0.300 | 0.38 | 0 | 0.292 |
| i = n-butylacetate | 0.300 | 0.301 | 0.292 | 0 |
| Virial coefficient [a] ($\eta_{ij}$) | j = acetic acid | j = n-butanol | j = water | j = n-butylacetate |
| i = acetic acid | 4.5000 | 2.5000 | 2.5000 | 2.0000 |
| i = n-butanol | 2.5000 | 2.2000 | 1.5500 | 1.3000 |
| i = water | 2.5000 | 1.5500 | 1.7000 | 1.3000 |
| i = n-butylacetate | 2.0000 | 1.3000 | 1.3000 | 0.5299 |

a)see Appendix A.

**Fig. 8**. Reactive azeotrope from distillation line calculation at 101.3 kPa. AA: acetic acid, BuOH: n-butanol, BA: n-butylacetate, W: water. Binary parameters from Table 1.

Table 5 reports calculations of the reactive azeotrope. The calculations were done with binary parameters from Table 1 (VLE phase data) and from Table 4 (LLE phase data) and for three values of the chemical equilibrium constant. The three values of the chemical equilibrium constant are inside the range of experimental information. Figure 8 displays a distillation diagram in transformed coordinates used to verify reactive azeotrope presence. The calculated reactive azeotrope in this work is consistent with previous calculated reactive azeotrope using UNIQUAC model for the liquid phase (Campanella and Mandagarán, 2003). As seen on Table 5 the value of the chemical equilibrium constant plays an important role in the conditions of the reactive azeotrope. The temperature of the reactive azeotrope moves from 93.51 ºC to 91.85 ºC when chemical equilibrium values are increased. Besides, composition moves from $X^T_1 = 0.0651$, $X^T_2 = 0.2328$ to $X^T_1 = 0.1849$, $X^T_2 = 0.2795$. On the other hand changes are smaller when different sets of parameters are used: from 93.06 ºC to 93.51 ºC, from $X^T_1 = 0.0606$, $X^T_2 = 0.2371$ to $X^T_1 = 0.0651$, $X^T_2 = 0.2328$. Increasing the value of the chemical equilibrium constant moves the reactive azeotrope from near the heterogeneous binary azeotrope BuOH-W to near the ternary heterogeneous azeotrope W-BuOH-BA (see Fig. 8), in agreement with the study of Okasinski and Doherty (2000).

**Table 5.** Calculated reactive azeotropic point for the system
acetic acid (1) - n-butanol (2) - water (3) - n-butylacetate (4) at 101.3 kPa

| Phase Data | Chemical Equilibrium Constant, T in K | T / °C (type [a]) | Calculated | | | |
|---|---|---|---|---|---|---|
| | | | $x'_1,x'_2,x'_3,x'_4$ $x^T_1,x^T_2,x^T_3,x^T_4$ | $X'_1,X'_2,X'_3$ $X^T_1,X^T_2,X^T_3$ | $x''_1,x''_2,x''_3,x''_4$ $y_1,y_2,y_3,y_4$ | $X''_1,X''_2,X''_3$ $Y_1,Y_2,Y_3$ |
| VLE | $\ln K_a =$ 0.4685+835.7/T | 93.06 (het.) | 0.0449, 0.2503, 0.6820, 0.0229 | 0.0678, 0.2732, 0.6591 | 0.0169, 0.0193, 0.9628, 0.0011 | 0.0180, 0.0204, 0.9617 |
| | | | 0.0409, 0.2173, 0.7220, 0.0197 | 0.0606, 0.2371, 0.7023 | 0.0038, 0.1803, 0.7591, 0.0568 | 0.0606, 0.2371, 0.7023 |
| LLE | $\ln K_a =$ 0.4685+835.7/T | 93.51 (het.) | 0.0513, 0.2819, 0.6369, 0.0299 | 0.0812, 0.3118, 0.6070 | 0.0234, 0.0372, 0.9369, 0.0025 | 0.0259, 0.0397, 0.9344 |
| | | | 0.0432, 0.2109, 0.7240, 0.0219 | 0.0651, 0.2328, 0.7020 | 0.0051, 0.1728, 0.7621, 0.0601 | 0.0651, 0.2328, 0.7020 |
| LLE | $\ln K_a =$ 1.0442+835.7/T | 92.65 (het.) | 0.0821, 0.2373, 0.5844, 0.0963 | 0.1784, 0.3336, 0.4881 | 0.0415, 0.0359, 0.9147, 0.0079 | 0.0494, 0.0438, 0.9068 |
| | | | 0.0719, 0.1871, 0.6667, 0.0743 | 0.1462, 0.2613, 0.5925 | 0.0091, 0.1243, 0.7296, 0.1371 | 0.1462, 0.2613, 0.5925 |
| LLE | $\ln K_a =$ 1.5671+835.7/T | 91.85 (het.) | 0.0720, 0.2533, 0.4434, 0.2313 | 0.3033, 0.4846, 0.2121 | 0.0335, 0.0227, 0.9361, 0.0077 | 0.0412, 0.0304, 0.9284 |
| | | | 0.0546, 0.1492, 0.6659, 0.1303 | 0.1849, 0.2795, 0.5356 | 0.0080, 0.1026, 0.7125, 0.1769 | 0.1849, 0.2795, 0.5356 |

a)het.= heterogeneous; hom. = homogeneous

## 4. CONCLUSIONS

To improve the process of production of n-butylacetate from acetic acid and n-butanol by reactive distillation, data and thermodynamic modeling are necessary. The acetic acid - n-butanol - water - n-butylacetate system has in the literature an extensive data base of binary, ternary and quaternary VLE and LLE. The thermodynamic modeling of the chemical equilibrium constant has a strong impact on the reactive azeotropic point.

## 5. APPENDIX A

- *Vapor pressure equation*

$$\ln P_{vap} = A + \frac{B}{C+T} + D \ln T + E\, T^F$$

where
$P_{vap}$ = vapor pressure (kPa)
$T$ = temperature (K)
$A, B, C, D, F$ = constants

- *NRTL equation*

The NRTL equation has the following form:

$$\ln \gamma_i = \frac{\sum\limits_{j=1}^{n} \tau_{ji}\, x_j\, G_{ji}}{\sum\limits_{k=1}^{n} x_k\, G_{ki}} + \sum\limits_{j=1}^{n} \frac{x_j\, G_{ij}}{\sum\limits_{k=1}^{n} x_k\, G_{ki}} \left( \tau_{ij} - \frac{\sum\limits_{m=1}^{n} \tau_{mi}\, x_m\, G_{mi}}{\sum\limits_{k=1}^{n} x_k\, G_{ki}} \right)$$

where
$\gamma_i$ = activity coefficient of component $i$

$G_{ij} = \exp\left[\, -\tau_{ij}\, \alpha_{ij}\, \right]$

$\tau_{ij} = \dfrac{aij + bijT}{RT}$

$x_i$ = mole fraction of component $i$

$T$ = temperature (K)

$n$ = total number of components

$a_{ij}$ = non-temperature-dependent energy parameter between components $i$ and $j$ (cal/gmol)

$b_{ij}$ = temperature-dependent energy parameter between components $i$ and $j$ (cal/gmol-K)

$\alpha_{ij}$ = NRTL non-randomness parameters for binary interaction ($\alpha_{ij} = \alpha_{ji}$ for all binaries)

The five adjustable parameters for the NRTL equation are the $a_{ij}$, $a_{ji}$, $b_{ij}$, $b_{ji}$ and $\alpha_{ij}$ terms.

- *Virial equation*

$$\ln \Phi_i = \left( 2 \sum_j y_i \, B_{ij} - B_{mix} \right) \frac{P}{RT}$$

with

$$B_{mix} = \sum_i \sum_j y_i \, y_j \, B_{ij}$$

The method of Hayden and O'Connell (1975) is used to calculate the second virial coefficient:

$$B_{ij} = B_{ij}^F + B_{ij}^D$$

where the superscript $F$ denotes the contribution from the polar and non-polar part due to physical interactions and the superscript $D$ the contribution due to the formation of metastable compounds (from dimerization), the formation of chemical bonds and the chemical reaction.

The required input parameters are, for each component: critical temperature $T_c$, critical pressure $P_c$, dipole moment $\mu$, mean radius of gyration $R_D$ and association parameter $\eta$; and for each binary pair, association parameter $\eta_{ij}$.

- *Azeotropes calculation*

Azeotropes were calculated with DISTIL using a homotopy continuation technique based on the work of Fidkowski et al. (1993).

The reactive azeotrope was calculated with HYSYS. The azeotrope was found adjusting two of the four pure component feeds to the reactive separator tank until two of the transformed coordinates reach the azeotropy condition. That is, for the quaternary system acetic acid(1)-n-butanol(2)-water(3)-n-butylacetate(4):

$$X_i = Y_i \qquad \text{, with i = 1, 2}$$
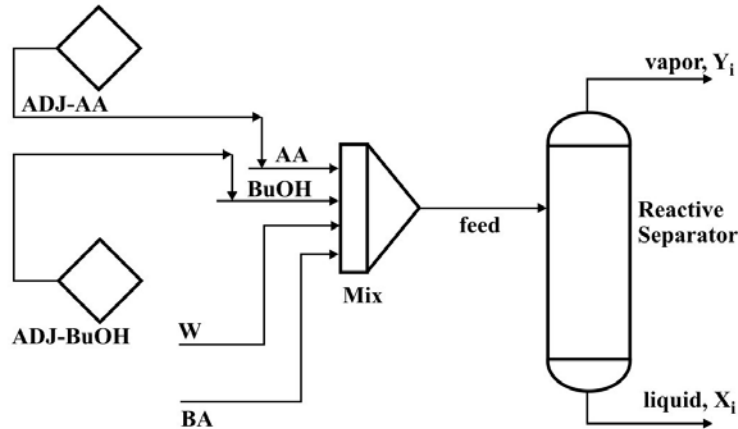


- *Residue curve and distillation line maps*

Residue curves were calculated with DISTIL solving:

$$H \frac{dx_i}{dt} = \frac{V}{H}(x_i - y_i)$$

where
$H$ = liquid holdup
$t$  = time
$V$ = vapor out flow
$x_i$ = liquid composition of component i
$y_i$ = vapor composition of component i

The residue curve describes the actual physical process of boiling off a mixture. The heavier boiling components in the system are being concentrated in the still. An azeotrope can be detected in the residue curve as a fixed point, which distils at fixed composition and temperature.
Distillation lines were calculated with HYSYS solving:

$$X_i^{k+1} = Y_i^k$$

The distillation line describes a condensation process and advances in the direction of decreasing the temperature of the system. A reactive azeotrope can be detected in the distillation line as a fixed point.

## 6. NOMENCLATURE

$f_i$ = fugacity of component i
$G$ = molar Gibbs energy
$K_a$ = equilibrium constant of reaction based on activity
$K_x$ = equilibrium constant of reaction based on liquid mole fraction
$K_\gamma$ = equilibrium constant of reaction based on activity coefficient
$L$ = liquid molar flow
$P$ = total pressure
$R$ = Universal gas constant
$T$ = temperature
$x_i$ = liquid phase mole fraction of component i
$X_i$ = transformed liquid phase coordinates of Ung and Doherty of component i (eq. 9)
$y_i$ = vapor phase mole fraction of component i
$Y_i$ = transformed vapor phase coordinates of Ung and Doherty of component i (eq. 10)

**Greek letters**

$\alpha$ = liquid fraction of phase $'$
$\Phi_i$ = fugacity coefficient of component i
$\gamma_i$ = activity coefficient of component i
$v_i$ = stecheometric coefficient of component i

**Subscripts**

$i$ = component
$k$ = reference component
$T$ = total

**Superscripts**

$^0$ = standard state
$^L$ = liquid phase
$^V$ = vapor phase
$^{'}$ = organic rich phase
$^{''}$ = water rich phase
$^T$ = total liquid composition

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