

SIMULATION OF N-PROPANOL DEHYDRATION PROCESS VIA HETEROGENEOUS AZEOTROPIC DISTILLATION USING THE NRTL EQUATION

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Numerical values of the NRTL equation parameters for calculation of the vapour – liquid – liquid equilibria (VLLE) at atmospheric pressures have been presented for 5 ternary mixtures. These values were fitted to the experimental VLLE and vapour – liquid equilibrium (VLE) data to describe simultaneously, as accurately as possible, the VLE and the liquid – liquid equilibria (LLE). The coefficients of this model called further NRTL-VLL were used for simulations of n-propanol dehydration via heterogeneous azeotropic distillation. The calculations performed by a ChemCAD simulator were done for 4 mixtures using hydrocarbons, ether and ester as an entrainer. In majority simulations the top streams of the azeotropic column had composition and temperature similar to the corresponding experimental values of ternary azeotropes. The agreement between the concentrations of both liquid phases formed in a decanter and the experimental values of the LLE was good for all four simulations. The energy requirements were the most advantageous for the simulation with di-n-propyl ether (DNPE) and isooctane. Simulations were performed also for one mixture using the NRTL equation coefficients taken from the ChemCAD database. In that case the compositions of the liquid organic phases leaving the decanter differed significantly from the experimental LLE data.

Keywords: dehydration of n-propanol, heterogeneous azeotropic distillation

1. INTRODUCTION

There is increasing interest in the use of dehydrated alcohols (ethanol, *n*-propanol, isopropanol and *n*-butanol) as a transport fuel. Biological fermentation delivers low concentration aqueous solutions of these alcohols. They may be relatively easily concentrated by a simple distillation. However, those alcohols form with water low boiling point azeotropes, which requires the use of other techniques to obtain anhydrous alcohols. One of them is a heterogeneous azeotropic distillation with the addition of a third component, which can form with water – an alcohol mixture, a ternary heteroazeotrope. A classic example is the dehydration of ethanol using benzene (Young, 1902). It has very good properties as an entrainer but carcinogenic nature. Therefore, it is proposed in the literature to use diisopropyl ether (DIPE) (Pienaar et al., 2013; Pla-Franco et al., 2014a) or other hydrocarbons: cyclohexane (Gomis et al., 2005), *n*-hexane (Gomis et al., 2007a), isooctane (Font et al., 2003) and *n*-heptane (Gomis et al., 2006). In the case of n-propanol dehydration process the following substances have been proposed to be used as an entrainer: cyclohexane (Lee and Shen, 2005), isooctane (Pla-Franco et al., 2014a), DNPE (Lladosa et al., 2008) and *n*-propyl acetate (Pla-Franco et al., 2014b).

The flowsheet of heterogeneous azeotropic distillation can be examined by professional simulators. Font et al. (2003) obtained the Uniquac equation parameters for the water – ethanol – isooctane system by correlation of the VLE and VLLE data and used them in the simulation of ethanol dehydration. The

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same system was investigated by Cairns and Furzer (1990). Pla-Franco et al. (2014b) proposed a flowsheet consisting of three columns for separation of the mixture water - *n*-propanol using *n*-propyl acetate. The same authors (Pla-Franco et al., 2014a) compared the simulations of ethanol dehydration process using benzene or DIPE. Arifin and Chien (2007), Chang et al. (2012) and Wu and Chien (2009) performed the simulations of isopropanol dehydration process using cyclohexane. Wyczesany (2011) applied the NRTL equation for the simulations of ethanol dehydration process using hydrocarbons such as cyclohexane, *n*-hexane, *n*-heptane, and isooctane. The parameters of this equation were fitted to the experimental VLLE data but the minimized objective function calculated separately the VLE and the LLE for these data. NRTL-VLL parameters obtained in the presented papers were fitted to the experimental data when the minimized objective function described the full VLLE. Gomis et al. (2015) compared the results of the experimental work of a semi-pilot plant scale distillation column with the calculated results obtained from the simulations for the process of ethanol dehydration using: *n*-hexane, cyclohexane, isooctane and toluene.

The calculation results of simulation are strongly dependent on a properly chosen thermodynamic model, which in heterogeneous azeotropic distillation should describe both the VLE and the LLE as accurately as possible. Equations such as the NRTL and the Uniquac can correlate the VLE and separately LLE with high precision. Unfortunately, the correlated parameters describing exactly the VLE predict the LLE very inaccurately and vice versa. The ChemCad data bank contains the coefficients of the NRTL and the Uniquac equations for the water - *n*-propanol mixture fitted with the VLE data. Both equations describe the VLE of this mixture with high precision but predict also the miscibility gap. (In reality water and *n*-propanol are miscible completely). The same phenomenon can be observed for the majority of the coefficients of both equations presented in literature for the water - *n*-propanol mixture.

The problem of parameter correlation for the VLLE was described in a previous work by the author (Wyczesany 2014), using the NRTL equation. Its parameters were fitted simultaneously to the experimental VLLE and VLE data. For 27 ternary systems measured at atmospheric pressure calculation results showed that the NRTL equation can describe quite accurately the VLLE and the VLE of ternary mixtures and their binary subsystems if the parameters of this equation were fitted simultaneously to three-phase and two-phase equilibrium data. The NRTL-VLL model parameters calculated in this paper were used to simulate the *n*-propanol dehydration process using a ChemCAD simulator (ChemCAD, 2010). The following entrainers were used: cyclohexane, isooctane, DNPE and *n*-propyl acetate. Therefore, in this work the NRTL-VLL parameters were fitted for ternary mixtures containing water, *n*-propanol and entrainer. The DIPE was tested also as the entrainer but it turned out that this ether did not form a heteroazeotrope with water and *n*-propanol and it was not used in the simulations. The correlated model parameters were used to: the VLLE calculations of the considered ternary mixtures, the VLE calculations of their binary subsystems (water - *n*-propanol and *n*-propanol - entrainer) and prediction of the temperature and concentrations of ternary and binary azeotropes. Calculation results showed that the NRTL-VLL parameters describe all these various properties with a good (but not perfect) accuracy. Therefore, the NRTL-VLL parameters were additionally tested in the simulations of *n*-propanol dehydration. It is known from literature that models describing the VLLE have the greatest difficulty with a precise description of LLE. Therefore, particular emphasis was placed on checking whether the concentrations of the liquid phases leaving the decanter are close to the experimental LLE data. Simulations presented in the literature do not contain such comparisons.

The results of simulations show also which variant of the *n*-propanol dehydration process is the most preferred from the standpoint of energy requirements. For comparison, calculations were also carried out for one mixture using the NRTL equation coefficients taken from the ChemCAD database.

2. CALCULATION OF VLLE

The article uses the classical version of the NRTL equation (Eq. 1) which has three adjustable parameters (A_{ij} , A_{ji} and α_{ij}), fitted to experimental equilibrium data.

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} + \sum_j \frac{x_j G_{ij}}{\sum_l G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_l G_{lj} x_l} \right), \quad \tau_{ji} = \frac{A_{ji}}{T}, \quad G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (1)$$

In my previous paper (Wyczesany, 2014) two approaches were used for the VLLE calculation depending on the availability of the experimental values of the total mixture mole fractions z_i . In the case of data containing T , P and the values z_i the classical method of the three-phase flash calculation was used. For systems considered in this paper the data contain the equilibrium compositions of all three phases in addition to T and P and do not present the mole fractions z_i . To be able to use this data at all, the last values must be assumed. We can assume that the mole fractions z_i refer to the total mixture or to the total liquid phase. In the first case the mole fractions z_i correspond to the arithmetic mean values of the experimental mole fractions of individual components in all three phases. In the second case these mean values refer to both liquid phases only. It is obvious that both assumptions cause some inaccuracies in the material balance of each component. The last assumption seems to be much more reliable and it was used in the second approach of the VLLE calculation. When z_i values are computed as in the first case the flash calculations often do not converge.

For isobaric data the known values are represented by the pressure and mole fractions z_i of the total liquid phase. The experimental temperature is treated in calculations as an initial value. For the known values z_i and T the algorithm calculates the LLE (aqueous phase fraction in the total liquid and the compositions of both liquid phases). In the next step the VLE is calculated for both liquid phases. For known values of P and the mole fractions of the liquid phase the algorithm computes the mole fractions y_i of the gas phase and the boiling temperature. The values of T obtained for both liquid phases are compared to each other. If they differ by more than the value of 0.001 K, the organic phase temperature is taken as a new one for further calculations. In the next step again the LLE and the VLE for both liquid phases are computed. Iterations are continued until the difference between the temperatures in both gas phases is lower than 0.001 K. Subsequently the algorithm computes for the same substances the differences between the mole fractions y_i calculated for both liquid phases. If they are greater than the value of 0.0001, the new temperature is assumed and the algorithm returns to the LLE and the VLE computations for both liquid phases. If not, the VLLE is calculated. A detailed description of the algorithm is given elsewhere (Wyczesany, 2014).

3. CALCULATION OF NRTL EQUATION PARAMETERS

NRTL equation parameters were calculated by the minimization of the objective function OF given by Eq. 2.

$$OF = \sum_{i=1}^{NLE} \sum_{j=1}^{Nc} \sum_{k=1}^2 (x_{\text{exp},k,j,i} - x_{\text{cal},k,j,i})^2 + W1 \sum_{i=1}^{NVLE} \sum_{j=1}^{Nc} (y_{\text{exp},j,i} - y_{\text{cal},j,i})^2 + W2 \sum_{i=1}^{NVLE} (T_{\text{exp},i} - T_{\text{cal},i})^2 \quad (2)$$

This function uses NLE experimental points for the LLE. The data may refer to the VLLE and the LLE of the given system or its subsystems. The first term of the function OF refers to Nc components and both liquid phases. The second term of the minimized function uses $NVLE$ experimental points of the VLE and also includes Nc components. The data may refer to the VLLE and the VLE for the given system or its subsystems. The last term of the function OF applies the differences between the

experimental and calculated temperatures and is calculated for *NVLE* experimental points. The values $W1$ and $W2$ are the weight parameters, which enable better fitting of the calculated values to the experimental data. For ternary mixtures the minimized objective function contains 9 parameters ($A_{12}, A_{21}, A_{13}, A_{31}, A_{23}, A_{32}, \alpha_{12}, \alpha_{13}, \alpha_{23}$).

4. RESULTS OF CALCULATION AND THEIR DISCUSSION

In a previous work by the author (Wyczesany, 2014) the coefficients of the NRTL equation were calculated for 27 mixtures determined at nearly atmospheric pressure. In this work these parameters were fitted for four new systems and calculated again for the mixture of water - *n*-propanol - DNPE putting emphasis on the better fitting of the concentration and temperature of the ternary heteroazeotrope. Table 1 lists the investigated mixtures and Table 2 presents the calculated values of the NRTL equation parameters.

The values representing the accuracy criteria of correlation and prediction of the VLLE and the VLE are the following: Δx_i and Δy_i - absolute mean deviations between experimental and calculated equilibrium compositions of species i in the liquid and vapour phases, respectively and ΔT - absolute mean difference between experimental and calculated equilibrium temperatures. Additionally, two mean deviations ΔX and ΔY were defined (Eq. 5). The first one refers to all the components (N_c) in a given liquid phase, the second one to all the components in the gas phase.

$$\Delta x_i = \frac{1}{NLE} \sum_{i=1}^{NLE} |x_{\text{exp},i} - x_{\text{cal},i}|, \quad \Delta y_i = \frac{1}{NVLE} \sum_{i=1}^{NVLE} |y_{\text{exp},i} - y_{\text{cal},i}| \quad (3)$$

$$\Delta T = \frac{1}{NVLE} \sum_{i=1}^{NVLE} |T_{\text{exp},i} - T_{\text{cal},i}| \quad (4)$$

$$\Delta X = \frac{1}{N_c} \sum_{i=1}^{N_c} \Delta x_i, \quad \Delta Y = \frac{1}{N_c} \sum_{i=1}^{N_c} \Delta y_i \quad (5)$$

Table 1. Experimental ranges of temperatures and pressures, number of the experimental points and references for the VLLE data of the considered systems

No.	System	T , K	P , bar	N_p	Ref.
1	water - <i>n</i> -propanol - cyclohexane	340-341	1.013	23	Lee and Shen (2003)
2	water - <i>n</i> -propanol - isooctane	348-352	1.013	17	Pienaar et al. (2013)
3	water - <i>n</i> -propanol - DNPE	347-352	1.0	11	Lladosa et al. (2008)
4	water - <i>n</i> -propanol - DIPE	335-346	1.013	18	Pienaar et al. (2013)
5	water- <i>n</i> -propanol - <i>n</i> -propyl acetate	355-357	1.013	11	Pla-Franco et al. (2014b)

Table 2. Coefficients of the NRTL equation for the systems (1) - (5)

No.	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	α_{12}	α_{13}	α_{23}
1	914.09	160.78	1771.1	1396.3	344.24	712.49	0.4589	0.3174	0.5661
2	903.93	333.92	2617.6	1354.9	460.63	759.68	0.5684	0.3196	0.5940
3	918.53	169.50	1598.3	901.75	159.43	254.75	0.4729	0.2904	0.2644
4	883.85	259.42	1921.0	893.44	159.47	152.23	0.5299	0.3209	0.5289
5	929.17	194.07	1500.8	537.60	-14.243	232.84	0.4971	0.3446	0.1200

Table 3 presents deviations obtained during the parameter correlation referring to the VLLE of the ternary systems. The mean deviations ΔX do not exceed 1 mol% and are generally significantly lower for the aqueous phase. The mean deviations ΔY are in the range of 1.07 - 1.54 mol%, and the mean deviations ΔT only in two cases exceed the value of 0.3 K. The maximum deviations ($\Delta x_{i,aq,max}$, $\Delta x_{i,org,max}$, $\Delta y_{i,max}$ and $\Delta T_{i,max}$) refer usually to one experimental point.

Table 3. Mean and maximum deviations obtained during the parameter correlation referring to the VLLE of the considered systems

	System				
	1	2	3	4	5
ΔX_{aq}	0.0015	0.0061	0.0059	0.0049	0.0033
ΔX_{org}	0.0062	0.0089	0.0086	0.0057	0.0094
ΔY	0.0154	0.0153	0.0127	0.0107	0.0114
ΔT	0.10	0.12	0.33	0.31	0.15
$\Delta x_{i,aq,max}$	0.0068	0.0229	0.0144	0.0723	0.0057
$\Delta x_{i,org,max}$	0.0208	0.0443	0.0660	0.0300	0.0452
$\Delta y_{i,max}$	0.0351	0.0406	0.0380	0.0410	0.0183
$\Delta T_{i,max}$	0.38	0.36	0.87	0.86	0.25

Table 4 presents deviations obtained during the parameter correlation referring to the VLE of the binary subsystems: water – *n*-propanol and *n*-propanol – entrainer (hydrocarbon, ether or ester). The accuracy of the description is quite good in spite of the fact that VLE temperatures often significantly differ from VLLE temperatures.

Table 4. Mean and maximum deviations obtained during the parameter correlation referring to the VLE of binary subsystems (water – alcohol and alcohol – entrainer).

		1	2	3	4	5
water <i>n</i> -propanol	Δy	0.0069	0.0122	0.0066	0.0089	0.0074
	$\Delta T/ref$	0.25 ^a	0.50 ^a	0.29 ^a	0.37 ^a	0.34 ^a
	$\Delta y_{i,max}$	0.0260	0.0343	0.0267	0.0255	0.0311
	$\Delta T_{i,max}$	1.52	1.85	1.56	1.53	1.75
<i>n</i> -propanol entrainer	Δy	0.0057	-	0.0025	-	0.0017
	$\Delta T/ref$	0.21 ^b	-	0.31 ^c	-	0.09 ^d
	$\Delta y_{i,max}$	0.0232	-	0.0115	-	0.0050
	$\Delta T_{i,max}$	0.70	-	0.60	-	0.21

^a – Mączyński and Mączyńska (1981); ^b – Mączyński et al. (1982); ^c – Lladosa et al. (2006);

^d - Mączyński et al. (1984)

Since the NRTL-VLL parameters can be used in a simulator for modelling *n*-propanol dehydration processes via heterogeneous azeotropic distillation, the model should accurately predict the composition, temperature and the type (homogeneous or heterogeneous) of the azeotropes. Table 5 presents the experimental and calculated compositions (in mole fractions) and temperatures of the azeotropes for the considered ternary systems and their binary subsystems. The necessary calculations were performed with ChemCAD. In most cases, the accuracy of the prediction is satisfactory. The best precision can be observed for the water - *n*-propanol – cyclohexane mixture. The least accuracy occurs for the water – *n*-propanol – DNPE system. If the system does not form any ternary azeotrope

(mixture 4), the NRTL-VLL parameters correctly predict this fact. Remaining ternary systems listed in Table 5 form heteroazeotropes. The NRTL-VLL parameters correctly predict this phenomenon also.

Table 5. Comparison of experimental and calculated compositions (in mole fractions) and temperatures of ternary and binary azeotropes of the considered systems

	system	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
1	water	0.256	0.261	0.568	0.577	0.300	0.301	- ^a	-
	<i>n</i> -propanol	0.132	0.132	0.432	0.423	- ^b	-	0.240	0.238
	cyclohexane	0.612 ^a	0.607	- ^c	-	0.700	0.699	0.760	0.762
	<i>T</i> , K	339.98	340.15	360.90	360.95	342.65	342.63	347.91	347.92
2	water	0.352	0.356	0.568	0.547	0.471	0.450	- ^c	-
	<i>n</i> -propanol	0.208	0.204	0.432	0.453	- ^c	-	0.453	0.433
	isooctane	0.440 ^c	0.440	- ^c	-	0.529	0.550	0.547	0.567
	<i>T</i> , K	347.04	347.38	360.90	360.62	352.28	352.21	357.93	357.93
3	water	0.383	0.367	0.568	0.578	0.396	0.386	- ^d	-
	<i>n</i> -propanol	0.103	0.117	0.432	0.422	- ^d	-	0.334	0.341
	DNPE	0.514 ^d	0.516	- ^c	-	0.604	0.614	0.666	0.659
	<i>T</i> , K	346.85	347.44	360.90	360.70	348.20	348.24	358.04	358.50
4	water	-	-	0.568	0.559	0.220	0.216		
	<i>n</i> -propanol	-	-	0.432	0.441	- ^c	-	-	-
	DIPE	-	-	- ^c	-	0.780	0.784	-	-
	<i>T</i> , K	-	-	360.90	360.74	335.35	335.09	-	-
5	water	0.525	0.507	0.568	0.577	0.520	0.520	- ^e	-
	<i>n</i> -propanol	0.081	0.095	0.432	0.423	- ^e	-	0.613	0.593
	<i>n</i> -propyl acetate	0.394 ^e	0.398	- ^c	-	0.480	0.480	0.387	0.407
	<i>T</i> , K	355.36	355.53	360.90	361.08	355.55	355.93	367.63	368.03

^a – Lee and Shen (2003); ^b – Horsley (1962); ^c – Pienaar et al. (2013); ^d – Lladosa et al. (2008); ^e – Pla-Franco et al. (2014b)

5. SIMULATIONS OF N-PROPANOL DEHYDRATION VIA HETEROGENEOUS AZEOTROPIC DISTILLATION

The NRTL-VLL parameters obtained in the presented works have been used in the simulation of dehydration processes of the mixtures: water - *n*-propanol via the heterogeneous azeotropic distillation. The calculations were performed with a ChemCAD simulator which contains numerical values of the coefficients of the NRTL equation for many binary systems in its database. They would correspond to the VLE parameters if the components are miscible completely. If the mixture exhibits a relatively small miscibility gap (as the water - *n*-butanol system), ChemCAD has usually two sets of parameters: for the VLE and the LLE. However, if the miscibility gap is large (as in the water - hydrocarbons systems) the NRTL equation parameters describe the LLE only. These coefficients taken from the database have been replaced by the NRTL-VLL parameters for the considered ternary systems. For comparison, in the case of the mixture with *n*-propyl acetate the simulations were also performed using the NRTL binary parameters taken from the ChemCAD database.

In the simulations of *n*-propanol dehydration the following entrainers were used: cyclohexane, isooctane, DNPE and *n*-propyl acetate. All simulations were performed using in the thermodynamic settings the following global phase option: "Vapor / Liquid / Liquid / Solid".

Figure 1 shows the flowsheet of this process (the numbers of streams are placed in squares and the numbers of unit operations in circles). Stream 1 contains 100 kmol/h of a mixture having the mole fractions of water and *n*-propanol equal to 0.5 and the vapour fraction equal to 0.5. It is separated in the distillation column 1 into water having a concentration of 99.9 mol% and the gaseous distillate which is an azeotropic mixture of water and *n*-propanol. This mixture is directed into the distillation column 2 which has not any condenser and is fed also by the organic phase from the decanter 3. Pure *n*-propanol (99.9 mol%) is obtained at the bottom of the column 2 and the top product of this column with a composition and temperature close to the ternary azeotrope is totally condensed at heat exchanger 4 and separated into two liquid phases in the decanter 3. The last unit can calculate the three-phase VLE. In all performed simulations the flow of the gaseous stream 12 was equal to zero and the decanter calculated only the LLE. (ChemCad has a flash unit which always treats the first output stream as vapour. Therefore, if we want to calculate the separation of two liquids only we must use the LLV flash.) The aqueous phase from the decanter is directed into the distillation column 1. The device 6 is a controller which counts the losses of the third component in the streams 3 and 7. These losses are supplemented by the stream 9.

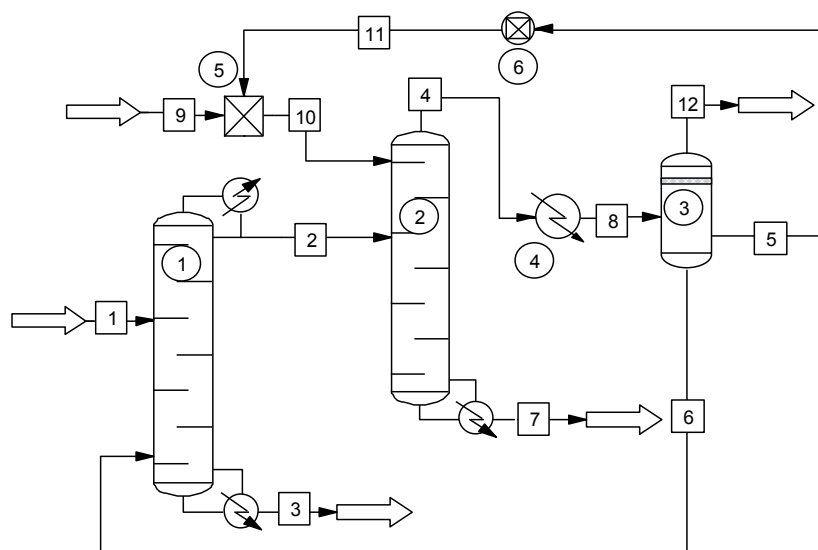


Fig. 1. Flowsheet of *n*-propanol dehydration

For all simulations carried out in the work the numbers of stages in columns have been established by trial method, so as the column was able to produce at the bottom water or alcohol of the assumed purity. The feed stage numbers of both columns were chosen also by trial method, based on conditions that the total heat delivered to the reboilers of both columns was the lowest. For the all performed simulation processes the reflux ratio at the top of the column 1 was fixed to 0.1.

Table 6 presents the total flow, composition and temperature of the streams 4, 5, 6 and 2 as well as the total number of stages and the feed stage numbers for both columns. For the mixtures with cyclohexane and DNPE Table 6 presents two solutions. For both mixtures in the first solution the top stream of the column 2 has the composition and the temperature close to the azeotrope. In the second solution these values are significantly different from those of the azeotrope. In the latter case, the streams 4 and 5 have significantly higher total flows, resulting in greater energy requirements for a given flowsheet.

Table 6. Total flow, composition and temperature of the streams 4, 5, 6 and 2. The total number of stages and the feed stage numbers for both columns. x_1 , x_2 and x_3 – mole fractions of water, *n*-propanol and entrainer, respectively

Entrainer		Stream					Column	
		4	5	6	2		1	2
cyclohexane first solution	kmol/h	276.32	208.29	68.03	118.503	no of stages	10	13
	x_1	0.2598	0.0360	0.9449	0.5451	feed stg. str. 1	3	
	x_2	0.1324	0.1589	0.0513	0.4528	feed stg. str. 6	9	
	x_3	0.6078	0.8051	0.0037	0.0021	feed stg. str. 10		1
	T, K	339.82	339.69	339.69	360.67	feed stg. str. 2		3
cyclohexane second solution	kmol/h	330.99	262.14	68.84	118.84	no. of stages	10	13
	x_1	0.2637	0.0858	0.9409	0.5454	feed stg. str. 1	3	
	x_2	0.2283	0.2738	0.0552	0.4523	feed stg. str. 6	9	
	x_3	0.5080	0.6404	0.0039	0.0022	feed stg. str. 10		1
	T, K	345.38	339.72	339.72	360.67	feed stg. str. 2		3
isooctane	kmol/h	232.55	161.21	71.34	121.32	no. of stages	10	15
	x_1	0.3428	0.0976	0.8970	0.5277	feed stg. str. 1	3	
	x_2	0.2182	0.2700	0.1011	0.4712	feed stg. str. 6	9	
	x_3	0.4390	0.6324	0.0019	0.0011	feed stg. str. 10		1
	T, K	348.05	347.37	347.37	360.43	feed stg. str. 2		5
DNPE first solution	kmol/h	231.35	167.20	64.15	114.14	no. of stages	10	20
	x_1	0.3318	0.0885	0.9660	0.5433	feed stg. str. 1	2	
	x_2	0.1599	0.2101	0.0292	0.4540	feed stg. str. 6	9	
	x_3	0.5083	0.7014	0.0048	0.0027	feed stg. str. 10		1
	T, K	348.69	347.38	347.38	360.76	feed stg. str. 2		3
DNPE second solution	kmol/h	289.93	223.73	66.20	116.20	no of stages	10	20
	x_1	0.3403	0.1591	0.9526	0.5431	feed stg. str. 1	2	
	x_2	0.2533	0.3159	0.0418	0.4537	feed stg. str. 6	9	
	x_3	0.4064	0.5250	0.0056	0.0032	feed stg. str. 10		1
	T, K	351.01	347.65	347.65	360.75	feed stg. str. 2		3
<i>n</i> -propyl acetate	kmol/h	266.73	204.08	62.65	112.60	no of stages	10	28
	x_1	0.4908	0.3428	0.9730	0.5414	feed stg. str. 1	2	
	x_2	0.1527	0.1938	0.0189	0.4541	feed stg. str. 6	9	
	x_3	0.3565	0.4634	0.0081	0.0045	feed stg. str. 10		1
	T, K	355.66	354.27	354.27	360.80	feed stg. str. 2		12
<i>n</i> -propyl acetate NRTL coefficients ChemCAD	kmol/h	241.69	177.98	63.71	113.67	no of stages	10	25
	x_1	0.4918	0.3191	0.9741	0.5461	feed stg. str. 1	3	
	x_2	0.2248	0.2973	0.0225	0.4520	feed stg. str. 6	9	
	x_3	0.2834	0.3836	0.0034	0.0019	feed stg. str. 10		1
	T, K	356.13	354.61	354.61	360.27	feed stg. str. 2		11

For a mixture with *n*-propyl acetate Table 6 shows also simulation results obtained for the NRTL equation coefficients taken from the ChemCAD database. The composition of the stream 4 differs here significantly from that of the azeotrope.

The vapour from the top of column 1 (stream 2) should have the composition and temperature close to the corresponding values for the binary azeotrope of water - *n*-propanol system. It can be seen that in all simulations this agreement is satisfactory.

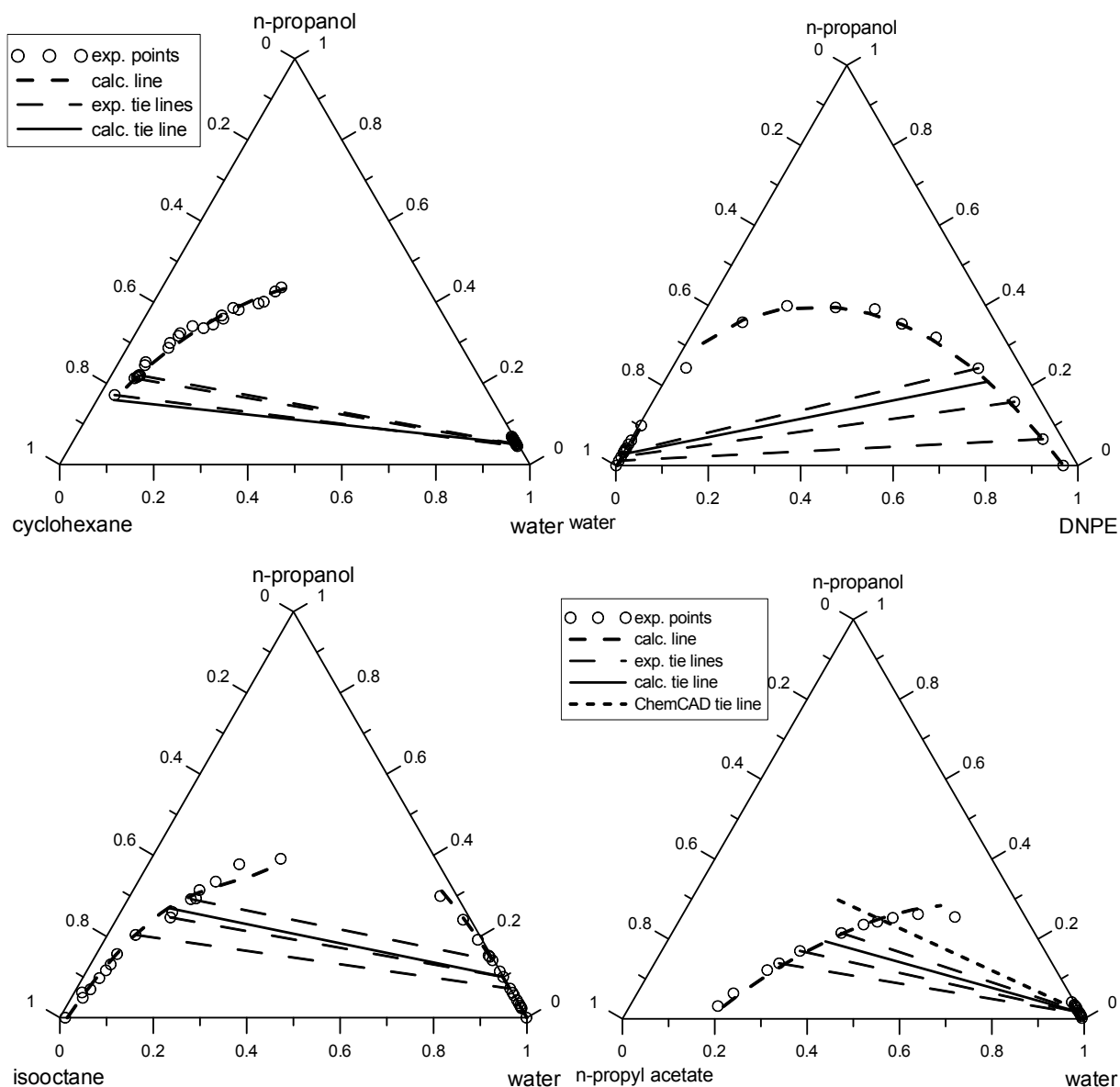


Fig. 2. The comparison of the concentrations of both liquid phases formed in the decanter with the experimental values of the LLE for the water - *n*-propanol - hydrocarbon (ether, ester) systems

The models describing the VLLE presented in the literature have the biggest problems with precise description of the LLE. Therefore, the agreement between the concentrations of both liquid phases formed in the decanter and the experimental LLE values is a very important factor that strongly affects the accuracy of the entire simulation. This agreement has been illustrated for the four considered systems in Fig. 2. It presents the experimental points of the LLE taken from the VLLE data, the lines describing these points by the NRTL-VLL parameters, tie lines drawn with a solid line on the base of the concentrations of the organic and the aqueous phases (respective streams 5 and 6) taken from the simulations and three experimental tie lines drawn with the dashed lines. In order to make the graphs clear, only three experimental tie lines closest to the tie line obtained from the simulation were placed on them. For the all four simulations, the line connecting the concentrations of the two phases obtained in the decanter fits very well into three experimental tie lines. In the case of mixtures with cyclohexane and DNPE the graphs were drawn for the first solution. For the system with *n*-propyl acetate the graph contains also the tie line plotted on the base of the simulation obtained using the NRTL equation

coefficients taken from the ChemCAD database. This line differs significantly from the experimental LLE data. It has an impact on the results of the entire simulation through the values of the molar flow and concentrations of the streams 4 and 5, which are here significantly different from those obtained for the NRTL-VLL parameters. So, the original coefficients taken from the ChemCAD database are not suitable for simulation of heterogeneous azeotropic distillation.

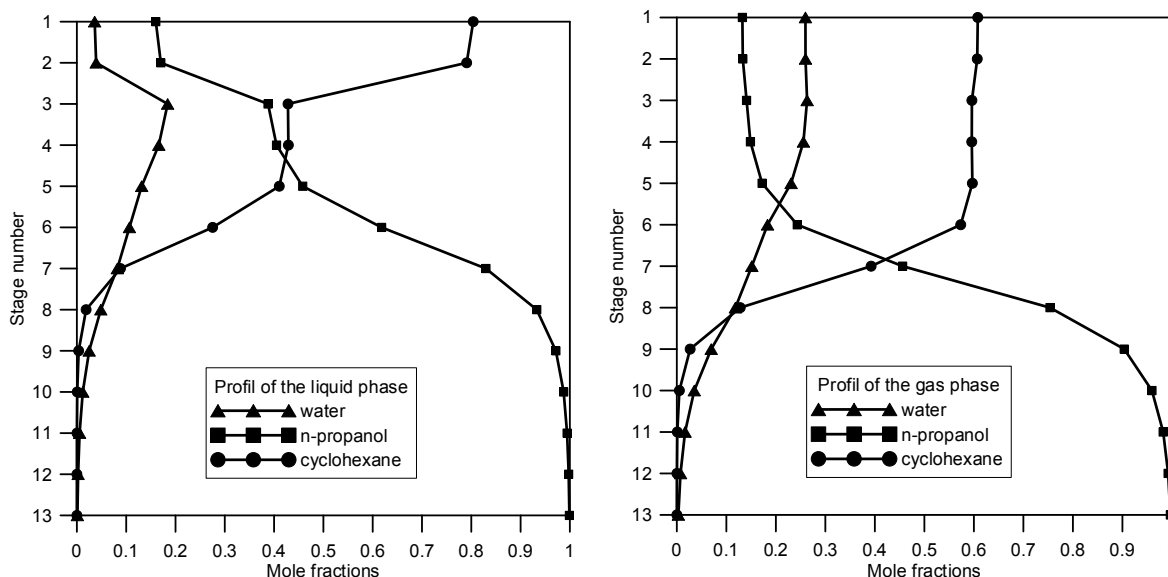


Fig. 3. Composition profiles of the liquid phase and the gas phase in the azeotropic column for the water - n-propanol - cyclohexane mixture.

Figure 3 presents the profile of the liquid phase and separately the profile of the gas phase in the azeotropic column for the water - n-propanol - cyclohexane mixture. For all simulations performed in the work only one liquid phase was present in the azeotropic column. No phase splitting was detected. The same phenomenon was observed for the simulation of ethanol dehydration with isooctane (Font et al., 2003) as well as in the experimental conditions of this process (Gomis et al., 2007b).

Table 7. Energy requirements for the investigated systems

Entrainer		col. 1	col. 2	ht. ex. 4	total
Cyclohexane first solution	Q_- , MJ/h	-495.4	-	-9781.4	-10276.8
	Q_+ , MJ/h	3484.7	4840.2	-	8324.9
Cyclohexane second solution	Q_- , MJ/h	-498.8	-	-12336.8	-12835.6
	Q_+ , MJ/h	3523.6	7360.5	-	10884.1
Isooctane	Q_- , MJ/h	-509.0	-	-8853.4	-9362.4
	Q_+ , MJ/h	3606.7	3805.8	-	7412.5
DNPE first solution	Q_- , MJ/h	-479.0	-	-8766.0	-9245.0
	Q_+ , MJ/h	3257.4	4034.7	-	7292.1
DNPE second solution	Q_- , MJ/h	-487.7	-	-11344.7	-11832.4
	Q_+ , MJ/h	3353.6	6526.2	-	9879.8
<i>n</i> -propyl acetate	Q_- , MJ/h	-472.4	-	-10602.6	-11075.0
	Q_+ , MJ/h	3149.5	5972.9	-	9122.4

Table 7 shows the energy requirements for each considered simulation. They take into account separately the heat duties in the column condensers and the coolers and the heat duties in the column reboilers. In the case of a mixture with cyclohexane and DNPE the first solutions have the lower total flows of the streams 4 and 5. These variants have also lower energy requirements. The simulations performed for the systems with isooctane and DNPE have lower energy requirements than the simulations with cyclohexane and *n*-propyl acetate.

6. CONCLUSIONS

For 5 ternary systems considered in this work calculation results showed that the NRTL equation can describe quite accurately the VLLE of ternary mixtures and the VLE of their binary subsystems if the binary parameters of this equation were fitted simultaneously to the three-phase and two-phase equilibrium data. The deviations ΔX do not exceed 1 mol % and they are usually lower for the aqueous phase. The deviations ΔY referring to the vapour phase are in the range of 1.07 - 1.54 mol%, and the differences ΔT only in two cases exceed the value of 0.3 K. The binary NRTL-VLL parameters describe the VLE of binary subsystems water – *n*-propanol and *n*-propanol – entrainer quite well despite the fact that VLE temperatures often significantly differ from VLLE temperatures. The NRTL-VLL parameters calculate the compositions and the temperatures of ternary azeotropes with good accuracy. The same conclusion refers to the binary subsystems of the considered ternary mixtures. The model also correctly predicts that the water – *n*-propanol – DIPE mixture does not form any azeotrope whereas the remaining ternary systems listed in Table 5 form heteroazeotropes. In the majority of simulations the top products from the azeotropic column have compositions and temperatures close to the corresponding experimental values of ternary azeotropes. The accuracy is very good for the mixtures: water - *n*-propanol – cyclohexane and water - *n*-propanol - isooctane. Examples referring to the water - *n*-propanol - cyclohexane and the water - *n*-propanol - DNPE mixtures indicate that if the top stream of the azeotropic column has the composition significantly different from that of azeotrope, then the recycle streams (especially organic phase) take higher values and the simulation results are energetically less favourable.

The top products from the first column are the mixtures having the compositions and temperatures close to the experimental values of the water - *n*-propanol azeotrope.

The accuracy of the entire simulation strongly depends on the correct prediction of the concentrations of both liquid phases formed in the decanter. Figure 2 shows that for all simulations (performed using the NRTL-VLL parameters) the lines connecting the concentrations of both liquid phases formed in the decanter fit very well to three closest experimental tie lines. For the simulation performed using the NRTL equation coefficients taken from the ChemCAD database the concentrations of the liquid organic phases obtained in the decanter differed very significantly from the experimental LLE data.

The energy requirements take into account for each simulation separately the heat duties in the column condensers, and coolers and separately the heat duties in the column reboilers. The simulations performed for the systems with isooctane and DNPE have the lowest energy requirements.

SYMBOLS

A_{ij}, A_{ji}	parameters of the NRTL equations, K
FC	objective function
Q^-	heat duty in the column condenser or cooler, MJ/h
Q^+	heat duty in the column reboiler or heater, MJ/h
T	temperature, K

ΔT	abs. mean deviation between experimental and calculated equilibrium temperature, K
$W1, W2$	weight factors
x, y	mole fractions in the liquid and the vapour phase, respectively
$\Delta X, \Delta Y$	mean deviation defined in Eq. (5)
$\Delta x, \Delta y$	absolute mean deviation between experimental and calculated equilibrium composition in the liquid and the vapour phase, respectively
z	assumed mole fraction of component i in the entire mixture or in the entire liquid phase

Greek symbols

α_{ij}	parameter of the NRTL equation
γ_i	activity coefficient of species i

Subscripts

exp	experimental
cal	calculated
aq	aqueous phase
org	organic phase
max	maximum

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