Chemical and Process Engineering 2012, 33 (3), 463-477
DOI: 10.2478/v10176-012-0039-5

CALCULATION OF VAPOUR - LIQUID - LIQUID – EQUILIBRIA IN QUATERNARY SYSTEMS

Andrzej Wyczesany*

University of Technology, Institute of Organic Chemistry and Technology, 31-155 Kraków, Poland

A method of parameters fitting to the experimental vapour - liquid - liquid equilibrium (VLLE) data is presented for the NRTL and the Uniquac equations for six quaternary mixtures. The same equations but with coefficients taken from the simulator Chemcad database were also used for calculation of the VLLE for the same mixtures. The calculated equilibrium temperatures and compositions for all the three phases were compared with the experimental data for these four cases. The investigated models were also applied for calculation of the compositions and temperatures of ternary azeotropes occurring in the considered quaternary mixtures. The computed values were compared with the experimental ones to appreciate the model's accuracy and to confirm whether the model correctly predicts the presence of homo- or heteroazeotrope. The NRTL equation with coefficients fitted to the VLLE data proved to be the most accurate model. For the mixtures containing water, ethanol and two different hydrocarbons this model shows particularly high accuracy. In three cases the mean deviations between the calculated and measured temperatures do not exceed 0.25 K, and for the fourth mixture the difference equals 0.33. Besides, the mean deviations between the calculated and the measured concentrations in the gas and liquid phases, with one exception do not exceed 1 mole %.

Keywords: vapor – liquid – liquid – equilibria, quaternary systems

1. INTRODUCTION

Mixtures water - ethanol - hydrocarbons are important in fuel industry because of ethanol containing gasolines. The presence of ethanol in gasoline increases its octane rating and promotes more complete combustion, reducing the content of harmful substances emitted with the flue gas. However, a small amount of water in the mixture can lead to phase splitting, which can cause troubles in the engine. For this reason, ethanol must be dehydrated before mixing with gasoline. Heterogeneous azeotropic distillation with an addition of hydrocarbon is often used for this purpose. This process can lead to pure ethanol or a "dry" mixture of ethanol with the hydrocarbon which can be directly blended with gasoline. A flow diagram of such a process can be analysed using a professional technological process simulator such as Chemcad. However, we should remember that the results of calculations are strongly dependent on a properly chosen thermodynamic model, describing as accurately as possible both the vapor - liquid equilibrium (VLE) and the liquid - liquid equilibrium (LLE).

In esterification processes or during regeneration of mixed solvents such as alcohol - ketone, alcohol - ether, or ketone – ester, which often absorb water, heteroazeotropes other than water-alcohol-hydrocarbon can also be formed.

---

*Corresponding author, e-mail: awyczes@chemia.pk.edu.pl

The available models correlate the VLE very precisely, and only slightly less accurately describe the LLE. Unfortunately, the parameters describing exactly one type of equilibrium very inaccurately predict the equilibrium of the second type. Fitting of the parameters for the VLLE is still insufficiently investigated.

Font et al. (2003) correlated the VLLE and the VLE data to obtain the parameters of the Uniquac equation for the system water – ethanol – isooctane. However, the minimised objective function was not given. The same equation was used by Asensi et al. (2002) for the system water – 1-propanol – 1-pentanol. The objective function contained the differences between the calculated and the experimental values of pressure, mole fractions in both liquid phases and activity coefficients. Ruiz et al. (1987) correlated the Uniquac parameters for the system water – ethanol – 2-ethylhexanol. The objective function consisted of two terms. The first one referred to the LLE data at 25 ^{o}C and the second one to the VLE data of two binary systems (water – ethanol and ethanol – 2-ethylhexanol) at P = 1.013 bar. Hsieh et al. (2006), Lee et al. (1996) and Hsieh et al. (2008) used the maximum likelihood principle to correlate the NRTL or Uniquac equation parameters for the following systems: water – propylene glycol monomethyl ether - propylene glycol methyl ether acetate, ethanol – ethyl acetate – water and water – methyl acetate – methyl propionate, respectively. The minimised objective function used the differences between the experimental and calculated pressure, temperature, mole fractions in both liquid phases and mole fractions in the vapour phase. Kosuge and Iwakabe (2005) applied two objective functions to correlate the parameters of Uniquac or NRTL equations for the systems water – ethanol – 1-butanol and water – ethanol – 2-butanol. One function used the VLE data and the second one the LLE data. Both methods were repeatedly used until the minimum values of the objective functions were obtained. Grigiante et al. (2008) and Ye et al. (2011) used the Peng – Robinson equation of state with Wong – Sandler mixing rule for description of the VLLE at elevated pressures for the systems isopropanol – water – propylene and water – methanol – dimethyl ether – carbon dioxide, respectively. Kundu and Banerjee (2011) applied the COSMO-SAC model to calculate the activity coefficients used for predicting the VLLE of eight systems.

The aim of this work was to develop computer programs fitting the model parameters to the experimental VLLE data available in the literature for quaternary systems. The NRTL (Renon and Prausnitz, 1968) and the Uniquac equations (Abrams and Prausnitz, 1975) were applied in the calculations. For the quaternary systems the first model is described by 18 parameters, the Uniquac equation needs 12 coefficients (the ternary systems are described in a previous article (Wyczesany, 2010). The computed coefficients were used for calculation of the VLLE of considered mixtures and for prediction of the compositions and temperatures of ternary azeotropes occurring in these systems. The same values were calculated using the NRTL and the Uniquac equations, for which the binary parameters were taken from a professional simulator Chemcad (Chemcad, 2010). These parameters describe the VLE for binary mixtures of completely miscible components and the LLE for the mixtures having a miscibility gap (with the exception of a mixture water – n-butyl acetate for the Uniquac model). Any user performing simulation calculations for the process based on the VLLE must use these parameters as the other ones are not available.

2. THERMODYNAMICS MODELS

The activity coefficients in the liquid phase can be calculated by the NRTL (Eq. 1) and the Uniquac (Eq. 3) equations.

$$\ln\gamma_i = \frac{\sum_{j=1}^{N}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{N}G_{li}x_l} + \sum_{j=1}^{N}\frac{x_j G_{ij}}{\sum_{l=1}^{N}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{k=1}^{N}\tau_{kj}G_{kj}x_k}{\sum_{l=1}^{N}G_{lj}x_l}\right) \qquad \tau_{ji} = \frac{A_{ji}}{T} \qquad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{1}$$

In the basic version the NRTL equation has three adjustable parameters for each binary mixture (A_{ij}, A_{ji} and α_{ij}) fitted to the experimental equilibrium data. Such a form is applied in the present paper. For the LLE in Chemcad a more extended expression for the parameter τ_{ij} (Eq. 2) is used by the NRTL model. In this case a binary mixture is described by 7 coefficients.

$$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} + C_{ij}\ln(T) \tag{2}$$

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_i} + 5q_i\ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{N} x_j l_j - q_i\ln\sum_{j=1}^{N}\theta_j\tau_{ji} + q_i - q_i\ln\sum_{j=1}^{N}\frac{\theta_j\tau_{ij}}{\sum\limits_{k=1}^{N}\theta_k\tau_{kj}} \tag{3}$$

where:

$$\Phi_i = \frac{r_i x_i}{\sum\limits_{j=1}^{N} r_j x_j}, \quad \theta_i = \frac{q_i x_i}{\sum\limits_{j=1}^{N} q_j x_j}, \quad l_i = 5(r_i - q_i) - (r_i - 1), \quad \tau_{ij} = \exp\left(-\frac{A_{ij}}{T}\right) \tag{4}$$

This paper uses the basic version of the Uniquac equation with two adjustable parameters: A_{ij} and A_{ji}. For the LLE Chemcad uses also a more complicated expression for the parameter τ_{ij} (Eq. 5). Such binary mixture has six parameters.

$$\tau_{ij} = \exp\left(A_{ij} - \frac{B_{ij}}{RT} + C_{ij}\ln(T)\right) \tag{5}$$

3. CALCULATION OF THE NRTL AND UNIQUAC EQUATIONS PARAMETERS

The parameters of correlation equations should allow to describe the VLLE as precisely as possible. To achieve the best precision the minimised objective function *FC* given by Equation (6) was formulated. The function has a slightly different form than that used in the previous work (Wyczesany, 2010).

$$FC = \sum_{i=1}^{NLLE}\sum_{j=1}^{4}\sum_{k=1}^{2}(x_{\exp,k,j,i} - x_{cal,k,j,i})^2 + W1\sum_{i=1}^{NVLE}\sum_{j=1}^{4}(y_{\exp,j,i} - y_{cal,j,i})^2 + W2\sum_{i=1}^{NVLE}(T_{\exp,i} - T_{cal,i})^2 \tag{6}$$

The objective function uses *NLLE* experimental points for the LLE. The data may refer to the VLLE and the LLE for the given quaternary system. The first term of the function *FC* refers to both (aqueous and organic) phases and four components. Therefore, the index *k* changes from 1 to 2 and index *j* from 1 to 4. The second term of the objective function includes *NVLE* experimental points of the VLE and also relates to four components. The data may describe the VLLE and the VLE for the given quaternary system. The last term of the minimised objective function applies to 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 allow to fit better the calculated values (temperature or the composition of the gas phase or both liquid phases) to the experimental data. The calculated temperatures and mole fractions in both phases appearing in Eq. (6) represent the full VLLE. For additional experimental data referring to the VLE or the LLE the calculated mole fractions describe appropriate phase equilibrium.

In the classical approach the VLLE is calculated for known constant values of *T*, *P* and mole fractions z_i of the total mixture. Unfortunately, the applied experimental data do not give the values z_i but only mole fractions of each component in all the three phases. Also, the temperature is different for each experimental point. Therefore, the calculations of the VLLE were performed with the method described below.

The known values are represented by the pressure and mole fractions z_i of the total liquid phase. The z_i values correspond to the arithmetic mean values of the experimental concentrations of individual components in both liquid phases. The experimental temperature is treated in calculations as the initial one. For such defined values z_i and T the LLE is calculated according to Equations (7) - (8).

$$\beta = \frac{L_{aq}}{L}, \quad x_{aq,i} = \frac{z_i}{\dfrac{\gamma_{aq,i}}{\gamma_{org,i}} + \beta\left(1 - \dfrac{\gamma_{aq,i}}{\gamma_{org,i}}\right)}, \quad x_{org,i} = \frac{\gamma_{aq,i}}{\gamma_{org,i}} x_{aq,i} \tag{7}$$

$$\sum_{i=1}^{N} x_{aq,i} - \sum_{i=1}^{N} x_{org,i} = 0 = \sum_{i=1}^{N} \frac{z_i\left(1 - \dfrac{\gamma_{aq,i}}{\gamma_{org,i}}\right)}{\dfrac{\gamma_{aq,i}}{\gamma_{org,i}} + \beta\left(1 - \dfrac{\gamma_{aq,i}}{\gamma_{org,i}}\right)} \tag{8}$$

We search for such a value β for which the sums of the mole fractions in both phases equal 1. The problem is reduced to one Equation (8) with one unknown β and the equation is solved in an iterative process. Subsequently, for a known value of P and the mole fractions of both liquid phases (aqueous $x_{aq,i}$ and organic $x_{org,i}$) the two VLE are calculated. For this type of equilibrium the boiling temperature and the mole fractions y_i of the gas phase are computed. The last ones are defined by Eq. (9) in which the saturated vapour pressure of pure component P_i^s is calculated from the Antoine equation and the activity coefficients γ_i from Eqs. (1) or (3).

$$y_i = \frac{\gamma_i P_i^s x_i}{P} \tag{9}$$

If in the first step the y_i sum is less than 1, the temperature increases by 2%. In the opposite case it decreases by 2%. For a the new temperature the values γ_i, P_i^s, y_i and the y_i sum are calculated. If the last one is not sufficiently close to 1, the next iterations are performed with the Newton method according to Eq. (10). The iterations are continued till the difference between 1 and the y_i sum is smaller than 10^{-6}.

$$slope = \frac{T - T_{old}}{\sum y - \sum y_{old}}, \quad T_{new} = T - slope \cdot \left(\sum y - 1\right) \tag{10}$$

In the next step the temperatures calculated for both liquid phases are compared. If the difference between them is higher than 0.001 K, the temperature of the organic phase is taken as the new one for further calculations. Subsequently the LLE and the VLE for both liquid phases are computed. The iterations are performed until the difference between the temperatures in both gas phases is lower than 0.001 K. In the next step algorithm checks whether the differences between the mole fractions y_i computed for both liquid phases exceed the value 0.0001 for the same components. If so, the new temperature is assumed as the arithmetic mean of the values obtained for both liquid phases and the algorithm returns to the LLE and the VLE calculations for both liquid phases. If not, the VLLE is computed.

A similar procedure of the VLLE calculations was applied by Liu and co-workers (Liu et al., 1993). However, they used two different sets of the NRTL equation parameters for the calculation of the LLE and the VLE. They also assumed that equilibrium is reached when the difference in boiling points calculated for the two liquid phases is less than 0.7 K and if the differences between the mole fractions y_i for the corresponding components calculated for the two liquid phases are less than 0.0035.

For quaternary mixtures and the NRTL equation the minimised objective function has 18 parameters (A_{12}, A_{21}, A_{13}, A_{31}, A_{14}, A_{41}, A_{23}, A_{32}, A_{24}, A_{42}, A_{34}, A_{43}, α_{12}, α_{13}, α_{14}, α_{23}, α_{24} i α_{34}) and for the Uniquac equation 12 coefficients (A_{12}, A_{21}, A_{13}, A_{31}, A_{14}, A_{41}, A_{23}, A_{32}, A_{24}, A_{42}, A_{34}, A_{43}). The problem is very difficult to solve from the computational point of view, since the minimum value of the objective function strongly depends on the starting values of such a large number of unknowns. In practice the number of unknowns was reduced twice according to the following reasoning:

Quaternary mixtures considered in the work can be classified into two types. The first one contains: water, ethanol, and two hydrocarbons (cyclohexane + isooctane, cyclohexane + toluene, cyclohexane + n-heptane or n-hexane + toluene), while the second one: water, ethanol, acetone and methyl ethyl ketone (MEK) or n-butyl acetate as the forth component. The systems water - hydrocarbon, water - MEK and water - n-butyl acetate are binary mixtures with the miscibility gap. The coefficients of the NRTL and the Uniquac equations were presented in a previous work (Wyczesany, 2010) for the ternary mixtures water - ethanol - hydrocarbon (for each of the above hydrocarbons) and water - ethanol - MEK, water - acetone - MEK, water - ethanol - n -butyl acetate and water - acetone - n-butyl acetate. In this situation, it was assumed that for the quaternary system water - ethanol - cyclohexane - isooctane the binary parameters of the ternary mixture water - ethanol – cyclohexane (A_{12}, A_{21}, A_{13}, A_{31}, A_{23}, A_{32}, α_{12}, α_{13}, α_{23}) are known and the fitted parameters refer only to the binary mixtures of isooctane with the rest of components (A_{14}, A_{41}, A_{24}, A_{42}, A_{34}, A_{43}, α_{14}, α_{24}, α_{34}). We can also assume that the binary parameters of the ternary mixture water – ethanol – isooctane are known and we should fit the coefficients for binary mixtures of cyclohexane with the remaining three components. The situation is similar for mixtures containing water and MEK or water and n-butyl acetate. We can assume that we know the binary coefficients for the ternary system containing two immiscible substances and ethanol or acetone. The size of deviations between the measured and calculated values of the VLLE for quaternary mixture determines which the ternary system should be selected as the mixture with the known binary parameters. Minimisation of the objective function *FC* was performed using the procedure MINUIT (James, 1967). It should be noted that computation of the optimal values of nine or six parameters is still a difficult task and requires a very careful selection of the starting point. However, reducing by half the number of parameters makes the task much easier. Calculation of the parameters by the above methodology differs from that described in the previous paper (Wyczesany, 2010) and gives better results for both ternary and quaternary mixtures. Therefore, for the ternary mixtures used in this paper the binary coefficients were fitted by the method described above. The computed parameters were applied as sets of known coefficients for calculation of the binary parameters for the quaternary systems. The parameters calculated in the previous work were used in the same manner. In most cases a better fit was obtained for the new coefficients. The set of parameters obtained in this way was treated as a carefully selected starting point for calculation of all the 18 coefficients for the NRTL equation and 12 coefficients for the equation Uniquac. Such procedure allows of better fit these parameters, although the increase in accuracy is rather small.

4. RESULTS OF CALCULATION AND THEIR DISCUSSION

The following values are the accuracy criteria of correlation and prediction of VLLE: Δx and Δy - absolute mean deviations between experimental and calculated equilibrium compositions 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. (12)). The first one refers to all the four components in both liquid phases, the second one to four components in the gas phase.

$$\Delta x = \frac{1}{N}\sum_{i=1}^{NLLE}\left|x_{\exp,i} - x_{cal,i}\right|, \quad \Delta y = \frac{1}{N}\sum_{i=1}^{NVLE}\left|y_{\exp,i} - y_{cal,i}\right|, \quad \Delta T = \frac{1}{N}\sum_{i=1}^{NVLE}\left|T_{i,\exp} - T_{cal,i}\right| \tag{11}$$

$$\Delta X = \frac{1}{8}\sum_{i=1}^{4}\sum_{j=1}^{2}\Delta x_{j,i}, \quad \Delta Y = \frac{1}{4}\sum_{i=1}^{4}\Delta y_i \tag{12}$$

Table 1 presents the values *NLLE* and *NVLE* as well as the experimental temperature ranges for the systems considered in the paper. All the data are isobaric. The calculated values of the parameters for both considered equations are presented in Tables 2 and 3.

Table 1. Values of *NLLE*, *NVLE*, experimental temperature ranges and pressure for all the considered mixtures (water + ethanol + comp. 3 + comp. 4)

No.	comp. 3	comp. 4	*NLLE*	*NVLE*	*T* [K]	*P* [bar]	Ref.
1	cyclohexane	isooctane	55	55	336.62–350.68	1.013	Pequenin et al., 2010
2	cyclohexane	toluene	29	29	336.98-353.75	1.013	Pequenin et al., 2011 a
3	cyclohexane	n-heptane	39	39	335.40-350.55	1.013	Pequenin et al., 2011 b
4	n-hexane	toluene	25	25	331.68-351.65	1.013	Pequenin et al., 2011 c
5	acetone	MEK	25	25	343.75-346.95	1.013	Younis et al., 2007
6	acetone	n-butyl acetate	35	35	345.35-365.15	1.013	Younis et al., 2007
7	acetone	n-butyl acetate	30	30	334.15-355.15	0.80	Younis et al., 2007
8	acetone	n-butyl acetate	29	29	321.25-345.15	0.48	Younis et al., 2007

Table 2. Coefficients of the NRTL equation

	System							
	1	2	3	4	5	6	7	8
A_{12}	921.21	924.24	902.99	498.80	490.89	348.95	790.16	373.20
A_{21}	-270.91	-283.42	-269.24	59.785	-70.249	434.09	88.369	453.23
A_{13}	1597.6	1901.2	1407.3	2370.3	632.14	557.95	555.42	591.08
A_{31}	1375.7	1440.4	2507.8	1823.6	370.67	245.00	531.58	168.59
A_{14}	1149.5	1449.1	755.52	1520.7	1008.0	2917.9	1616.0	2917.5
A_{41}	1154.2	1071.3	1122.4	822.10	500.87	448.94	659.57	496.29
A_{23}	484.92	514.70	573.25	335.72	679.43	70.655	244.78	-275.39
A_{32}	750.88	814.87	645.19	818.97	-480.34	71.690	16.132	2932.8
A_{24}	639.17	423.33	770.04	410.85	377.15	-360.45	631.76	-243.57
A_{42}	777.84	469.78	967.06	550.17	-71.286	743.58	-138.70	609.29
A_{34}	380.43	170.67	681.27	101.09	-285.05	127.14	78.884	-235.29
A_{43}	-214.74	15.903	-407.74	121.77	573.85	-123.76	-51.990	1341.1
α_{12}	0.1460	0.1500	0.1420	0.3771	0.3129	0.6000	0.5479	0.6252
α_{13}	0.2622	0.2542	0.2494	0.1933	0.5239	0.5834	0.4775	0.1883
α_{14}	0.1976	0.3091	0.1522	0.3379	0.4296	0.2410	0.3390	0.2392
α_{23}	0.5089	0.4918	0.4935	0.5051	0.6999	0.1500	0.5381	0.2479
α_{24}	0.5480	0.4513	0.5291	0.5306	0.4863	0.1527	0.1857	0.2356
α_{34}	0.4527	0.2003	0.2503	0.2805	0.3273	0.1507	0.6988	0.7000

Table 3. Coefficients of the Uniquac equation

	System							
	1	2	3	4	5	6	7	8
A_{12}	200.88	98.686	198.70	-249.27	700.19	391.59	430.45	231.73
A_{21}	-7.6794	49.559	-18.524	913.54	-278.71	-158.52	-137.91	-43.737
A_{13}	4828.2	746.79	89.549	481.48	-123.38	29.093	44.535	-6.7337
A_{31}	1050.2	1670.8	1165.8	8195.3	599.61	156.18	208.09	231.87
A_{14}	2988.8	191.26	1045,0	61.536	67.032	56.713	52.366	1.9279
A_{41}	910.51	636.22	1439.1	612.19	282.93	524.96	566.11	624.31
A_{23}	-97.865	-95.989	41.883	-132.41	-187.37	-171.65	179.44	-196.48
A_{32}	561.44	575.47	430.39	647.63	4938.0	341.05	70.830	1453.1
A_{24}	-88.881	-115.20	-83.068	-98.747	-394.13	-70.788	147.61	92.358
A_{42}	537.06	496.87	563.49	516.66	8197.2	273.54	92.512	76.457
A_{34}	65.842	177.01	252.21	44.128	-236.24	-65.672	265.72	.63108
A_{43}	-40.477	-85.134	-164.01	20.692	1400.6	105.89	-131.64	15.131

Table 4. Mean deviations of VLLE prediction for water – ethanol – cyclohexane – isooctane system

	NRTL-Chemcad	Uniquac-Chemcad	NRTL-VLL	Uniquac-VLL
$\Delta x_{aq,1}$	0.0126	0.0166	0.0112	0.0197
$\Delta x_{aq,2}$	0.0213	0.0207	0.0067	0.0264
$\Delta x_{aq,3}$	0.0066	0.0042	0.0060	0.0034
$\Delta x_{aq,4}$	0.0038	0.0032	0.0094	0.0072
$\Delta x_{org,1}$	0.0115	0.0146	0.0063	0.0110
$\Delta x_{org,2}$	0.0525	0.0515	0.0099	0.0484
$\Delta x_{org,3}$	0.0267	0.0253	0.0057	0.0219
$\Delta x_{org,4}$	0.0356	0.0382	0.0088	0.0372
Δy_1	0.0111	0.0148	0.0105	0.0190
Δy_2	0.0066	0.0069	0.0034	0.0072
Δy_3	0.0127	0.0150	0.0108	0.0115
Δy_4	0.0056	0.0043	0.0059	0.0077
ΔX	0.0213	0.0218	0.0080	0.0219
ΔY	0.0090	0.0102	0.0077	0.0114
ΔT	0.32	0.84	0.15	0.14

Tables 4 - 7 present the mean deviations in predicting the VLLE for all the systems. For mixtures containing water – ethanol – cyclohexane – isooctane and water – ethanol – cyclohexane – toluene all the deviations Δx, Δy, ΔX, ΔY and ΔT are shown whereas for the remaining systems only the values ΔX, ΔY and ΔT are given. The following conclusions can be drawn. In almost every case the deviations are significantly smaller for the models in which the coefficients were fitted to the VLLE data (NRTL-VLL and Uniquac-VLL). The NRTL-VLL model is much more precise. For the three mixtures consisting of water - ethanol - hydrocarbons the mean deviation between the calculated and measured temperatures does not exceed 0.25 K, for the fourth mixture it equals 0.33 K. Also, the mean deviations between the calculated and the measured concentrations in the gas phase and the liquid phases, with one exception do not exceed 1 mole %. In the case of VLLE such an accuracy is really very high. The NRTL-VLL model is also the most precise one for mixtures containing MEK or n-butyl acetate in addition to water, ethanol and acetone, although the accuracy is no longer as good as in the case of water – ethanol – hydrocarbons mixtures. For the system containing MEK ΔT equals 0.5 and for mixtures containing n-butyl acetate this value is close to 1 K. Deviations ΔX are generally less than 1 mole % and the values ΔY exceed 1%. The models with coefficients taken from the Chemcad database (NRTL-Chemcad and Uniquac-Chemcad) give much poorer accuracy in spite of the fact that some of the binary mixtures are described by a larger number of parameters (Eq. (2) or (5)). Also in this case the NRTL model shows higher accuracy than the Uniquac equation. For systems containing MEK or n-butyl acetate the binary parameters for mixtures of these components and water taken from Chemcad related to the VLE instead of LLE. The deviations ΔX, ΔY and ΔT were smaller for this type of coefficients.

Sample figures show pseudoternary representations of the VLLE. In Figures 1 - 2 two hydrocarbons were combined in one pseudocomponent whereas in Figures 3 - 4 the pseudocomponents represent the sums of ethanol and acetone mole fractions. The experimental data of systems containing two hydrocarbons were measured for the four mixtures of a defined initial ratio $M = x_4/(x_3+x_4)$ (M = 0.2, 0.4, 0.6 and 0.8). The experimental data of systems containing ethanol and acetone also referred to four mixtures having the same values of the initial ratio M. However, in this case, the definition of M was as follows: $M = x_{acetone}/(x_{ethanol}+x_{acetone})$. In order to make the graphs clear, only the lines representing the experimental data and the models NRTL-VLL and NRTL-Chemcad were placed on them. In all the figures we can observe a significant advantage of the model for which the coefficients were fitted to the VLLE data. Lower accuracy obtained for the systems with MEK or n-butyl acetate with the models NRTL-VLL and Uniquac-VLL can be partly explained by the quality of the experimental data. Figure 4 shows that the experimental points representing the composition of the liquid organic phase are not lying on smooth but highly corrugated curves.

Table 5. Mean deviations of VLLE prediction for water – ethanol – cyclohexane – toluene system

	NRTL-Chemcad	Uniquac-Chemcad	NRTL-VLL	Uniquac-VLL
$\Delta x_{aq,1}$	0.0156	0.0204	0.0117	0.0176
$\Delta x_{aq,2}$	0.0360	0.0234	0.0064	0.0103
$\Delta x_{aq,3}$	0.0103	0.0104	0.0046	0.0057
$\Delta x_{aq,4}$	0.0162	0.0157	0.0084	0.0076
$\Delta x_{org,1}$	0.0431	0.0419	0.0102	0.0175
$\Delta x_{org,2}$	0.0645	0.0382	0.0083	0.0183
$\Delta x_{org,3}$	0.0382	0.0237	0.0073	0.0182
$\Delta x_{org,4}$	0.0690	0.0538	0.0094	0.0136
Δy_1	0.0105	0.0141	0.0094	0.0128
Δy_2	0.0173	0.0341	0.0056	0.0127
Δy_3	0.0367	0.0449	0.0144	0.0127
Δy_4	0.0130	0.0120	0.0098	0.0106
ΔX	0.0366	0.0284	0.0083	0.0136
ΔY	0.0194	0.0263	0.0098	0.0122
ΔT	0.31	0.68	0.24	0.29

An accurate prediction of temperature and concentrations of azeotropes is an important feature of a model. According to the experimental data quaternary azeotropes are not formed in the considered mixtures. However, we can observe the formation of ternary azeotropes listed in Table 8. The first four are heteroazeotropes, and the last two are homoazeotropes. A comparison of the experimental and calculated compositions and temperatures for azeotropes presented in Table 8 leads to the conclusion that again these models in which the coefficients were fitted to the VLLE data show higher precision.

The NRTL-VLL model is more accurate for mixtures containing isooctane, n-hexane or toluene, and the Uniquac-VLL model for mixtures containing cyclohexane and n-heptane. In reality the mixture water - ethanol - toluene forms homoazeotrope. The models NRTL-VLL and VLL-Uniquac predict the correct type of this azeotrope. However, models with the coefficients taken from Chemcad databank predict the occurrence of heteroazeotrope. This suggests that dehydration of ethanol by heterogeneous azeotropic distillation with toluene may be achieved, which in practice is not possible.

Table 6. Mean deviations of VLLE prediction for the following systems: a) water – ethanol – cyclohexane – n-heptane, b) water – ethanol – n-hexane – toluene and c) water – ethanol – acetone – MEK

system		NRTL-Chemcad [d]	Uniquac-Chemcad	NRTL-VLL	Uniquac-VLL
a	ΔX	0.0161	0.0170	0.0092	0.0154
	ΔY	0.0141	0.0186	0.0121	0.0150
	ΔT	0.26	0.54	0.17	0.12
b	ΔX	0.0302	0.0273	0.0086	0.0111
	ΔY	0.0290	0.0331	0.0099	0.0124
	ΔT	1.25	1.41	0.33	0.36
c	ΔX	0.0237	0.0309	0.0156	0.0177
	ΔY	0.0137	0.0151	0.0133	0.0175
	ΔT	0.71	2.11	0.50	0.39

[d] for system (c) parameters describe the VLE for all binary mixtures

Table 7. Mean deviations of VLLE prediction for water – ethanol – acetone – n-butyl acetate system

P, bar		NRTL-Chemcad [a]	Uniquac-Chemcad	NRTL-VLL	Uniquac-VLL
1.013	ΔX	0.0186	0.0317	0.0060	0.0066
	ΔY	0.0326	0.0349	0.0118	0.0114
	ΔT	2.65	2.92	1.08	1.10
0.8	ΔX	0.0173	0.0281	0.0064	0.0058
	ΔY	0.0232	0.0264	0.0192	0.0216
	ΔT	1.18	0.80	0.95	0.85
0.48	ΔX	0.0182	0.0292	0.0093	0.0080
	ΔY	0.0325	0.0366	0.0185	0.0167
	ΔT	1.68	2.08	0.97	1.03

[a] parameters describe the VLE for all binary mixtures

For homoazeotrope water - ethanol - MEK models with coefficients taken from Chemcad predicted correctly the type of azeotrope, but the temperature and concentrations were obtained with poor precision. The models NRTL-VLL and Uniquac-VLL do not predict the formation of this homoazeotrope at all. However, the coefficients of the last two models were fitted to the experimental VLLE data, but concentrations at these equilibria are significantly different from the composition of the homoazeotrope of this particular system. The values of the correlation equations coefficients fitted to the experimental VLLE data are the result of a compromise between the accuracy of the VLE and LLE description and they are not able to predict concentrations significantly different from the VLLE compositions with high accuracy.

Table 8. Comparison of experimental and calculated temperatures and compositions of ternary azeotropes

	exper.	NRTL-VLL	Uniquac-VLL	NRTL-Chemcad	Uniquac-Chemcad	Ref.
water	0.188	0.170	0.183	0.151	0.162	Gomis et al., 2005
ethanol	0.292	0.303	0.295	0.325	0.316	
cyclohexane	0.520	0.525	0.522	0.524	0.522	
T, K	335.60	335.55	335.61	335.41	335.95	
water	0.198	0.206	0.217	0.192	0.203	Font et al., 2003
ethanol	0.436	0.438	0.438	0.445	0.439	
isooctane	0.366	0.356	0.345	0.362	0.358	
T, K	341.85	341.89	342.00	342.10	342.52	
water	0.105	0.124	0.110	0.129	0.130	Gomis et al., 2007
ethanol	0.236	0.240	0.270	0.242	0.249	
n-hexane	0.658	0.636	0.620	0.629	0.621	
T, K	329.20	329.53	329.61	330.18	330.55	
water	0.205	0.196	0.210	0.188	0.175	Gomis et al., 2006
ethanol	0.432	0.441	0.436	0.457	0.471	
n-heptane	0.363	0.363	0.355	0.355	0.354	
T, K	341.83	341.83	342.06	341.83	342.05	
water	0.332	0.271	0.199	0.263	0.270	Gomis et al., 2008
ethanol	0.412	0.474	0.604	0.468	0.457	
toluene	0.256	0.255	0.198	0.269	0.273	
T, K	347.60	347.68	347.24	346.08	346.40	
water	0.3124	-	-	0.222	0.245	Szanyi et al., 2004
ethanol	0.1555	-	-	0.232	0.210	
MEK	0.5321	-	-	0.546	0.545	
T, K	346.35	-	-	345.56	345.55	

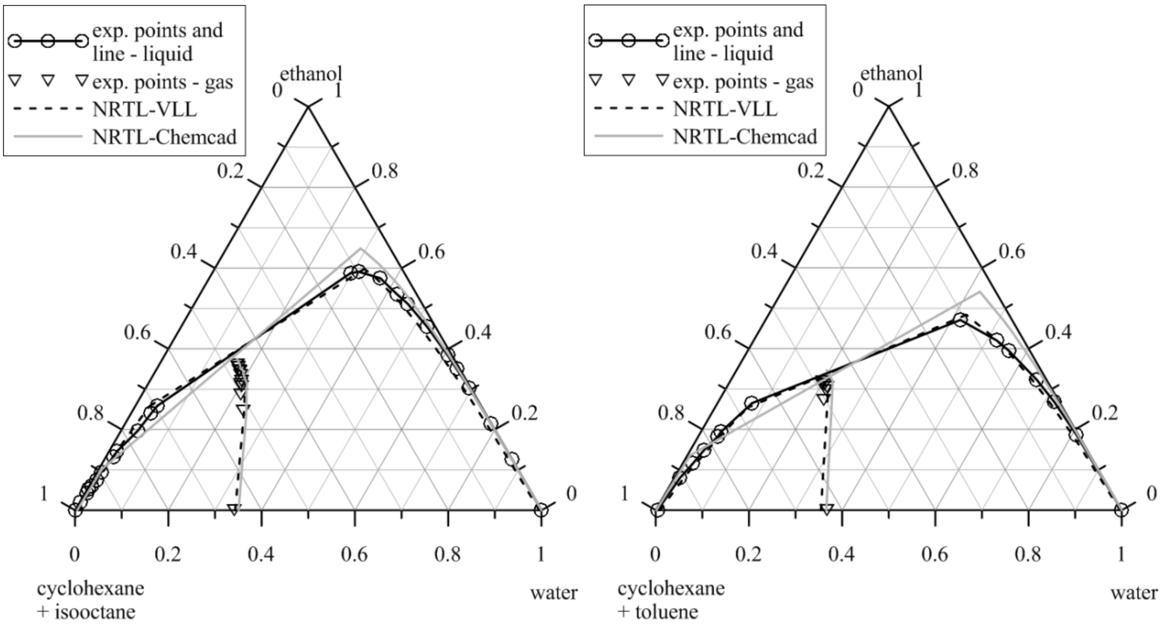

Fig. 1. Experimental and calculated pseudoternary VLLE for water – ethanol – cyclohexane - isooctane ($M = 0.4$) and water – ethanol – cyclohexane - toluene ($M = 0.4$) systems

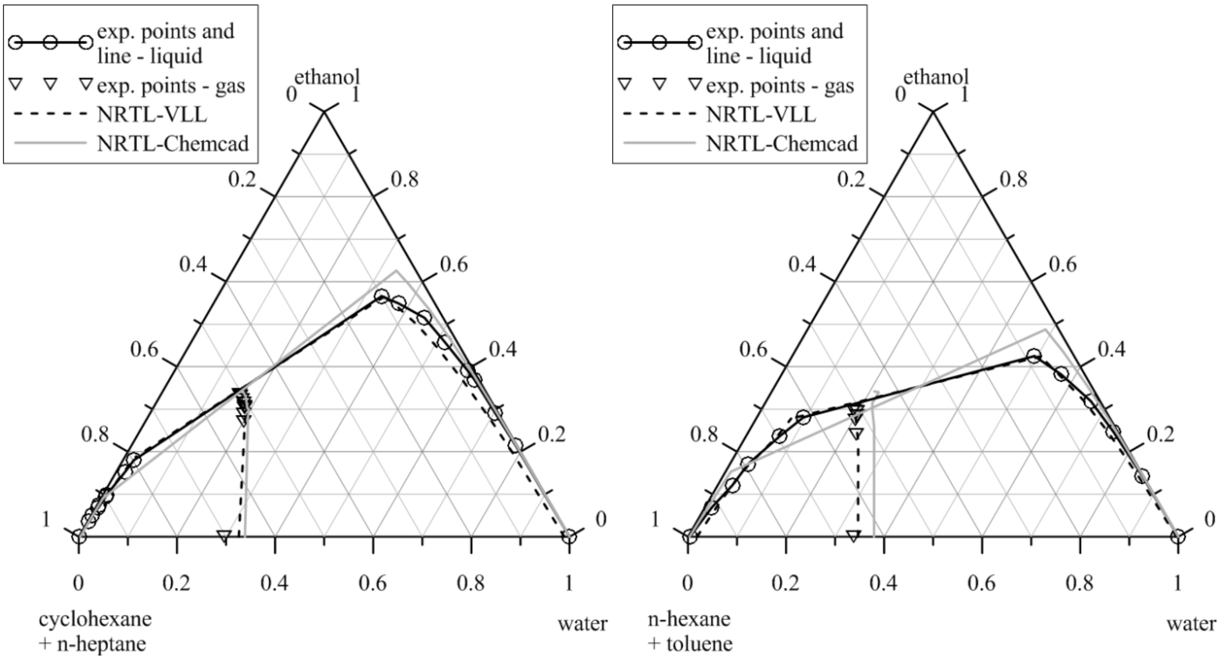

Fig. 2. Experimental and calculated pseudoternary VLLE for water – ethanol – cyclohexane – n-heptane ($M = 0.2$) and water – ethanol – n-hexane - toluene ($M = 0.6$) systems

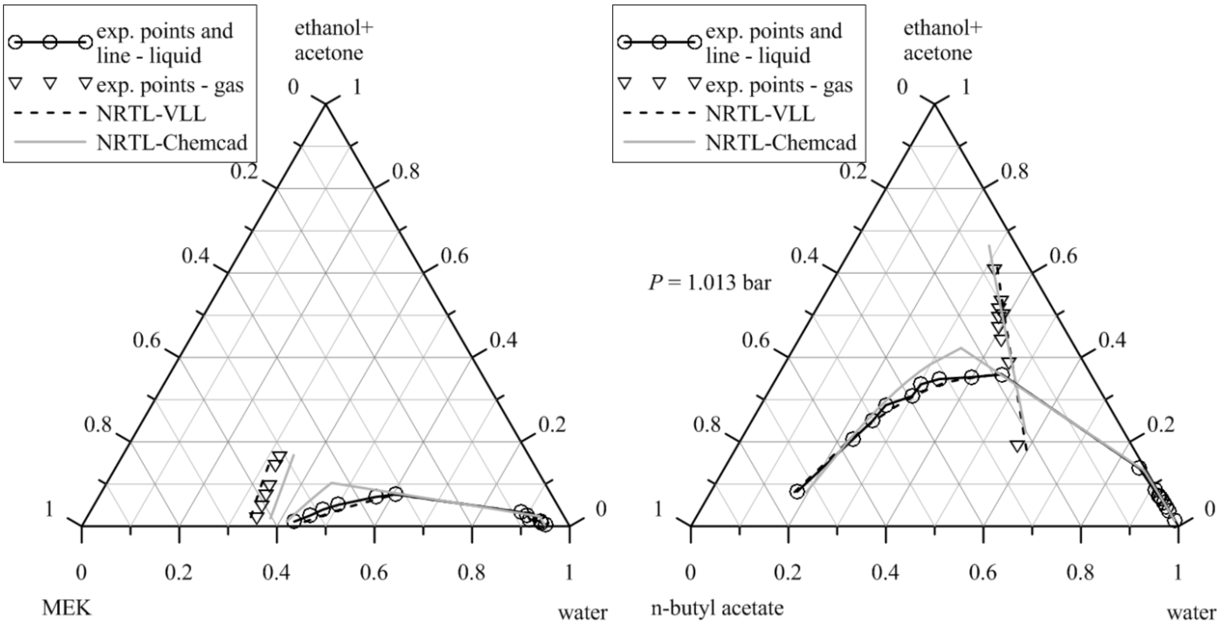

Fig. 3. Experimental and calculated pseudoternary VLLE for water – ethanol – acetone - MEK ($M = 0.4$) and water – ethanol – acetone – n-butyl acetate ($M = 0.4$) systems

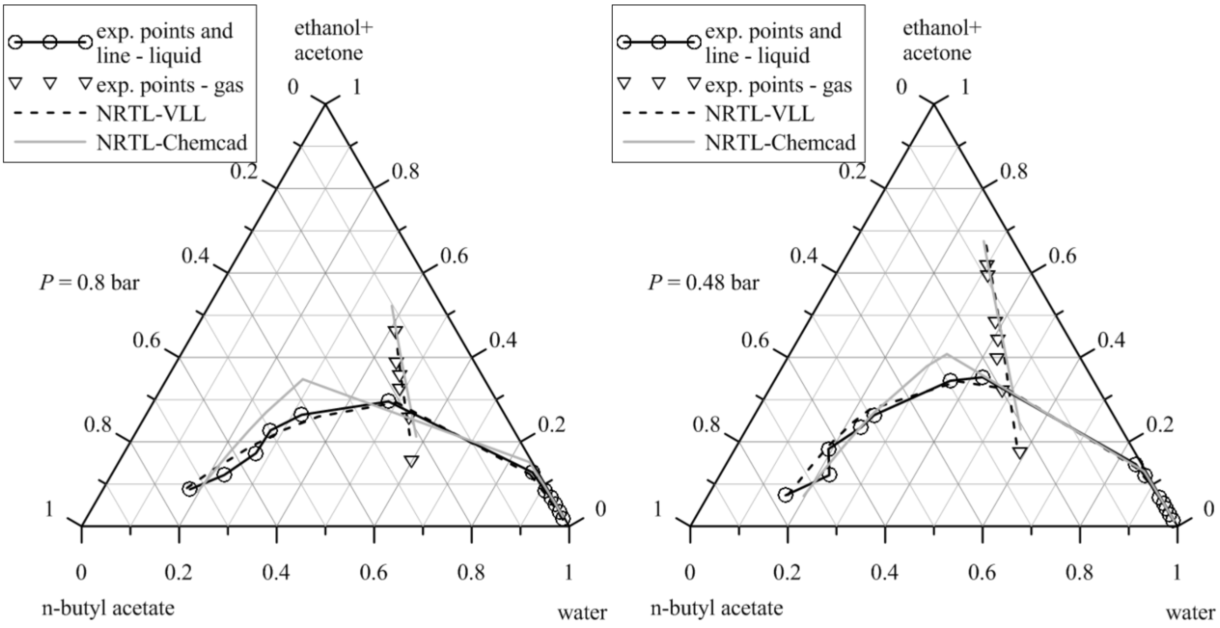

Fig. 4. Experimental and calculated pseudoternary VLLE for water – ethanol – acetone – n-butyl acetate system. For P = 0.8 bar M = 0.2, and for P = 0.48 bar M = 0.6

5. CONCLUSIONS

For each experimental point the minimised objective function *FC* calculates the full VLLE and it can compute the VLE or the LLE when such types of data are used. The function is flexible because it has two weight parameters *W1* and *W2*. They allow to fit the calculated equilibrium temperatures and compositions of the VLE and the LLE to the experimental data with a varying degree of accuracy. The parameters *W1* and *W2* are chosen by a trial and error method to get the best fit. In the case of the NRTL equation a quaternary system is described by 18 parameters and in the case of the Uniquac model by 12 coefficients. In the first stage of parameter fitting the number of these coefficients was halved by treating the previously calculated parameters for the ternary mixtures (being the part of the considered quaternary system) as known values. The coefficients obtained in this way were used in the second stage as a carefully selected starting point for the calculation of all the 18 or 12 parameters. The calculated coefficients more precisely described the VLLE than in the first stage, but the accuracy increased only slightly. A comparison of the calculated results with the experimental data for all the four investigated models shows that in almost every case the deviations Δx, Δy, ΔX, ΔY and ΔT are the lowest for the models NRTL-VLL and Uniquac-VLL, with a significant predominance of the former. For the first four systems (water - ethanol - two hydrocarbons) the prediction accuracy is really high. In three cases ΔT does not exceed 0.25 K and for the fourth system it equals 0.33 K. Also, the deviations ΔX and ΔY, with one exception do not exceed 1 mole %. The Model NRTL-VLL is also the most precise one for mixtures of water, ethanol and acetone with MEK or n-butyl acetate, although the accuracy is no longer as high as in the case of mixtures containing water, ethanol and two hydrocarbons. The deviation ΔT equals 0.5 for the system containing MEK, and for the mixtures with n-butyl acetate this value is slightly less than 1 K. In most cases the values ΔX are less than 1 mole %, whereas the deviations ΔY do not exceed 2 %. The models with the coefficients taken from Chemcad have a much worse accuracy. But also in this case higher accuracy of the NRTL equation can be observed. Figures showing the pseudoternary VLLE confirm high accuracy of the NRTL-VLL model. They also indicate that a slightly worse fitting of the coefficients for the systems containing MEK or n-butyl acetate may be explained by the quality of the experimental data. Figure 4 shows that the experimental points representing the composition of the liquid organic phase are not lying on smooth but highly corrugated curves. In the case of temperature and composition predicting for ternary azeotropes (which can be formed in the considered quaternary mixtures) the models NRTL-VLL and Uniquac-VLL are also much more accurate than those using the coefficients from the Chemcad database. Models with parameters fitted to the VLLE data correctly predict that the mixture of water - ethanol - toluene forms homoazeotrope. Models using the coefficients from the Chemcad database predict that this ternary mixture can form heteroazeotrope, suggesting that ethanol could be dehydrated by heterogenic azeotropic distillation with toluene, which is not possible in practice. These models correctly predict that the system water - ethanol – MEK can form homoazeotrope, but the temperature and compositions are calculated with poor precision. On the contrary, the models NRTL-VLL and Uniquac-VLL do not predict the formation of this homoazeotrope. This phenomenon may be explained by the fact that the coefficients of these last two models were fitted to the experimental VLLE data, but concentrations at these equilibria are significantly different from the composition of the homoazeotrope of this particular system.

SYMBOLS

A_{ij}, A_{ji}	parameters of the NRTL and the Uniquac equations, K
FC	objective function
N	number of experimental points
P	total pressure, bar
P_i^s	saturated vapour pressure of pure component *i* at *T*, bar
q	van der Waals molecular surface area parameter
R	gas constant, J/(mol · K)
r	van der Waals molecular volume parameter
T	temperature, K
ΔT	absolute 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
ΔX, ΔY	mean deviation defined in Equation (12)
Δx, Δy	absolute mean deviation between experimental and calculated equilibrium composition in the liquid and the vapour phase, respectively
z	mole fraction of component *i* in the entire mixture or in the entire liquid phase

Greek symbols

α_{ij}	parameter of the NRTL equation
β	aqueous phase fraction in total liquid
γ_i	activity coefficient of species *i*

Subscripts

exp	experimental
cal	calculated
aq	aqueous phase
org	organic phase

REFERENCES

Abrams D.S., Prausnitz J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.*, 21, 116-128. DOI: 10.1002/aic.690210115.

Asensi J.C., Molto J., del Mar Olaya M., Ruiz F., Gomis V., 2002. Isobaric vapour – liquid equilibria data for the binary system 1-propanol + 1-pentanol and isobaric vapour – liquid – liquid equilibria data for the ternary system water + 1-propanol + 1-pentanol at 101.3 kPa. *Fluid Phase Equil.*, 200, 287-293. DOI: 10.1016/S0378-3812(02)00040-7.

Chemcad VI. Process Flowsheet Simulator, v. 6.4.0.5052, Chemctations Inc., Huston 2010.

Font A., Asensi J.C., Ruiz F., Gomis V., 2003. Application of isooctane to the dehydration of ethanol. Design of a column sequence to obtain absolute ethanol by heterogeneous azeotropic distillation. *Ind. Eng. Chem. Res.*, 42, 140-144. DOI: 10.1021/ie0204078.

Gomis V., Front A., Pedraza R., Saquete M.D., 2005. Isobaric vapor – liquid and vapor – liquid – liquid equilibrium data for the water + ethanol + cyclohexane system. *Fluid Phase Equil.*, 235, 7-10. DOI: 10.1016/j.fluid.2005.07.015.

Gomis V., Front A., Saquete M.D., 2006. Vapour – liquid – liquid and vapour – liquid equilibrium of the system water + ethanol + heptane at 101.3 kPa. *Fluid Phase Equil.*, 248, 206 – 210. DOI: 10.1016/j.fluid.2006.08.012.

Gomis V., Front A., Pedraza R., Saquete M.D., 2007. Isobaric vapor – liquid and vapor – liquid – liquid equilibrium data for the water – ethanol – hexane system. *Fluid Phase Equil.*, 259, 66-70. DOI: 10.1016/j.fluid.2007.04.011.

Gomis V., Front A., Saquete M.D., 2008. Homogenity of the water + ethanol + toluene azeotrope at 101.3 kPa. *Fluid Phase Equil.*, 266, 8-13. DOI: 10.1016/j.fluid.2008.01.018.

Grigiante M., Stringari P., Scalabrin G., Ihmels E.C., Fischer K., Gmehling J., 2008. (Vapour + liquid + liquid) equilibria and excess molar enthalpies of binary and ternary mixtures of isopropanol, water, and propylene. *J. Chem. Therm.*, 40, 537-548. DOI: 10.1016/j.jct.2007.12.002.

Hsieh C.T., Lee M.J., Lin H.M., 2006. Multiphase equilibria for mixtures containing acetic acid, water, propylene glycol monomethyl ether, and propylene glycol methyl ether acetate. *Ind. Eng. Chem. Res.*, 45, 2123-2130. DOI: 10.1021/ie051245t.

Hsieh C.T., Ji W.Y., Lin H.M., Lee M.J., 2008. Multiphase equilibria for mixtures containing water, acetic acid, propionic acid, methyl acetate and methyl propionate. *Fluid Phase Equil.*, 271, 69-75. DOI: 10.1016/j.fluid.2008.07.004.

James F., 1967. *FOWL, CERN Program Library, program D506*. Available at http://c-minuit.sourceforge.net.

Kosuge H., Iwakabe K., 2005. Estimation of isobaric vapor – liquid – liquid equilibria for partially miscible mixture of ternary system. *Fluid Phase Equil.*, 233, 47-55. DOI: 10.1016/j.fluid.2005.04.010.

Kundu D., Banerjee T., 2011. Multicomponent vapor – liquid – liquid equilibrium prediction using an a priori segment based model. *Ind. Eng. Chem. Res.*, 50, 14090-14096. DOI: 10.1021/ie201864y.

Lee L.S., Chen W.C., Huang J.F., 1996. Experiments and correlations of phase equilibria of ethanol – ethyl acetate – water ternary mixture. *J. Chem. Eng. Jap.*, 29, 427-438.

Liu F.Z., Mori H., Hiraoka S., Yamada I., 1993. Phase equilibria and simulation method for beterogeneous azeotropic distillation. *J. Chem. Eng. Jap.*, 26, 41-47.

Pequenin A., Asensi J.C., Gomis V., 2010. Isobaric vapor-liquid-liquid equilibrium for the quaternary system water-ethanol-cyclohexane-isooctane at 101.3 kPa. *J. Chem. Eng. Data*, 55, 1227-1231. DOI: 10.1021/je900604a.

Pequenin A., Asensi J.C., Gomis V., 2011a. Vapor-liquid-liquid equilibrium and vapor-liquid equilibrium for the quaternary system water-ethanol-cyclohexane-toluene and the ternary system water-cyclohexane-toluene. Isobaric experimental determination at 101.3 kPa. *Fluid Phase Equil.*, 309, 62-67. DOI: 10.1016/j.fluid.2011.06.033.

Pequenin A., Asensi J.C., Gomis V., 2011b. Quaternary isobaric (vapor-liquid-liquid) equilibrium and (vapor-liquid) equilibrium for the system water-ethanol-cyclohexane-heptane at 101.3 kPa. *J. Chem. Therm.*, 43, 1097-1103. DOI: 10.1016/j.jct.2011.02.016.

Pequenin A., Asensi J.C., Gomis V., 2011c. Experimental determination of quaternary and ternary isobaric vapor-liquid-liquid equilibrium and vapor-liquid equilibrium for the systems water-ethanol-hexane-toluene and water-hexane-toluene at 101.3 kPa. *J. Chem. Eng. Data*, 56, 3994-3998. DOI: 10.1021/je2002072.

Renon H., Prausnitz J.M., 1968. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.*, 14, 135-144. DOI: 10.1002/aic.690140124.

Ruiz F., Gomis V., Botella R.F., 1987. Extraction of ethanol from aqueous solution. 1. Solvent less volatile than ethanol: 2-ethylhexanol. *Ind. Eng. Chem. Res.*, 26, 696-699.

Szanyi A., Mizsey P., Fonyo Z., 2004. Novel hybrid separation processes for solvent recovery based on positioning the extractive heterogeneous-azeotropic distillation. *Chem. Eng. Process.*, 43, 327–338. DOI: 10.1016/S0255-2701(03)00132-6.

Wyczesany A., 2010. Calculation of vapour-liquid-liquid equilibria. *Chem. Proc. Eng.*, 31, 333-353.

Ye K., Freund H., Sundmacher K., 2011. Modelling (vapour + liquid) and (vapour + liquid + liquid) equilibria of {water (H_2O) + methanol (MeOH) + dimethyl ether (DME) + carbon dioxide (CO_2)} quaternary system using the Peng – Robinson Eos with Wong – Sandler mixing rule. *J. Chem. Therm.*, 43, 2002-2014. DOI: 10.1016/j.jct.2011.07.016.

Younis O.A.D., Pritchard D.W., Anwar M.M., 2007. Experimental isobaric vapour-liquid-liquid equilibrium data for the quaternary systems water (1)-ethanol (2)-acetone (3)-n-butyl acetate (4) and water (1)-ethanol (2)-acetone (3)-methyl ethyl ketone (4) and their partially miscible-constituent ternaries. *Fluid Phase Equil.*, 251, 149-160. DOI:10.1016/j.fluid.2006.11.011.

Received 26 June 2012
Received in revised form 05 September 2012
Accepted 07 September 2012