# Simulation of Toluene Extractive Distillation from a Mixture with Heptane\*

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Comparison of simulated equilibrium data and extractive distillation simulations accomplished by the use of different model parameters sources is presented. Sets of experimental binary vapourliquid and liquid-liquid equilibrium data were used to estimate the binary parameters of the NRTL model equation. Furthermore, UNIFAC method predicted binary NRTL parameters were obtained from the HYSYS simulation environment.

Both sets of model parameters were used to model the vapour-liquid equilibrium of ternary mixture containing heptane, toluene, and *N*-methylpyrrolidone (NMP). The influence of the NRTL model parameters on the efficiency of extractive distillation unit used for toluene separation from a mixture with heptane in the presence of NMP was further investigated.

Simulation of extractive distillation column gave similar results for both sets of NRTL model parameters when the use of a large quantity of extractive solvent was assumed. However, for solvent to feed ratio lower than 3, higher separation efficiency of the column was observed for original model parameters compared to HYSYS supplied ones. This fact seems to correlate with the feed component's relative volatility variation with the amount of extractive solvent present in the mixture.

It was found that the source of model parameters influences essentially the quality of binary and ternary equilibria prediction. Important differences between experimental and modelled equilibrium data could be expected when unreliable model parameters are used. Especially, model parameters predicted by the UNIFAC LLE method gave mistaken liquid-liquid and vapour-liquid equilibrium data fit. As a consequence, at certain simulation conditions the choice of improper phase-equilibrium model parameters led to wrong separation unit design.

Aromatics are valuable intermediates in chemical industry. Although their content in crude does not exceed a few percent, naphtha is their principal source. Benzene, toluene, and xylenes (BTX fraction) are produced via pyrolysis and reforming of different naphtha fractions obtained from oil by fractional distillation. The reactions occurring during these processes are too fast to be fully controlled and, therefore, a mixture of different hydrocarbons is obtained. The content of aromatics varies upon the reaction conditions; still, in order to get pure BTX aromatics, it should be separated from the remaining hydrocarbons [1]. The other reasons for aromatics separation from reformat fuel are the successively stringent requirements on the fuel aromatics content. BTX fraction is believed to be the main source of polyaromatic hydrocarbons produced inside the car engines and emitted to the environment. Thus, according to European Union legislation, since

January 2005 the content of aromatic hydrocarbons in fuels for spark-ignition engines should fall below 30 % and that of benzene should not exceed 1 % [2].

In case of aromatics—nonaromatics mixtures separation, fractional distillation is of limited use only, due to similarity of the mixture components' boiling points. Moreover, various azeotropes restrain required hydrocarbons separation, *e.g.* benzene forms azeotropic mixtures with variety of nonaromatics and oxygenates [3]. Therefore, other separation processes for aromatics recovery were developed, of which liquidphase extraction is successfully employed for this purpose. Probably, the most widespread extraction process used for aromatics separation nowadays is SUL-FOLANE process introduced in [1, 4].

An alternative to extraction, namely extractive distillation, was proposed combining advantages of both liquid-phase extraction and distillation. As in the case

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of extraction, addition of a solvent (entrainer) to the original mixture is needed. However, different properties of the entrainer are required compared to the solvent used in liquid-phase extraction [5]. Subsequently, the mixture containing solvent undergoes fractional distillation.

In the case of hydrocarbons mixture separation, extractive solvent is a polar compound, thus exhibiting higher affinity to the mixture components with higher polarity – aromatics. Due to its low volatility, the presence of extractive solvent in the mixture causes the rise of the relative volatility of the nonpolar mixture components, *i.e.* nonaromatics. Basic information about this separation procedure was given in [6].

In this study, a system composed of alkane (heptane), aromatic compound (toluene), and a solvent (Nmethylpyrrolidone) was chosen with the aim to model the vapour-liquid equilibrium in an extractive distillation column. Based on experimental binary equilibrium data measured within the temperature interval of 40—60 °C, binary parameters of the NRTL equation were obtained. Subsequently, they were used to predict the ternary equilibria and to simulate extractive distillation of the above-mentioned mixture. Then, the same simulation procedure was carried out using a set of alternative NRTL parameters supplied by the HYSYS simulation program.

#### THEORETICAL

Ideal behaviour of the vapour phase was considered, as relatively low total pressure, P = 12 kPa, for all simulations was assumed. This value of the total pressure reflects the conditions, at which the experimental equilibrium data were obtained. Then, the vapour-liquid equilibrium could be described by the modified Raoult law equation

$$Py_i = P_i^{\mathbf{o}} x_i \gamma_i \qquad i = 1, 2, \dots, K \tag{1}$$

where P represents the total pressure,  $P_i^{\text{o}}$  vapour pressure of the pure component i,  $\gamma_i$  its activity coefficient, x and y the component's liquid- and gas-phase mole fraction, respectively, and K the number of mixture components.

Vapour pressure of pure components was calculated using semiempiric Antoine equation in the form

$$\log(P^{\circ}/\mathrm{kPa}) = A - B/(C + t/^{\circ}\mathrm{C})$$
(2)

A, B, and C are the parameters and t temperature.

When describing the liquid-liquid equilibrium, isoactivity condition must be fulfilled

$$a_{i1} = a_{i2}$$
  $x_{i1}\gamma_{i1} = x_{i2}\gamma_{i2}$   $i = 1, 2, \dots, K$  (3)

 $a_{ij}$  being the *i*-th component's activity in the *j*-th equilibrium liquid phase.

In order to evaluate components' activity coefficients variation with the mixture composition, the NRTL model [7] was chosen

$$\ln \gamma_{i} = \frac{\sum_{j=1}^{K} \tau_{ji} G_{ji} x_{j}}{\sum_{l=1}^{K} G_{li} x_{l}} + \sum_{j=1}^{K} \frac{G_{ij} x_{j}}{\sum_{l=1}^{K} G_{lj} x_{l}} \left( \tau_{ij} - \frac{\sum_{n=1}^{K} \tau_{nj} G_{nj} x_{n}}{\sum_{l=1}^{K} G_{lj} x_{l}} \right)$$
$$i = 1, 2, \dots, K$$
(4)

The model parameters  $\tau_{ij}$  and  $G_{ij}$  are defined as follows

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$$
$$i, j = 1, 2, \dots K \quad i \neq j \tag{5}$$

 $g_{ij}$  being the interaction parameter between the molecules *i* and *j*, *R* gas constant, *T* absolute temperature, and  $\alpha_{ij}$  nonrandomness model parameter.

To improve the experimental data fit, variation of interaction parameters with temperature was assumed in the form

$$g_{ij} - g_{jj} = D + ET \quad i, j = 1, 2, \dots K \quad i \neq j \quad (6)$$

where D and E are the model parameters and T absolute temperature.

#### EXPERIMENTAL

Antoine equation parameters of the model mixture components were found in the literature [8, 9] as shown in Table 1. Vapour-liquid equilibrium (VLE) data of the binary systems heptane—toluene and toluene— N-methylpyrrolidone at three temperatures, namely 40 °C, 50 °C, and 60 °C, as well as the liquid-liquid equilibrium (LLE) and available VLE data of the system heptane—N-methylpyrrolidone were taken from experiments described elsewhere [10—13] (see Table 2).

For fully miscible systems heptane—toluene and toluene—NMP, the model parameters were calculated from the isothermal P-x and/or P-x, y equilibrium data by minimization of the objective function, F. For N experimental points the objective function adopts the form

$$F = \sum_{k=1}^{K} \left( x_1 - x_{\text{calc},1} \right)_k^2 + \sum_{k=1}^{K} \left( \frac{P - P_{\text{calc}}}{P} \right)_k^2 \quad (7)$$

 Table 1. Antoine Equation Parameters of the Mixture Components

Antoine equation parameters	Heptane $[8]$	Toluene [8]	NMP [9]
Α	6.02633	6.08627	6.43532
B	1268.583	1349.122	1846.874
C	217.096	219.996	214.131

 Table 2. Sources of Experimental Binary VLE and LLE Data

Dimension	Temperature, $t/{}^{\circ}\!\mathrm{C}$		
Binary system	40	50	60
Heptane—toluene Heptane—NMP Toluene—NMP	[10] LLE, [13]	[11] VLE [11] [13]	$[12] \\ [12] \\ [13]$

For each binary system, this optimization problem was solved for the three sets of isothermal (40 °C, 50 °C, and 60 °C) vapour-liquid equilibrium data simultaneously using the maximum likelihood method [14]. For the two binary systems nonrandomness parameter  $\alpha_{ij}$ was set to 0.3, a value typical for binaries not presenting an important deviation from the ideal behaviour.

The NRTL model parameters of the third binary system, heptane—NMP, were estimated from the component's mutual solubility measured within the temperature range of  $29.9 \,^{\circ}\text{C}$ — $53.1 \,^{\circ}\text{C}$  [11]. Similar optimization procedure was applied for the model parameters estimation as previously. For this binary system, the objective function was defined as follows

$$F = \sum_{k=1}^{K} (x_{11} - x_{\text{calc},11})_k^2 + \sum_{k=1}^{K} (x_{12} - x_{\text{calc},12})_k^2 \quad (8)$$

In this case, the nonrandomness model parame-

ter  $\alpha_{ij} = 0.4$  was assumed reflecting the liquid phase strong nonideality. The set of model parameters obtained by the direct fitting of experimental data is hereinafter denoted as the original one.

HYSYS simulation engine supplied the second set of binary NRTL model parameters. Only the binary parameters corresponding to the system heptane toluene were directly available in the HYSYS (DECHEMA) database. Remaining binary parameters were either UNIFAC LLE (heptane—NMP) or UNIFAC VLE (toluene—NMP) predicted [15]. Table 3 summarizes both sets of the NRTL model parameters.

# **RESULTS AND DISCUSSION**

For the sake of brevity, just the equilibrium data for the binary system heptane—NMP at 50 °C are presented. Serious differences between the two predicted vapour-liquid-liquid equilibria could be seen in Fig. 1. Both, original and HYSYS supplied, sets of NRTL model parameters were able to predict the immiscibility region. However, the position of immiscibility region calculated for the two parameters' sets overlapped only partially. Moreover, a great difference between the vapour pressures of the predicted vapour-liquid-liquid equilibria was found. When using the original model parameters the vapour pressure of about 17 kPa was obtained; meanwhile, the value calculated for the HYSYS supplied parameters was P =11.39 kPa.

These differences were caused by the values of model parameters used. Original ones were obtained by the direct fitting of experimental data. Meanwhile, the HYSYS supplied binary parameters for the system heptane—NMP were UNIFAC predicted; thus, less precise. Accuracy of the liquid-liquid equilibria fit for the same binary system is shown in Fig. 2. One can observe that the UNIFAC prediction does not match with the experimental data at all.

Fig. 3 shows the flow sheet of an extractive distil-

 Table 3. Binary Model Parameters and Objective Function Values Estimated from Experimental Data and Model Parameters

 Supplied by the HYSYS Simulation Program

		Binary system		
	Heptane-toluene	Heptane-NMP	Toluene—NMP	
	Parameters and o	bjective function values derived	from the equilibrium data	
$g_{ij} - g_{jj}$	$43.0068 - 0.1877 \times T$	$6700 - 17.315 \times T$	904.6165 + 0.0711  imes T	
$g_{ji} - g_{ii}$	$225.1605 + 0.1805 \times T$	4000 - 9.1  imes T	-381.9910 - 0.0420  imes T	
$\alpha_{ij}$	0.3	0.4	0.3	
F	$1.889 imes10^{-3}$	$7.342 imes10^{-3}$	$1.617 imes 10^{-3}$	
	Parame	eters supplied by the HYSYS sin	nulation program	
$g_{ij} - g_{jj}$	-160.0340	-480.8750	734.9159	
$g_{ji} - g_{ii}$	425.1932	2468.5830	-456.5560	
$\alpha_{ij}$	0.302	0.2	0.3	



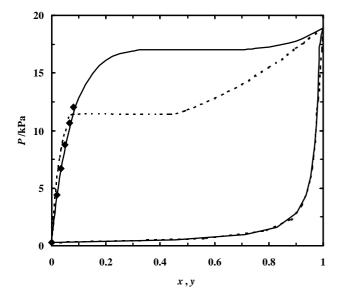


Fig. 1. Experimental (symbols) [11] and NRTL modelled (solid line – original parameters, dotted line – HYSYS prediction) VLE data of the binary system heptane—NMP at 50 °C.

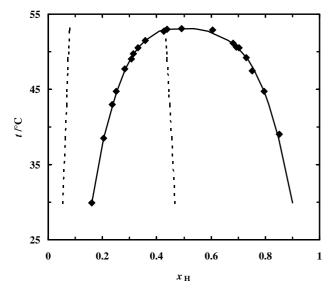


Fig. 2. Experimental (symbols) [11] and modelled (solid line – original parameters, dotted line – HYSYS prediction) LLE data of the binary system heptane—NMP.

lation column for toluene separation from a mixture with heptane using NMP as an extractive solvent. For this purpose HYSYS simulation program (version 2.1) was used. Counter-current flow of feed and extractive solvent within the distillation column was assumed in order to improve the contact of NMP with separated mixture. Extractive solvent is effective only in the liquid phase and, being the least volatile component of all, it is present primarily in the liquid phase flowing from the column top downwards [1]. Therefore, the inlet tray for NMP was situated at the fifth stage

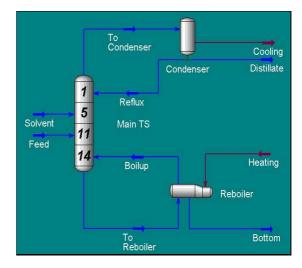


Fig. 3. HYSYS flow sheet of extractive distillation column.

counting from the column top, allowing good contact of the extractive solvent with the separated mixture, but not as close to the column top to get NMP in the distillate. Reflux ratio, RR = 3, was selected according to preliminary calculations. This value allowed optimum contact of the vapour and liquid phases preserving good separation efficiency of the column. Liquid backflow was formed in a total condenser situated at the column top. The amount of distillate corresponded to the input molar flow of heptane in the feed. Bottom product, containing main portion of toluene and practically all the extractive solvent, was withdrawn from the reboiler. There, the vapour flow passing through the column was formed. All simulations were carried out at a column total pressure of 12 kPa. This pressure was chosen with the aim to work roughly within the temperature range, for which the original model parameters were obtained. The composition of hydrocarbons feed was chosen arbitrarily (heptane to toluene mole ratio of 1), as the content of aromatics in reformat fuel varies within a broad concentration range. Column operation conditions applied during the column simulation are shown in Table 4.

In order to evaluate quantitatively the column separation efficiency,  $\eta$ , the amount of separated heptane in distillate was compared to its amount in the feed. Fig. 4 shows that the purity of distillate is gradually improved, increasing the amount of NMP used. For the solvent to feed mole ratio of about 2.5 practically pure heptane is obtained at the column head independently of the model parameters set used for the column simulation. However, the curve form differs substantially for the two sets of NRTL model parameters when looking at the extractive solvent to hydrocarbons mixture ratio lower than 2. At these conditions, higher-purity distillate was obtained for the original model parameters compared to the distillate composition calculated for the HYSYS parameters' set.

 
 Table 4. Experimental Conditions for Simulation of Extractive Distillation Column

Distinguish Column	
Parameter	Value
Column pressure, $P/kPa$	12
Number of stages (without reboiler)	15
Feed composition $\dot{n}(\text{heptane})/\dot{n}(\text{toluene})$	1:1
Feed temperature, $t_{\rm F}/{}^{\circ}{\rm C}$	43.33
Feed stage	11
Extractive solvent temperature, $t_{\rm E}/{}^{\circ}{\rm C}$	50
Extractive solvent stage	5
Solvent to feed ratio, $\dot{n}_{\rm E}$ : $\dot{n}_{\rm F}$	0:1 - 5:1
Total molar flow rate,	40
$(\dot{n}_{\rm tot} = \dot{n}_{\rm E} + \dot{n}_{\rm F})/({\rm kmol}\ {\rm h}^{-1})$	
Reflux ratio, RR	3
Distillate molar flow rate, $\dot{n}_{\rm D}/(\text{kmol } h^{-1})$	Heptane molar
	flow in feed

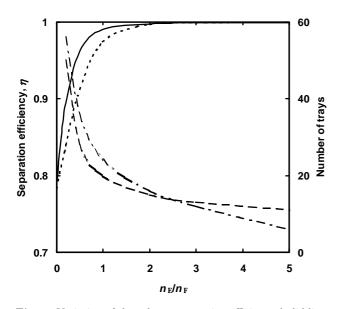


Fig. 4. Variation of the column separation efficiency (solid line – original parameters, dotted line – HYSYS prediction) and of the number of equilibrium stages necessary to reach 99.5 % yield of heptane in distillate (dashed line – original parameters, dotted-dashed line – HYSYS prediction) with the solvent to feed mole ratio.

The number of trays, on which NMP is in contact with the mixture to be separated, seems to be important for the distillate purity. Therefore, the column operation conditions, at which 99.5 % separation efficiency was achieved, *i.e.* heptane mole fraction of 0.995 in distillate, and no NMP loss observed, were investigated. The corresponding data are shown in Fig. 4.

All calculations of the minimum number of equilibrium stages were carried out for the reflux ratio RR = 8. At these conditions, intensive-enough contact of vapour and liquid phases was achieved, allowing reaching prescribed distillate purity even if relatively small amount of extractive solvent was used. As expected,

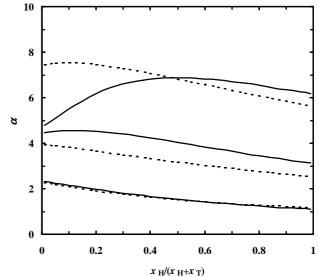


Fig. 5. Variation of heptane to toluene relative volatility with heptane content in the mixture for the (NMP) : (heptane + toluene) mole ratios of 0 : 1, 1 : 1, and 3 : 1 (from bottom to top): solid line – original parameters, dotted line – HYSYS prediction.

variation of the number of column stages is indirectly proportional to the extractive solvent molar flow. At low values of solvent to feed ratio, the number of equilibrium stages determined using the set of parameters calculated from the original experimental data was lower compared to the number of stages obtained for the predicted parameters' set. The opposite was true for  $\dot{n}_{\rm E}$  to  $\dot{n}_{\rm F}$  ratio higher than about 2.5.

To explain such behaviour of the model ternary mixture, additional calculations of the components relative volatility variation with the mixture composition at 12 kPa were performed.

The three pairs of curves shown in Fig. 5 correspond to different extractive solvent to hydrocarbons mixture mole ratios. The pair of curves situated at the chart bottom represents relative volatility of heptane in the mixture with toluene only. The intermediate couple of curves was obtained for the equimolar extractive solvent—feed mixture. By addition of NMP to the hydrocarbons mixture, the relative volatility of heptane with respect to toluene was increased from the value of about 1—2 to 3—5. Moreover, the heptane to toluene relative volatility calculated using the original NRTL binary parameters was higher than the value obtained for the model parameters supplied by the HYSYS simulation program within the whole concentration range.

Further increase of the solvent to hydrocarbons mixture mole ratio to 3 : 1 causes even higher values of heptane relative volatility, 5—8. This time however, the values of heptane to toluene relative volatility calculated for the HYSYS parameters prevail over those obtained for the set of original model parameters, es-

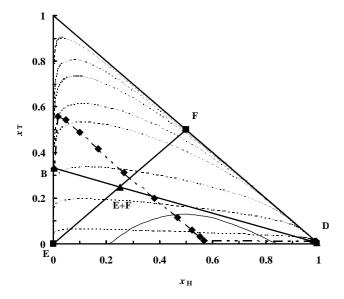


Fig. 6. Residue curve map of the system heptane-toluene NMP at a pressure of 12 kPa calculated using original NRTL model parameters: thin dotted lines - residue curves, thin solid line - immiscibility region border, thick dotted-dashed line - liquid-phase composition within the extractive distillation column, thick solid line – graphical representation of the column overall material balance. B - residue, D - distillate, E - extractive solvent, F - hydrocarbons feed.

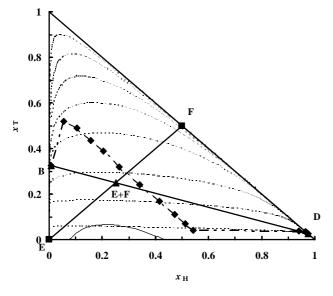


Fig. 7. Residue curve map of the system heptane-toluene-NMP at a pressure of 12 kPa calculated using HYSYS supplied NRTL model parameters: thin dotted lines residue curves, thin solid line - immiscibility region border, thick dotted-dashed line - liquid-phase composition within the extractive distillation column, thick solid line - graphical representation of the column overall material balance. B - residue, D - distillate, E extractive solvent, F – hydrocarbons feed.

pecially in the case of mixtures with high toluene content. At these conditions the mixture boiling temperature exceeded the temperature window  $(40-60^{\circ}\text{C})$ , for which the original model parameters were obtained. Then, the accuracy of the vapour-liquid equilibrium prediction, based on the original set of NRTL model parameters, was not assured.

Figs. 6 and 7 present residue curve maps (RCM) of the ternary system heptane-toluene-NMP calculated by the original and the HYSYS supplied model parameters, respectively. Both charts are qualitatively similar, showing small immiscibility region resulting from heptane-NMP partial miscibility. Over each RCM, graphical representation of the corresponding material balance and the liquid-phase concentration profile of the extractive distillation column is superimposed. Presented tray liquid compositions were calculated by the HYSYS simulation program taking into account the conditions shown in Table 4 and extractive solvent to feed mole ratio  $\dot{n}_{\rm E} : \dot{n}_{\rm F} = 1 : 1$ .

One can see that the liquid composition on several column trays lays within the immiscibility region. This is not true for the RCM chart calculated using the HYSYS model parameters (Fig. 7), as the immiscibility region is shallower and shifted towards lower heptane concentrations. Moreover, higher-purity distillate was found for the simulation based on original model parameters compared to the result obtained by the set of UNIFAC predicted parameters.

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# SYMBOLS

- A, B, C Antoine equation parameters, eqn (2)
- activity of component  $\boldsymbol{i}$  $a_i$
- D, Emodel parameters, eqn (6)F
- objective function defined by eqn (7) or (8)
- $G_{ij}$ NRTL model parameter
- NRTL model interaction para $g_{ij}$  $cal^* mol^{-1}$ meter Knumber of mixture components N
- total number of experimental points n
  - experiment

 $\dot{n}$ 

y

- $\rm kmol \ h^{-1}$ molar flow
- Psystem pressure kPa
- $P_i^{\rm o}$ vapour pressure of pure component ikPa Rgas constant
- $(= 1.98721 \text{ cal mol}^{-1} \text{ K}^{-1})$ cal mol<sup>-1</sup> K<sup>-1</sup> RR reflux ratio
- Τ thermodynamic temperature Κ  $^{\circ}\mathrm{C}$ temperature
- tcomponent's liquid-phase mole fraction x
  - component's vapour-phase mole fraction

<sup>\*</sup> The HYSYS software required the unit cal instead of J.

# **Greek Letters**

- $\alpha$  heptane to toluene relative volatility
- $\alpha_{ij}$  nonrandomness NRTL model parameter
- $\gamma_i$  activity coefficient of pure component i
- $\eta$  separation efficiency
- $\tau_{ij}$  NRTL model parameter

#### Subscripts

- calc calculated
- D distillate
- E extractive solvent
- F feed
- H heptane
- i, j component or equilibrium phase
- T toluene
- tot total

### REFERENCES

- 1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th Edition. Wiley, New York, 1992.
- Zierock, K. H., in 2nd CEN/TC 19 Symposium: Automotive Fuels 2003, Amsterdam, The Netherlands, 2003.
- Gmehling, J., Menke, J., Krafczyk, J., and Fischer, K., Azeotropic Data, 2nd Edition. Wiley—VCH, Weinheim, 2004.

- 4. http://www.uop.com/techsheets/sulfolane.pdf, Sulfolane Process.
- 5. Müller, E., Chem. Ind. (London) 1973, 518.
- Steltenpohl, P. and Graczová, E., in Proceedings of the 31st International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, Slovak Republic, 2004.
- Renon, H. and Prausnitz, J. M., AIChE J. 14, 135 (1968).
- Dykyj, J., Repáš, M., and Svoboda, J., *Tlak nasýtenej pary organických zlúčenín*. (Saturated Vapour Pressure of Organic Compounds.) Veda, Bratislava, 1984.
- 9. Aim, K., Fluid Phase Equilib. 2, 119 (1978).
- Gmehling, J., Onken, U., and Arlt, W., Vapor-Liquid Equilibrium Data Collection, Vol. I, 6b. DECHEMA, Frankfurt/Main, 1980.
- Graczová, E., *PhD. Thesis.* Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, 1989.
- 12. Chlebovec, M., *Bachelor Project*. Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, 2004.
- Graczová, E. and Surový, J., Chem. Pap. 53, 428 (1999).
- 14. Graczová, E. and Surový, J., Chem. Pap. 50, 1 (1996).
- Fredeslund, A., Gmehling, J., and Rasmussen, P., Vapour-Liquid Equilibria Using UNIFAC, a Group-Contribution Method. Elsevier, Amsterdam, 1977.