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Extractive Distillation of C7 Hydrocarbon Mixture in the Presence of Furfural

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Separation of heptane–methylcyclohexane–toluene mixture in the presence of furfural was investigated at atmospheric pressure. Multi-component vapor–liquid equilibrium (VLE) of the chosen system was simulated employing the NRTL equation. In order to improve the accuracy of the multi-component VLE prediction, the NRTL model extended by the universal ternary contribution was used. Binary parameters of the NRTL model were taken from DECHEMA VLE database. Parameters of the universal ternary contribution were obtained independently from the VLE of ternary subsystems constituting the four-component mixture.
Original and extended NRTL model was employed for simulation of aromatics separation from hydrocarbon mixtures in the presence of extractive solvent. The influence of the VLE prediction accuracy on the separability of the chosen mixture was deduced on the basis of the distillate and bottom product composition as well as the variation of relative volatility with the mixture composition.

1. Introduction

Aromatics with their annual production exceeding 12.5 millions ton at the end of the past century represent one of the most important intermediates in chemical industry (The Aromatics Producers Association, 2001).
Principal source of these compounds remains crude and its derivatives, from which aromatics should be separated (Kirk-Othmer, 1992). Distillation of hydrocarbons mixtures is, however, of a limited use only owing to the similar boiling temperatures of various hydrocarbons as well as due to the formation of azeotropes. This problem could be effectively overcome employing extractive distillation, which presents integration of the traditional liquid-phase extraction with further separation step – distillation (Steltenpohl and Graczová, 2004; Steltenpohl et al., 2005).
In the present study, the accuracy of multi-component vapor–liquid equilibrium (VLE) prediction was tested assuming extractive distillation of a model hydrocarbons mixture comprising alkane, cycloalkane, and aromatic compound in the presence of an extractive solvent (furfural). For this purpose, the multicomponent VLE was predicted either considering the binary equilibrium data only or both binary and ternary VLE were taken into account (Surový et al., 1982).

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2. Theoretical

Non-ideal behavior of the liquid phase was described employing the NRTL model. For the excess molar Gibbs energy calculations either original NRTL equation (Renon and Prausnitz, 1968) or the model equation extended by the ternary contribution proposed by Surový et al. (1982) was used.

The original NRTL model allows prediction of three- and more-component VLE on basis of binary VLE data only. Then, employing the NRTL model binary and non-randomness parameters, τ_{ij}, τ_{ji}, and α_{ij}, the component activity coefficient could be calculated as follows

$$\ln \gamma_i = \frac{\sum_{j=1}^{K} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{K} G_{li} x_l} + \sum_{j=1}^{K} \frac{G_{ij} x_j}{\sum_{l=1}^{K} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{n=1}^{K} \tau_{nj} G_{nj} x_n}{\sum_{l=1}^{K} G_{lj} x_l} \right) \qquad i = 1,\ 2,\ ...,\ K \tag{1}$$

However, this approach does not account for the interactions of more than two different molecules. Surový et al. (1982) concluded that the difference between the measured value of the excess Gibbs energy of a ternary mixture and the value calculated on basis of the binary equilibrium data is caused by the ternary intermolecular interactions. Consequently, the authors postulated the ternary contribution to the component activity coefficient in the form

$$\Delta_t \ln \gamma_i = x_j x_k \left[E_i x_i \left(2 - 3x_i\right) + E_j x_j \left(1 - 3x_i\right) + E_k x_k \left(1 - 3x_i\right) \right] \qquad i, j, k = 1,2,3 \tag{2}$$

where E represents the ternary contribution parameter and x mole fraction of the ternary mixture components. Activity coefficient of the ternary mixture component is then obtained as a sum of the value obtained from the original model equation (Eq. (1)) and the ternary contribution to the component activity coefficient expressed by Eq. (2).

Graczová and Surový (1992) and Graczová (2002) proved that the ternary contribution concept could be applied also for the prediction of equilibrium of quaternary liquid–liquid and vapour–liquid systems. Taking into account, that the probability of intermolecular interactions with the number of molecules involved decreases exponentially, the authors suggested that quaternary and higher order interactions between molecules could be omitted. Then, the ternary contribution to the activity coefficient of the component of a quaternary system could be expressed as linear combination of the ternary contributions to the activity coefficient resulting from the four ternary subsystems constituting the four-component mixture

$$\begin{aligned} \left(\Delta_t \ln \gamma_i\right)_q = {} & x_j x_k \left[E_{il} x_i \left(2 - 3x_i\right) + E_{jl} x_j \left(1 - 3x_i\right) + E_{kl} x_k \left(1 - 3x_i\right) \right] + \\ & + x_k x_l \left[E_{ij} x_i \left(2 - 3x_i\right) + E_{kj} x_k \left(1 - 3x_i\right) + E_{lj} x_l \left(1 - 3x_i\right) \right] + \\ & + x_j x_l \left[E_{ik} x_i \left(2 - 3x_i\right) + E_{jk} x_j \left(1 - 3x_i\right) + E_{lk} x_l \left(1 - 3x_i\right) \right] - \\ & - 3 x_j x_k x_l \left(E_{ji} x_j + E_{ki} x_k + E_{li} x_l \right) \qquad i, j, k, l = 1,2,3,4 \end{aligned} \tag{3}$$

3. Results and Discussion

Isobaric binary and ternary VLE of systems comprising heptane, methylcyclohexane, toluene, and furfural as well as the binary NRTL model parameters were taken from DECHEMA VLE database (Gmehling et al., 1979, 1980, 1993). Parameters of the ternary contribution were evaluated from the respective ternary VLE data considering that all variables, liquid- and vapour-phase component mole fractions as well as temperature are subject of experimental error. Thus, corresponding objective function adopted the following form

$$F = \sum_i \left[\sum_n \left(x_i - x_{\mathrm{calc},i} \right)_n^2 + \sum_n \left(y_i - y_{\mathrm{calc},i} \right)_n^2 \right] + \sum_n \left(\frac{t - t_{\mathrm{calc}}}{t} \right)_n^2 \quad i = 1,...,4 \quad n = 1,...,N \qquad (4)$$

where t denotes temperature and N number of experiments.
Complete sets of binary NRTL and ternary contribution parameters are given in Tables 1 and 2. Quality of the ternary VLE prediction by the original and extended NRTL model was evaluated on basis of the standard deviation of experimental and calculated vapour-phase composition. It was found that the introduction of the ternary contribution to the original NRTL model increased accuracy of the VLE prediction by about three to four times (Table 2, rows denoted with $E_i = 0$ for the ternary VLE prediction by the original NRTL model equation and $E_i \neq 0$ for the prediction employing extended NRTL model).

Table 1 Binary NRTL model parameters for the quaternary system heptane (1) – methylcyclohexane (2) – toluene (3) – furfural (4) at P = 101 kPa

Parameter	Binary system					
	1 – 2	1 – 3	1 – 4	2 – 3	2 – 4	3 – 4
$(g_{12} - g_{22})$/(cal mol^{-1})	-410.4052	-30.5760	1727.6480	96.8077	1029.9084	452.2016
$(g_{21} - g_{11})$/(cal mol^{-1})	517.0045	268.3335	12.7446	97.2195	553.2400	316.4811
α_{ij}	0.3046	0.2986	0.0132	0.3019	0.0008	0.2952

Table 2 Ternary contribution parameters and statistical indices for the ternary systems constituting quaternary system heptane (1) – methylcyclohexane (2) – toluene (3) – furfural (4) at P = 101 kPa

Parameter		Ternary system			
		1 – 2 – 3	1 – 2 – 4	1 – 3 – 4	2 – 3 – 4
E_i		-0.53405	0.20407	-1.56487	-1.65549
E_j		-0.50459	-1.01010	-0.54689	-0.32955
E_k		0.64464	-4.95225	-1.30861	-1.40039
σ	$E_i = 0$	0.0111	0.0613	0.0331	0.0324
	$E_i \neq 0$	0.0046	0.0167	0.0095	0.0095

Simulation of extractive distillation of the chosen quaternary system was carried out assuming distillation column with total condenser (denoted as the stage No. 1), 18 equilibrium plates (stages No. 2–19), and a reboiler (stage No. 20). In order to avoid its presence in distillate, extractive solvent (pure furfural) entered column at the stage No. 7 (6^{th} equilibrium plate). On the other hand, to prevent excess amount of non-aromatics in the bottom stream, the equimolar hydrocarbons mixture was fed to the column stage No. 16 (15^{th} equilibrium plate). Both streams were entering column at their respective boiling temperature. Reflux ratio inside the separation module was kept constant $R = 3$. Feed to extractive solvent molar flow was set to 1 : 3, a value typical for this kind of technologies (Gentry et al., 2002). Molar flow of distillate was preset so that it should contain heptane and methylcyclohexane only. Consequently, it was expected that majority of toluene and furfural would by found in the bottom product. The results of simulations assuming the original and extended NRTL model are presented in Figure 1 in form of the component concentration profiles.

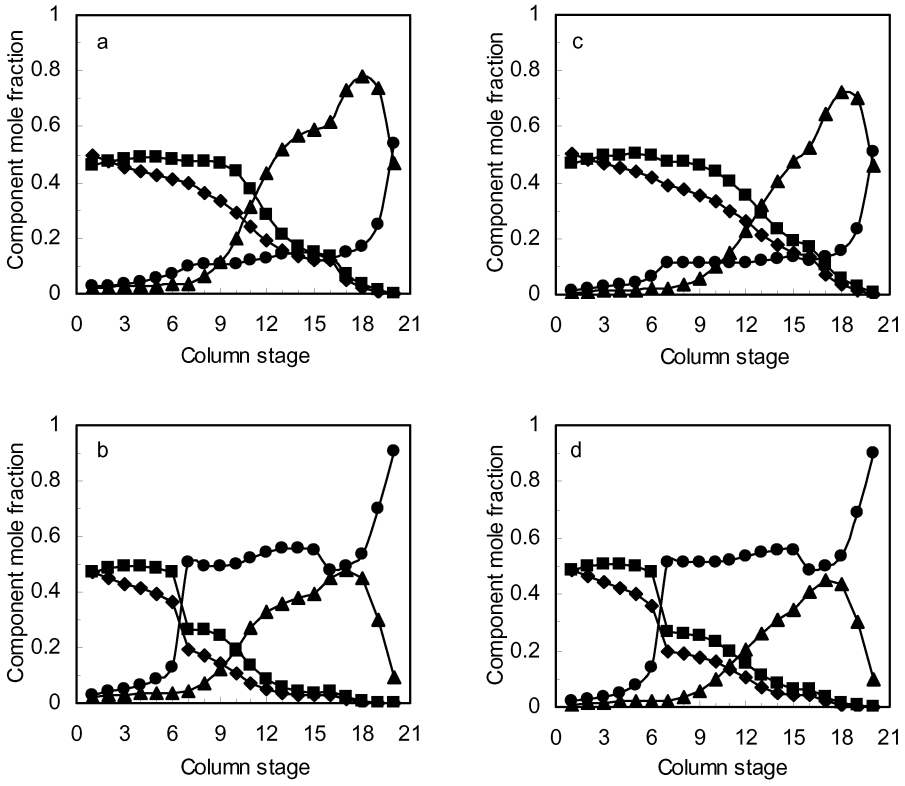

Figure 1. Vapor- (a, c) and liquid-phase (b, d) composition profiles within the column for extractive distillation of toluene (▲) from the mixture with heptane (◆) and methylcyclohexane (■) in the presence of furfural (●) at atmospheric pressure. Simulation based on the original NRTL equation (a, b) and the NRTL model extended by the ternary contribution (c, d).

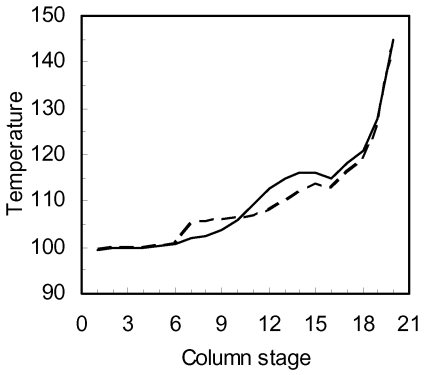

Figure 2. Temperature profiles within the column for extractive distillation of toluene from hydrocarbons mixture in the presence of furfural at atmospheric pressure. Simulation based on the original NRTL equation (solid line) and the NRTL model extended by the ternary contribution (dashed line).

Apparently, very similar concentration profiles were obtained for both models. However, slightly higher purity of both distillate and bottom product were obtained when the extended NRTL equation was used for the extractive distillation simulation, i.e. toluene and furfural mole fraction in the distillate 0.010 and 0.020, respectively, vs. the values of 0.023 and 0.031 observed for toluene and furfural, respectively, in case of simulation based on the binary NRTL parameters only. On the other hand, purity of bottom streams was almost the same for both simulations never exceeding the heptane and methylcyclohexane mole fraction the value of 0.002.

More important differences were observed while comparing the temperature profiles within the distillation column (Figure 2). Temperature profile computed using the extended NRTL model (dashed line) offers more realistic view allowing to distinguish both feed and extractive solvent input stages within the distillation column. The largest differences in the temperature profiles for both simulation cases are seen between the stages No. 7 and 17, the region corresponding to the most intense contact of extractive solvent with the mixture to be separated.

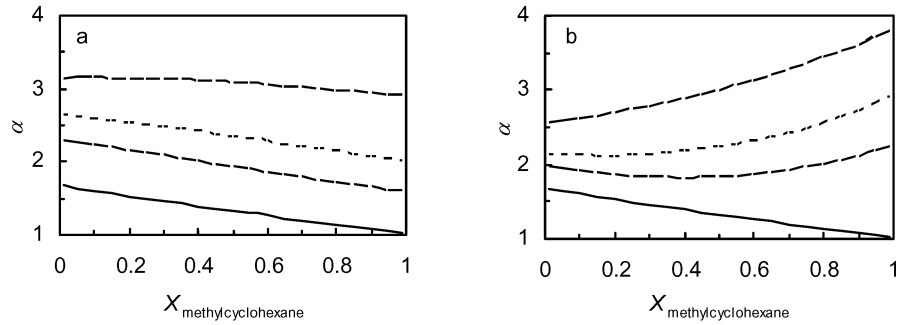

Figure 3. Variation of methylcyclohexane vs. toluene relative volatility with cykloalkane relative mole fraction calculated using original (a) and extended (b) NRTL model. Binary methylcyclohexane–toluene mixture (solid line), hydrocarbon mixture to furfural mole ratio of 2 : 1 (dashed line), 1 : 1 (dotted line), and 1 : 3 (dotted-dashed line).

In order to elucidate this behavior, variation of the toluene relative volatility (vs. heptane and vs. methylcyclohexane) in the absence or presence of furfural was calculated using both original and extended NRTL model. Essentially, the same picture was obtained, thus only the results of relative volatility calculation for methylcyclohexane vs. toluene is presented (Figure 3).

The only similarity between the two diagrams is that the presence of extractive solvent has positive effect on the cykloalkane relative volatility. When looking at the results obtained employing the original NRTL model, almost constant relative volatility of methylcyclohexane is observed throughout the whole concentration range when the feed to extractive solvent is 1 : 3 (condition similar to that of extractive distillation simulation). On the other hand, continuous increase of the α value could be seen, when also ternary equilibrium data are considered. This corresponds with the fact that higher purity distillate was obtained for the second simulation. Curiously, at higher toluene content in the mixture, relative volatility of methycyclohexane computed using the original model is higher than that obtained for the extended NRTL model.

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References

APA, The Aromatics Producers Association, 2001, Aromatics - Improving the Quality of Your Life. European Chemical Industry Council (CEFIC), Brussels.

Gentry J.C., Kumar S. and Lee H.M., 2002, Operational Experience with GT-BTX^{TM} Aromatics Recovery Technology. GTC Technology Corporation, Houston.

Gmehling J., Onken U. and Arlt W., 1979, DECHEMA Chemistry Data Series, Vol. I. Vapor–Liquid Equilibrium Data Collection, Part 3. DECHEMA, Frankfurt am Main.

Gmehling J., Onken U. and Arlt W., 1980, DECHEMA Chemistry Data Series, Vol. I. Vapor–Liquid Equilibrium Data Collection, Part 6b. DECHEMA, Frankfurt am Main.

Gmehling J., Onken U. and Rarey J.R.., 1993, DECHEMA Chemistry Data Series, Vol. I. Vapor–Liquid Equilibrium Data Collection, Part 3a. DECHEMA, Frankfurt am Main.

Graczová E., 2002, Habilitation. Slovak University of Technology in Bratislava, Bratislava.

Graczová E. and Surový J., 1992, Collect. Czech. Chem. Commun. 57, 16.

Kirk-Othmer, 1992, Encyclopedia of Chemical Technology. J. Wiley: New York.

Renon H. and Prausnitz J.M., 1968, AICHE J., 14, 135.

Steltenpohl P., Chlebovec M. and Graczová E., 2005, Chem. Pap. 59, 421.

Steltenpohl P. and Graczová E., 2004, New Technologies for BTX Aromatics Recovery. In Markoš J. and Štefuca V., Eds., 31st International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, Slovak Republic.

Surový J., Dojčanský J. and Bafrncová S., 1982, Collect. Czech. Chem. Commun. 47, 1420.