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Incorrect Ternary Liquid–Liquid Equilibria Description versus Extractor Design Simulation

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The presented study focuses on the separation of aromatics from aliphatic hydrocarbons by liquid-phase extraction using ionic liquids. The aim of this study was to show the impact of incorrect description of liquid–liquid equilibria of the separated system on the extractor design parameters.

Extraction is usually applied for the separation or concentration of dilute solutions with the aim to achieve minimum concentration of the separated component in the final raffinate. Therefore, correct description of the liquid–liquid (L-L) equilibrium in this concentration region is very important for the industrial practice. For thermodynamic description of a ternary L-L equilibrium, excess Gibbs energy dependencies on the mixture composition are applied. Model parameters of the mentioned equations can be evaluated from different experimental equilibrium data. The most commonly used experimental data are ternary tie lines. Parameters of the G^E equations evaluated from experimental tie lines usually provide good or even excellent description of the given ternary L-L area. Extrapolation of the L-L data beyond this region, however, can sometimes lead to incorrect L-L equilibrium description. This problem is shown on the real ternary system heptane – toluene – 3-methyl-*N*-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)$_4$)]). This study proves serious discrepancies in the extractor design parameters using the NRTL equation parameters evaluated from experimental ternary equilibrium data. Depending on the initial guess, the mathematical model of a continuous counter-current extraction column offered at least three different values of the extraction solvent consumption for the preset purity of the final raffinate and of the number of theoretical stages.

1. Introduction

Conventional process for the separation of an aromatic and aliphatic hydrocarbons mixture (C_4 to C_{10}) is the liquid–liquid extraction suitable for the range of 20–65 mass % of the aromatics content. For this separation process, usually polar solvents, e.g. sulfolane, *N*-methylpyrrolidone, *N*-formyl morpholine, ethylene glycol, and propylene carbonate (Meindersma et al., 2005) or Techtiv 100^{tm} (Gentry and Kumar, 2002) are used. According to Weissermel and Arpe (2003), no feasible processes for the separation of aromatic and aliphatic hydrocarbons are available in below 20 mass % of aromatics in feed. For this purpose, ionic liquids have been identified as alternative solvents to replace conventional solvents in the liquid–liquid extraction (Perreiro et al., 2012), e.g. Meindersma and de Haan (2008) tested 4-methyl-*N*-butylpyridinium tetrafluoroborate ([mebupy]BF$_4$) in toluene separation from heptane – toluene mixture. Compared to traditional solvents, ILs show remarkable advantages; their miscibility with other liquids can be tuned by selecting the appropriate anions and cations. This makes ILs suitable “designer solvents” (Perreiro et al., 2012) for a wide range of processes.

Particularly useful is the application of ILs in separation processes, e.g. liquid–liquid extraction or extractive distillation, due to their negligible volatility and tunable solubility. The latter one allows selecting IL with substantially higher affinity to one of the components of the liquid mixture while the other mixture component(s) are poorly soluble in the chosen IL. Negligible volatility of ILs is beneficial considering the effortlessness of their regeneration in further separation steps.

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Meindersma et al. (2010) selected as the most promising ILs used for the aromatics separation from hydrocarbons mixture via liquid–liquid extraction the following ones: 1-ethyl-3-methylimidazolium ethylsulfate ([EMim][ESO$_4$]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMim][NTf$_2$]), 3-methyl-*N*-butylpyridinium tetracyanoborate ([3-mebupy][B(CN)$_4$)], and 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([EMpy][NTf$_2$]).

2. Theoretical

In liquid–liquid extraction, a solute is distributed between two immiscible liquid phases. For two coexisting equilibrium liquid phases at constant temperature, *T*, and pressure, *P*, the following relation is valid:

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \qquad \left[T,P\right] \qquad i = \mathrm{A,B,C} \tag{1}$$

Superscripts I and II denote the equilibrium liquid phases and x_i^{I} and x_i^{II} are the mole fractions of component *i* in the respective equilibrium phases. γ_i^{I} and γ_i^{II} represent the activity coefficients of *i*-th component in the two equilibrium liquid phases and are expressed in form of excess molar Gibbs energy dependence on the composition of the liquid phase using the NRTL equation (Renon and Prausnitz, 1968):

$$\ln\gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} + \sum_j \frac{x_j G_{ij}}{\sum_l G_{lj} x_l}\left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_l G_{lj} x_l}\right) \qquad i,j,k,l = \mathrm{A,B,C} \tag{2}$$

Binary parameters τ_{ij} and G_{ij} are defined by the following expressions:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \qquad G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \qquad i,\ j = \mathrm{A,B,C} \qquad i \neq j \tag{3}$$

where $\tau_{ij} \neq \tau_{ji}$, $\tau_{ii} = \tau_{jj} = 0$, *R* is the universal gas constant, g_{ij} and g_{jj} represent the energies of the interaction between molecule pairs, α_{ij} characterizes the tendency of species *i* and *j* to be distributed in non-random form.

3. Experimental

The present study focuses on the separation of aromatics from their mixtures with aliphatic hydrocarbons in the presence of a ionic liquid using the extraction process. As a model system, the heptane – toluene mixture was chosen. As the extractive solvent, the [3-mebupy][B(CN)$_4$)] ionic liquid was applied (Figure 1).

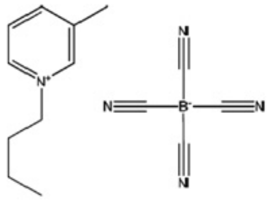

Figure1: Structure of [3-mebupy][B(CN)$_4$)].

3.1. L-L equilibrium description of the studied ternary system

In liquid–liquid extraction, at least three substances are involved. Proper description of ternary L-L equilibria is necessary for reliable design of the extraction equipment.

NRTL parameters (parameters of the Gibbs free-energy model for calculation of liquid-phase activity coefficients) can be determined directly using the ternary equilibrium data only. This method gives a reasonably accurate description of the L-L equilibria within the experimental composition range and is commonly used in literature to describe ternary systems (e.g. DECHEMA Data Collection). Extrapolation of the L-L data beyond the experimental ternary region can sometimes lead to incorrect L-L equilibrium prediction (Graczová and Steltenpohl, 2013). Since the NRTL parameters evaluated using this method have no physical meaning, they can lead to unrealistic or even multiple solutions using interpolation also within the experimental data range. This problem is shown on the real ternary heptane – toluene – [3-mebupy][B(CN)$_4$)] system with two pairs of partially miscible components. L-L equilibrium data of this ternary system were published by Meindersma et al. (2011) at 303.2 K and 328.2 K. Published regressed NRTL parameters were determined directly from the ternary tie lines using ASPEN Plus V7.2 (Meindersma et al., 2011) for the temperature range of 303.2–328.2 K and are summarized in Table 1.

Table 1: NRTL equation parameters for the ternary system heptane (A) – toluene (B) – [3-mebupy][B(CN)$_4$] (C) (Meindersma et al., 2011)

Binary	a_{ij}	b_{ij}/K	a_{ji}	b_{ji}/K	α_{ij}
Heptane (A) – toluene (B)	–7.7238	2,152.19	5.0166	–715.589	0.30
Heptane (A) – [3-mebupy][B(CN)$_4$] (C)	58.867	–5,850.99	5.1218	–472.15	0.20
Toluene (B) – [3-mebupy][B(CN)$_4$] (C)	9.3178	–1,443.4	–6.5559	1,687.21	0.30

Parameters ($g_{ij} - g_{jj}$) were considered to be linear in temperature. Then, the NRTL parameters, τ_{ij}, were expressed as follows:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = a_{ij} + \frac{b_{ij}}{T} \qquad i, j = \text{A, B, C} \qquad i \neq j \tag{4}$$

The NRTL non-randomness parameters, α_{ij}, of individual pairs of molecules were fixed (Table 1). According to the common rules (Seader and Henley, 1998), for immiscible components the value of α_{ij} usually lies between 0.2 and 0.47. In general, the value of α_{ij} = 0.2 is recommended for mixture of saturated hydrocarbons and polar non-associated species, α_{ij} = 0.3 for mixtures of non-polar compounds, and α_{ij} = 0.47 for mixtures of strongly self-associated species with non-polar species. Considering the values presented in Table 1, these general rules were not satisfied. An exception is the value of the non-randomness parameter for the binary mixture heptane (A) – toluene (B).

Original NRTL parameters (Table 1) evaluated for the ternary system heptane (A) – toluene (B) – [3-mebupy][B(CN)$_4$] (C) provide multiple solutions of the L-L equilibria. Instead of a smooth continuous raffinate and extract part of the binodal curve, discontinuities in the branches of binodal curve were observed and, moreover, precise continuation calculations identified isola solutions for mixtures with low toluene content. Calculated compositions of the ternary system are represented using the right-triangle (Figure 2a) and distribution (Figure 2b) diagrams; a detail of the region of lower toluene mole fractions is given in Figure 3.

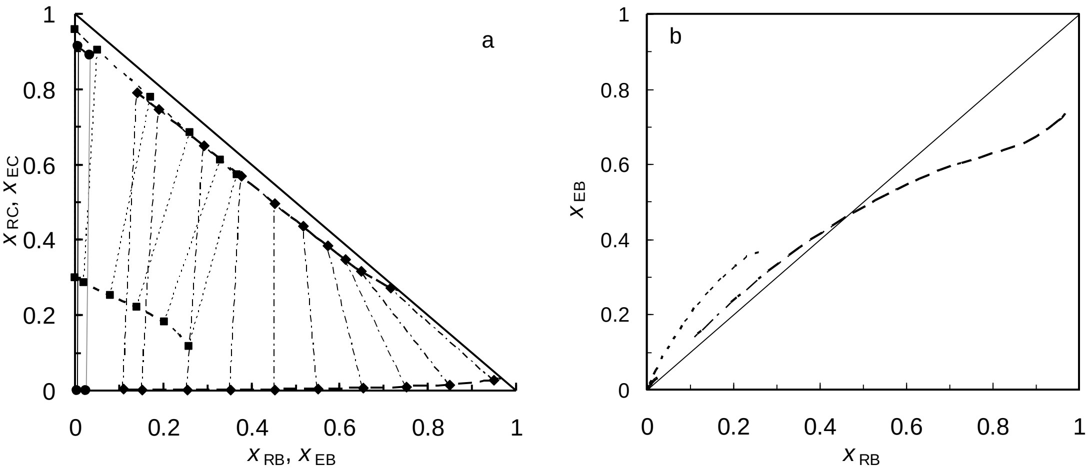

Figure 2: Calculated equilibrium (a) and distribution (b) diagrams for the ternary system heptane (A) – toluene (B) – [3-mebupy][B(CN)$_4$)] (C) at T = 313.2 K computed using original NRTL parameters (Table 1). Equilibrium diagram: lower (diamonds), upper (squares), and isola (circles) stable steady states; tie lines for lower (dotted-dashed lines), upper (dotted lines), and isola (solid lines) stable steady states. Distribution diagram: computed distribution curve for lower (dotted-dashed line), upper (dotted line), and isola (solid line) stable steady states

3.2. Design calculations

The NRTL equation with the above mentioned binary parameters was used for the simulation of toluene extraction from hydrocarbons mixtures in a multi-compartment column employing [3-mebupy][B(CN)$_4$)] as the extraction solvent.

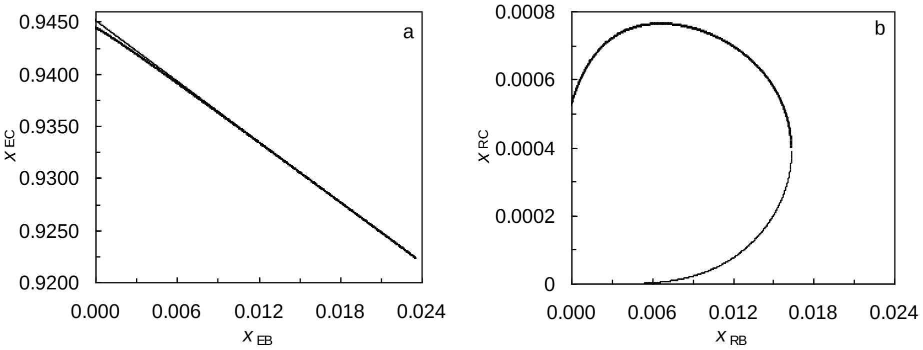

Figure 3: Magnification of computed isola solutions at low toluene concentration in extract (a) and raffinate (b) phases. Stable (thick curve) and unstable (thin curve) steady states

For the column simulation, an equilibrium model of a counter-current extractor (Steltenpohl and Graczová, 2014) was developed. Input data used in the calculations were as follows: number of theoretical stages N = 10, feed (F) composition x_{FA} = 0.85 and x_{FB} = 0.15, solvent (S) composition x_{SC} = 1, and the required maximum toluene content in the final raffinate $x_{\mathrm{R}N\mathrm{B}}$ = 0.005.

Computation of the concentration profiles in the extraction column was carried out in two cycles. Based on a guess of the solvent to feed mole ratio and the component distribution coefficients, D_{ji}, mass balances were solved to determine the raffinate compositions at individual equilibrium stages. Computed composition profiles were checked and normalized to fulfil the summation equation:

$$\sum_i x_{\mathrm{R}ji} = 1 \qquad i = \mathrm{A, B, C} \qquad j = 1, 2, \ldots, N \tag{5}$$

In the second cycle, normalized raffinate concentration profiles were used as a guess for the calculation of the equilibrium extract (E) and raffinate (R) phase compositions at each equilibrium stage, j. These values, satisfying the iso-activity criterion:

$$x_{\mathrm{R}ji}\gamma_{\mathrm{R}ji} = x_{\mathrm{E}ji}\gamma_{\mathrm{E}ji} \qquad i = \mathrm{A, B, C} \qquad j = 1, 2, \ldots, N \tag{6}$$

were used to calculate corrected components' distribution coefficients:

$$D_{ji} = x_{\mathrm{E}ji} / x_{\mathrm{R}ji} = \gamma_{\mathrm{R}ji} / \gamma_{\mathrm{E}ji} \qquad i = \mathrm{A, B, C} \qquad j = 1, 2, \ldots, N \tag{7}$$

New guess of the distribution coefficients was returned back to the first computation cycle.

The procedure was repeated until the two consecutive concentration profiles showed lower difference of the components mole fractions than the preset accuracy:

$$\sum_{j=1}^{N} \sum_i \left[\left(x_{\mathrm{R}ji}^{f} - x_{\mathrm{R}ji}^{f+1} \right)^2 + \left(x_{\mathrm{E}ji}^{f} - x_{\mathrm{E}ji}^{f+1} \right)^2 \right] \le \varepsilon \qquad i = \mathrm{A, B, C} \tag{8}$$

where f in the superscript denotes the iteration and ε is the computation accuracy (typically 10^{-16}).

4. Results and Discussion

Using different initial guesses of the components distribution coefficients (Eq(7)), at least three different concentration profiles were obtained within the extraction column. In Figures 4 and 5, two of these profiles, the most different ones, are shown. Component A, B, and C mole fractions in the equilibrium raffinate phases at individual extraction column stages are compared in Figures 4(a), 4(b), and 4(c). Figure 5 shows a comparison of the equilibrium extract phases at the column stages.

Serious discrepancies between the heptane and IL content in the raffinate and extract phases were observed without influencing the simulation quality (objective function, Eq(8), was fulfilled in both simulations). Moreover, very different values of the extraction solvent specific consumption (solvent to feed mole ratio) of 0.648 (squares, Figures 4 and 5) and of 0.329 (triangles, Figures 4 and 5) were obtained when the preset raffinate purity criterium, $x_{R/NB}$ = 0.005, was reached.

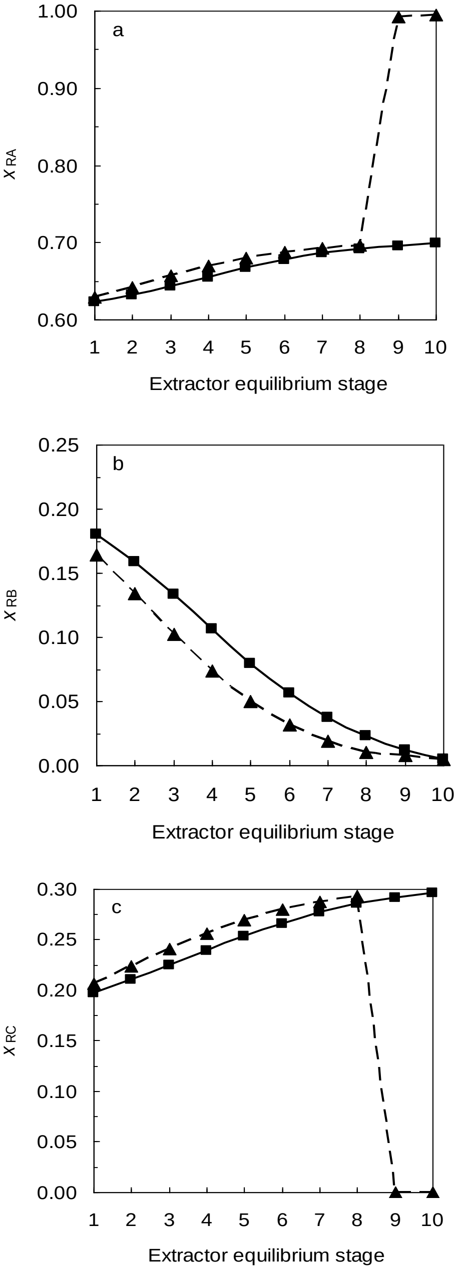

Figure 4. Component A (a), B (b), and C (c) concentration profiles in raffinates obtained by simulation of the counter-current extraction column with ten equilibrium stages. Results for two different guesses of the component distribution coefficients yielding the solvent to feed mole ratio of 0.329 (▲) and 0.648 (■)

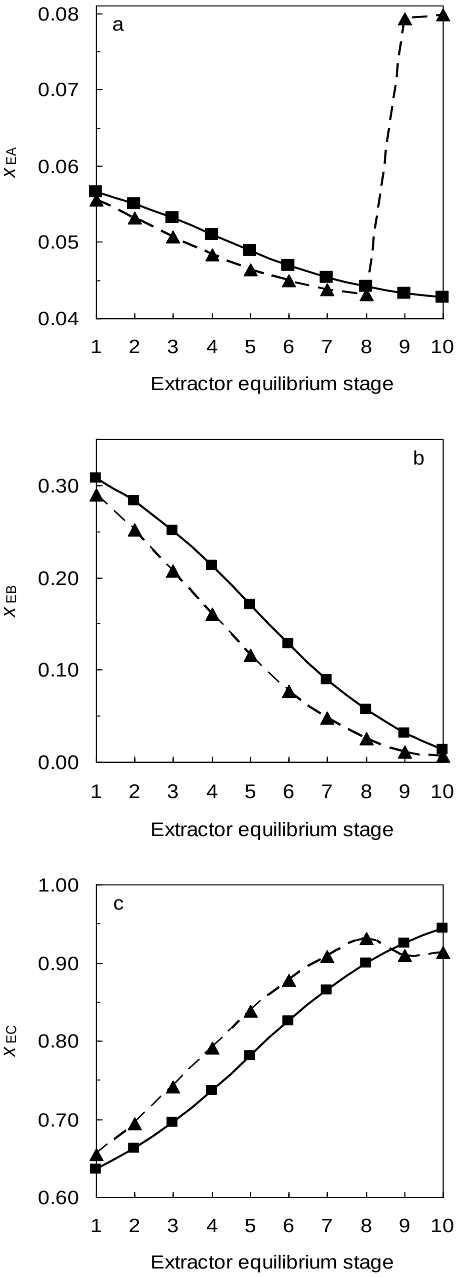

Figure 5. Component A (a), B (b), and C (c) concentration profiles in extracts obtained by simulation of the counter-current extraction column with ten equilibrium stages. Results for two different guesses of the component distribution coefficients yielding the solvent to feed mole ratio of 0.329 (▲) and 0.648 (■)

In case of lower solvent specific consumption, the computed extract and raffinate compositions at the equilibrium stages 1–8 correspond to the upper stable steady states (Figure 2), while isola solutions (Figure 3) represent the compositions of extract and raffinate phases at equilibrium stages 9 a 10. This conclusion was deduced from a sudden change in the composition of the raffinate and extract phases moving from the 8th to the 9th equilibrium stage, e.g. x_{R8C} = 0.285 and x_{R9C} = 6 × 10^{-6} as well as x_{E8A} = 0.043 and x_{E9A} = 0.079.

Similar analysis for the solvent to feed mole ratio of 0.648 shows that the equilibrium phase compositions computed for all column stages correspond to the upper stable steady state solutions (Figure 2).

5. Conclusions

Presented data show that the quality of the L-L equilibrium description plays an important role in the extraction column design calculations. Depending on the initial guess, very different values of the solvent specific consumption as well as of the final product compositions were obtained, while the quality of computation was not questioned. This has serious impact on the design of the separation unit dimensions (solvent to feed mole ratios of 0.329 and 0.648) as well as on the necessity of additional separation steps (solvent regeneration from one/both phases as the solvent mole fraction in raffinate, x_{R10C}, varying from 0.296 to 3 × 10^{-7}). Then, completely different investment and operational cost are predicted for the two cases considered.

Regarding the ternary system heptane – toluene – [3-mebupy][B(CN)$_4$], the original NRTL parameters taken from the literature were not reliable for the L-L equilibrium calculations. This was clearly evidenced by the occurrence of multiple steady states in the ternary equilibrium diagram (Figures 2 and 3). This problem can be avoided considering also the solubility of both partially miscible pairs (heptane – [3-mebupy][B(CN)$_4$] and toluene – [3-mebupy][B(CN)$_4$]) during the NRTL parameters evaluation. Moreover, bearing in mind that the non-randomness parameter value affects the quality of the L-L equilibrium description of dilute systems, we recommend fitting this parameter to the limiting activity coefficients (Graczová and Steltenpohl, 2013).

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