Modelling of Liquid–liquid Equilibria in Quasi-seven-component Systems with Deep Eutectic Solvents as Extraction Media

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Abstract

Liquid-liquid equilibria were experimentally investigated in systems in which the first component was aliphatic (*n*-hexane, *n*-heptane or *i*-octane) or aromatic hydrocarbon (toluene), the second component was pyridine or thiophene, and the third quasi-component was DES consisting of choline chloride and glycerol or choline chloride and ethylene glycol, at 25 °C and atmospheric pressure. The equilibria were successfully described by the NRTL and UNIQUAC models. The same models were successfully applied to describe the liquid-liquid equilibria in quasi-seven-component systems that comprised all the mentioned low molecular weight components and one DES. The restrictions of the models were discussed; it seems that the preference can be given to the UNIQUAC model.

Keywords

Deep eutectic solvents, NRTL, UNIQUAC, model fuel, liquid-liquid equilibria

1 Introduction

By definition, green solvents are solvents that have minimal negative environmental impact arising from the use of these solvents in industry. Most industrial processes use harmful organic solvents. For such a process to be ecologically acceptable, it is necessary to replace the harmful solvents with solvents that have more favourable EHS (environmental, health and safety) properties, biosolvents, supercritical fluids, ionic liquids or deep eutectic solvents.[1]

Deep eutectic solvents (DES) are mixtures of hydrogen bond donors and acceptors with a melting point lower than the melting point of their individual components.[2] The most important properties for their application in separation processes are: non-flammability, negligible vapour pressure, chemical and thermal stability, and high capacity for dissolution of various types of substances.[3] Moreover, it is relatively easy to regenerate them and even to use them several times without purification.[4,5] The easy adjustment of their properties by simple replacement of the hydrogen bond donor or acceptor allows them to be widely applied, so they have found their place in the treatment of motor fuels.[6]

Among the motor fuel treatment processes, those used for removing harmful sulphur and nitrogen compounds are particularly important, which is also stipulated by the legislation. The most commonly used commercial process of desulphurization of hydrocarbon fuels is hydrodesulphurization (HDS).[7] Due to high consumption of energy, hydrogen and catalysts, the commercial HDS process has to be replaced by cheaper and more efficient ones.[8] Among the alternative processes, extractive desulphurization (EDS) is particularly interesting, being characterized by mild extraction conditions (low temperature and atmospheric pressure). In particular, extraction desulphurization using ionic liquids was investigated. However, authors who have used model solutions containing sulphur, nitrogen and aromatic compounds as well as real refinery samples have proven that denitrification and dearomatization are being carried out simultaneously with desulphurization.[9–11] Because of the toxicity of ionic liquids and their high cost, DESs are being investigated more recently in the processes of extractive desulphurization,[12–14] denitrification[15,16] and dearomatization.[17] In all the mentioned cases, model fuels, i.e. mixtures of one hydrocarbon and one characteristic sulphur or nitrogen compound, were investigated, and the observed extraction equilibrium was described by NRTL model[16,17] with a slightly larger success or with COSMO-RS model,[16] somewhat less successfully.

According to our best knowledge, there is no research to deal with the simultaneous extraction of aromatic, sulphur and nitrogen compounds by a DES, and only such studies may point to effects such as the possible suppression of the solubility of paraffins in ionic liquids by aromatic, sulphur and nitrogen compounds.[18] In our previous works[19,20] similar studies have been described on model seven-component systems containing three aliphatic hydrocarbons, one aromatic hydrocarbon, one nitrogen- and one sulphur-containing compound and an ionic liquid (IL). Those studies also contain a thermodynamic description of the extraction equilibrium by the NRTL and UNIQUAC models, including a detailed description of the method of transferring the parameters from the three-component to the seven-component systems. The described procedure will be adapted in this paper for the systems containing DESs instead of ionic liquids as extraction media. Particular emphasis will be placed on the limitations of thermodynamic modelling in DES-containing systems that did not exist in the systems with ionic liquids.

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2 Experimental

2.1 Chemicals

The list of chemicals is given in Table 1. The chemicals were used without further purification. DES components, choline chloride and glycerol, or choline chloride and eth-ylene glycol were mixed at the given molar ratios. The re-sulting mixtures were stirred in a rotary vacuum evaporator at 60 °C and 250 mbar until a homogeneous colourless liquid was obtained, presumably anhydrous. The density of the prepared DESs was measured by a Mettler Toledo densitometer Densito 30PX at 25 °C.

2.2 DES as a quasi-component

Unlike ionic liquids, DESs themselves are not well-defined chemical compounds, but rather two-component systems consisting of a hydrogen bond donor and hydrogen bond acceptor in the ratio determined by the very preparation process. The components of DES are kept together by stronger or weaker hydrogen bonds, whereby the hydro-gen bonds themselves do not determine the eutectic char-acter of the mixture. Namely, the phenomenon of binary eutectics is characteristic for all two-component systems that are completely immiscible in solid phase or exhibit limited immiscibility, which means that they cannot crys-tallize in a common crystal lattice. Since the latter systems are relatively rare, binary eutectics are rather a rule than an

exception. Hydrogen bonds here only induce the non-ide-ality of the liquid phase, which can produce shifting of the characteristic parameters of the binary eutectic mixture, *i.e.* its melting point and composition, with respect to the parameters expected for the ideal solutions. The addition of any component to a system commonly referred to as DES, can affect the strength of hydrogen bonding between its components, or their mutual miscibility. This fact influ-enced the experimental procedure applied in this paper. DESs prepared and investigated in this paper are listed in Table 2.

2.3 Tie lines in quasi-three-component systems

The quasi-three-component systems in which the first component is aliphatic (*n*-hexane, *n*-heptane or *i*-octane) or aromatic hydrocarbon (toluene), the second component is pyridine or thiophene, and the third quasi-component is DES consisting of choline chloride and glycerol, or choline chloride and ethylene glycol may be considered as class II systems with respect to the liquid-liquid equilibrium. Namely, pyridine and thiophene are completely miscible with all investigated hydrocarbons. Hydrocarbons and DESs are completely immiscible, as confirmed by NMR. Namely, the ^{1}H NMR spectra collected on a Bruker AV300 apparatus did not indicate measurable traces of DESs in hydrocarbons or hydrocarbons in DESs. Regarding the mis-cibility of pyridine with DESs or thiophene with DESs, DESs

Table 1   – Chemicals
Tablica 1 – Kemikalije

Chemical Kemikalija	Manufacturer Proizvođač	Purity / mass % Čistoća / mas. %	CAS number CAS (registarski) broj	Molar mass / g mol⁻¹ Molarna masa / g mol⁻¹
n-hexane	Carlo Erba Reagenti	>98.5	110-54-3	86.18
n-heptane	Carlo Erba Reagenti	99	142-82-5	100.21
i-octane	Kemika	>99.5	540-84-1	114.23
toluene	Lachner	99.28	108-88-3	92.14
thiophene	Acros Organics	99	110-02-1	84.14
pyridine	Carlo Erba Reagenti	>99	110-86-1	79.10
choline chloride	Acros Organics	99	67-48-1	139.62
glycerol	Kemika	>99.5	56-81-5	92.10
ethylene glycol	VWR Chemicals	99.7	107-21-1	62.07

Table 2   – Deep eutectic solvent systems studied
Tablica 2 – Istraživana niskotemperaturna eutektička otapala

Hydrogen bond acceptor Akceptor vodikove veze	Hydrogen bond donor Donor vodikove veze	Molar ratio Molarni omjer	Molar mass / g mol⁻¹ Molarna masa / g mol⁻¹	Density / g cm⁻³ Gustoća / g cm⁻³
choline chloride (ChCl)	ethylene glycol (EG)	1:2	263.760	1.1260
choline chloride (ChCl)	ethylene glycol (EG)	1:3	325.830	1.1241
choline chloride (ChCl)	ethylene glycol (EG)	1:3.5	356.865	1.1231
choline chloride (ChCl)	glycerol (Gly)	1:1.5	277.755	1.1888
choline chloride (ChCl)	glycerol (Gly)	1:2	323.800	1.2006
choline chloride (ChCl)	glycerol (Gly)	1:3	415.890	1.2082

are dissolved neither in pyridine nor in thiophene; the solubility of pyridine and thiophene in DESs is determined by a simple combination of titration and gravimetry. Pyridine or thiophene is added dropwise into the DESs until turbidity is observed indicating the appearance of the second phase in the system. Maximum solubility was determined from the mass of the added pyridine or thiophene. Regarding the immiscibility of hydrocarbons and DESs, the results are consistent with literature findings in similar systems.[16] In pyridine systems, at higher pyridine content (w_2 higher than approximately 0.4–0.6, depending on the DES), at least one additional phase appears, *i.e.* the DES becomes unstable. This phenomenon was not observed in thiophene systems.

From this, an appropriate experimental procedure for the determination of tie lines was constructed. Mixtures of hydrocarbons and pyridine of different compositions were prepared, whose refractive index at 25 °C was determined on Abbe's refractometer (Model RMI, Exacta Optech, precision ± 0.0001). The obtained dependence of the refractive index on composition can be described by the empirical expression:

$$w_2 = A \cdot n_{D,25}^3 + B \cdot n_{D,25}^2 + C \cdot n_{D,25} + D \qquad (1)$$

which serves as a calibration function of the raffinate phase.

Subsequently, by weighing on an analytical balance, quasi-three-component mixtures were prepared with approximately equal masses of hydrocarbons and DES and a varying pyridine content. The exact composition was calculated from the component masses. The resulting two-phase mixtures were stirred for 24 h in a thermostated air bath at 25 °C (220 rpm). After separation of equilibrium phases, the refractive indices were measured, which were converted into raffinate phase compositions by means of the calibration functions. Compositions of extract phases were determined from the mass balance, from the known overall compositions and compositions of the raffinate phase, whereby preliminary experiments verified the assumption that there are no measurable hydrocarbon quantities in the extract phase.

2.4 Extraction experiments in quasi-seven-component systems

The quasi-seven-component model systems consist of a six-component model fuel comprising three aliphatic hydrocarbons: *n*-hexane, *n*-heptane and *i*-octane, toluene as an aromatic hydrocarbon, as well as thiophene and pyridine as a sulphur and nitrogen compound representative, respectively; the seventh quasi-component is DES as an extraction medium. The model fuel solution was prepared to mimic the composition of Fluid Catalytic Cracking (FCC) gasoline.[10] It consisted of approximately 26 % of *n*-hexane, 26 % of *n*-heptane, 26 % of *i*-octane, 10 % of toluene, 6 % of thiophene and 6 % of pyridine.

Experiments were performed at different mass ratios of DES/model fuel (0.25, 0.50, 0.75, and 1.00 kg kg⁻¹) in a single-stage mode. DES and model fuel were mixed vigorously for 150 min (preliminary experiments showed this to be sufficient time for equilibration). The phases were then left to separate in a settling unit at 25 °C and atmospheric pressure for 24 h.

Raffinate phase compositions after extraction were determined by gas chromatography [GC-2014-Shimadzu / autosampler / FID detector / fused silica capillary column CBP1-S25-050 (length: 25 m, inner diameter: 0.32 mm) system]. Extract phase compositions were calculated by mass balance.

3 Results and discussion

3.1 Tie lines in quasi-three-component systems

The first step in the determination of tie lines is the preparation of calibration curves for the determination of the raffinate phase composition according to Eq. (1). The raffinate phase refractive indices for all the two-component systems ranged from 1.25 to 1.55 and for each system at least 11 data points (21 for the toluene systems) were determined, and the correlation coefficients for all systems were at least $R^2 = 0.999$. The calibration curve parameters are shown in Table 3.

Table 3 – Parameters of composition *vs.* refractive index correlations (Eq. 1)
Tablica 3 – Parametri ovisnosti indeksa loma o sastavu (jedn. 1)

System Sustav	A	B	C	D
n-hexane (1) – pyridine (2)	0	−18.39	60.20	−47.96
n-heptane (1) – pyridine (2)	220.39	−978.55	1454.93	−723.50
i-octane (1) – pyridine (2)	262.15	−1155.75	1705.50	841.61
toluene (1) – pyridine (2)	0	0	79.73	−119.09
n-hexane (1) – thiophene (2)	0	−20.98	67.16	−52.63
n-heptane (1) – thiophene (2)	161.27	−727.45	1098.95	−555.07
i-octane (1) – thiophene (2)	141.40	−644.03	982.82	−501.51
toluene (1) – thiophene (2)	0	−208.93	661.64	−522.14

The solubility of pyridine or thiophene in DESs is shown in Table 4. The measurement uncertainty here is estimated at a relatively high value of $u(w) \leq 0.01$. Significantly higher solubility of pyridine than thiophene has been observed, which can immediately point to the higher suitability of investigated DESs for denitrification than for desulphurization.

As far as the tie lines in the three-component pyridine systems are concerned, it has already been stated that it was not possible to investigate the entire range of compositions, because the systems with a higher mass fraction of pyridine separated into more than two phases, that is, DESs became unstable. Twelve systems of the hydrocarbon (1) – pyridine (2) – DES (3) type were investigated. Complete experimental data (initial compositions and equilibrium compositions) are available only on request, as supplemental information, due to their extensiveness. Here, the measurement uncertainty is estimated relatively high as well, at $u(w) \leq 0.005$ for initial compositions and for the raffinate phase compositions, and at $u(w) \leq 0.01$ for the extract phase compositions. The graphical representation,

Table 4 – Solubility of pyridine or thiophene in investigated DESs at 25 °C

Tablica 4 – Topljivost piridina ili tiofena u istraživanim DES-ovima pri 25 °C

DES	Maximal mass fraction of pyridine/w_2 Maksimalni maseni udjel piridina/w_2	Maximal mass fraction of thiophene/w_2 Maksimalni maseni udjel tiofena/w_2
ChCl-EG 1:2	0.630	0.092
ChCl-EG 1:3	0.746	0.102
ChCl-EG 1:3,5	0.787	0.106
ChCl-Gly 1:1,5	0.744	0.057
ChCl-Gly 1:2	0.761	0.051
ChCl-Gly 1:3	0.766	0.039

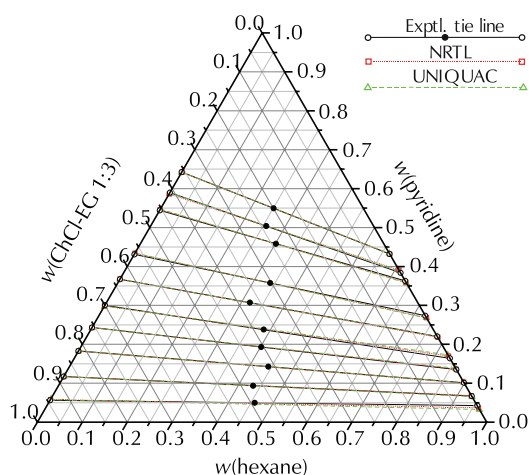*i.e.* triangular diagrams are shown only for four characteristic systems in Figs. 1–4.

Fig. 1   – Tie lines in the system *n*-hexane (1) – pyridine (2) – ChCl-EG 1:3 (3)

Slika 1 – Vezne linije u sustavu *n*-heksan (1) – piridin (2) – ChCl-EG 1:3 (3)
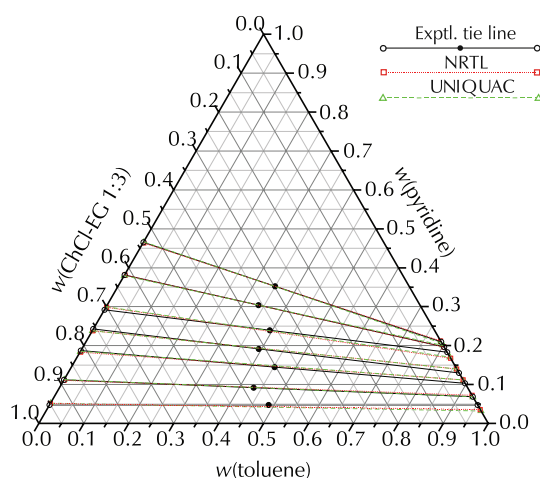

Fig. 2   – Tie lines in the system toluene (1) – pyridine (2) – ChCl-EG 1:3 (3)

Slika 2 – Vezne linije u sustavu toluen (1) – piridin (2) – ChCl-EG 1:3 (3)
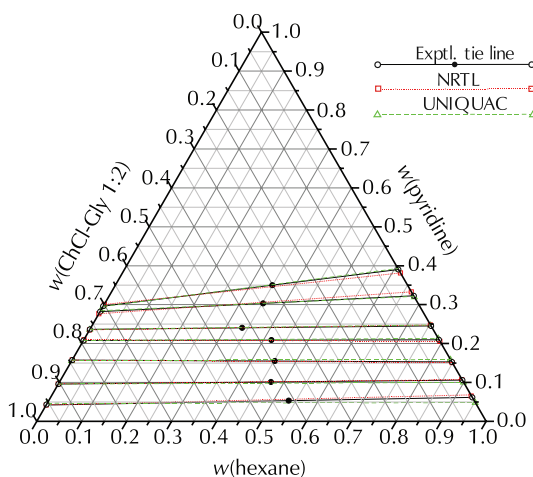

Fig. 3   – Tie lines in the system *n*-hexane (1) – pyridine (2) – ChCl-Gly 1:2 (3)

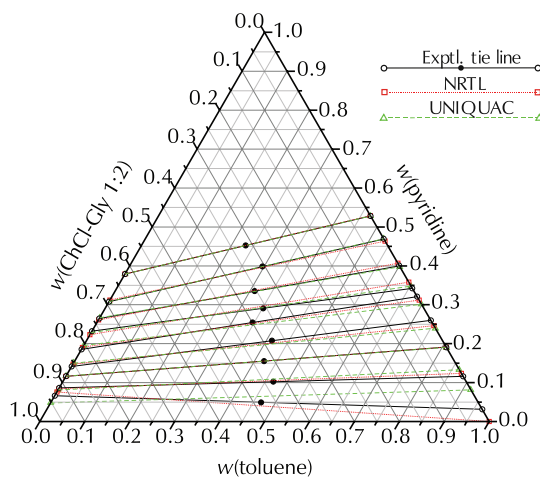*Slika 3* – Vezne linije u sustavu *n*-heksan (1) – piridin (2) – ChCl-Gly 1:2 (3)

Fig. 4   – Tie lines in the system toluene (1) – pyridine (2) – ChCl-Gly 1:2 (3)

Slika 4 – Vezne linije u sustavu toluen (1) – piridin (2) – ChCl-Gly 1:2 (3)
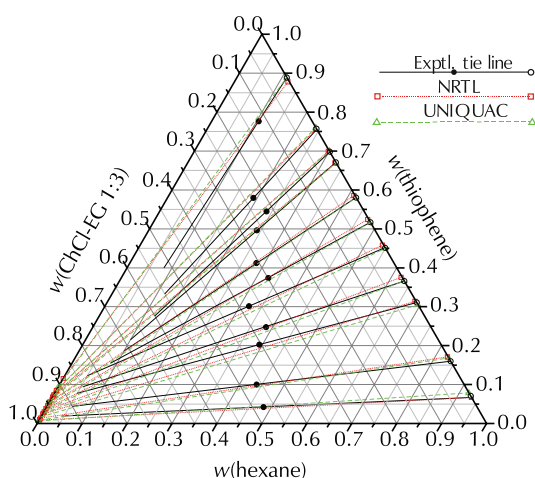
Fig. 5 – Tie lines in the system *n*-hexane (1) – thiophene (2) – ChCl-EG 1:3 (3)
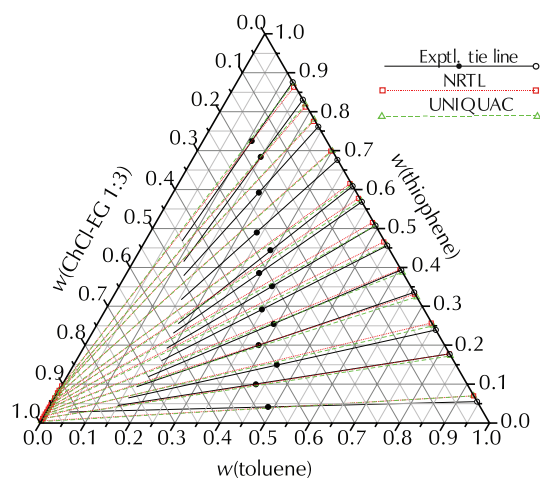*Slika 5* – Vezne linije u sustavu *n*-heksan (1) – tiofen (2) – ChCl--EG 1:3 (3)

Fig. 6 – Tie lines in the system toluene (1) – thiophene (2) – ChCl-EG 1:3 (3)
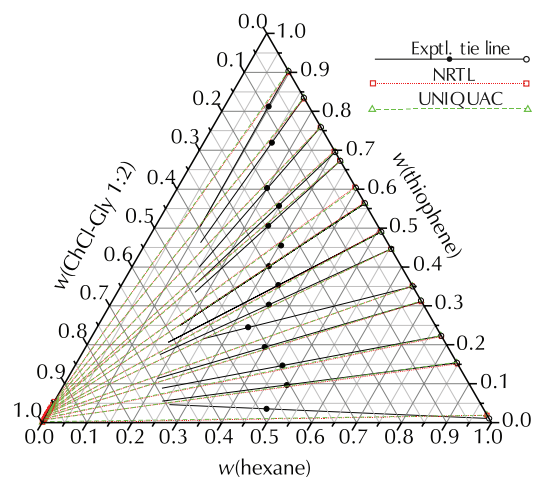*Slika 6* – Vezne linije u sustavu toluen (1) – tiofen (2) – ChCl-EG 1:3 (3)

Fig. 7 – Tie lines in the system *n*-hexane (1) – thiophene (2) – ChCl-Gly 1:2 (3)
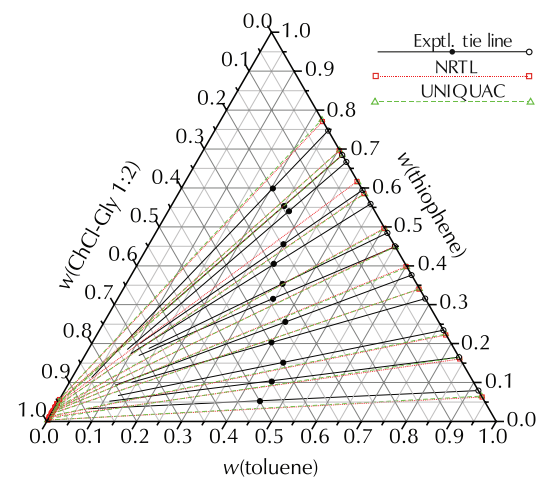*Slika 7* – Vezne linije u sustavu *n*-heksan (1) – tiofen (2) – ChCl--Gly 1:2 (3)

Fig. 8 – Tie lines in the system toluene (1) – thiophene (2) – ChCl-Gly 1 : 2 (3)
Slika 8 – Vezne linije u sustavu toluen (1) – tiofen (2) – ChCl-Gly 1:2 (3)

With respect to tie lines in thiophene systems, the experimental procedure described above proved to be insufficiently precise. Namely, the estimated uncertainty of $u(w) \leq 0.005$ both for the initial composition and the refractive phase was not sufficient to determine the composition of the extract phase with enough certainty by means of the mass balance, due to the relatively high slope of the tie lines, especially at higher thiophene content. Complete experimental data (initial compositions and equilibrium compositions of the raffinate phase) are available only on request, as supplemental information, due to their extensiveness. In Figs. 5–8, only four characteristic systems are shown. The tie lines were not drawn up to the point of the extract phase because some of them would intersect due to the large measurement uncertainty.

3.2 Thermodynamic modelling in quasi-three-component systems

For describing liquid-liquid phase equilibria in quasi-three-component systems containing DES, NRTL model[16,17] and COSMO-RS model[16] have been used so far; thereby NRTL gave significantly better results.

With respect to our previous studies in systems containing ionic liquids,[19,20] in this paper we have tried to compare NRTL and UNIQUAC model in their appropriate variants. NRTL model calculates local concentrations of solution components that can be different from global ones due to particle interactions, as described by two interaction energy parameters per pair of molecules or other particles, τ_{ij} and τ_{ji}. The third, nonrandomness parameter, $\alpha_{ij} = \alpha_{ji}$, is

introduced to account for other effects. Excess Gibbs energy, g^{ex}, is calculated according to:

$$g^{ex}/RT = \sum_{i=1}^{n_c} x_i \left[\sum_{j=1}^{n_c} \tau_{ji} G_{ji} x_j \middle/ \sum_{k=1}^{n_c} G_{ki} x_k \right] \qquad (2)$$

with:

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \qquad (3)$$

n_c is the number of components (or other particles, e.g. quasi-components) in the system. α parameters are usually fixed at empirical values; here they will be set to the value of 0.3 for all component pairs.[10,19,20] Interaction parameters are determined by regression from experimental tie line data.

UNIQUAC model takes into account the combinatorial contribution, $g^{ex,C}$ which describes the non-ideality of the liquid solution as a result of differences in the size and shape of molecules or of other particles according to:

$$g^{ex,C}/(RT) = \sum_{i=1}^{n_c} x_i \ln\left(\Phi_i/x_i\right) + (z/2)\sum_{i=1}^{n_c} q_i x_i \ln\left(\Theta_i/\Phi_i\right) \quad (4)$$

The residual contribution, $g^{ex,R}$, describes the non-ideality as a consequence of interaction of molecules or of other particles according to:

$$g^{ex,R}/(RT) = -\sum_{i=1}^{n_c} q_i x_i \ln\left(\sum_{j=1}^{n_c} \Theta_j \tau_{ji}\right) \qquad (5)$$

In previous expressions Φ_i, Θ_i and x_i denote volume, surface and mole (number) fractions, respectively, of components or any other chemical units, and they are interrelated by the following expressions:

$$\Phi_i = x_i r_i \middle/ \sum_{j=1}^{n_c} x_j r_j \qquad (6)$$

$$\Theta_i = x_i q_i \middle/ \sum_{j=1}^{n_c} x_j q_j \qquad (7)$$

r_i and q_i are characteristic volume and surface parameters, respectively, of molecules or any other particles. For most simple substances (hydrocarbons, pyridine and thiophene in this article) they can be calculated by structural group approach according to:

$$r_i = \sum_{k=1}^{n_g} v_{ki} R_k \qquad (8)$$

$$q_i = \sum_{k=1}^{n_g} v_{ki} Q_k \qquad (9)$$

using corresponding volume and surface structural group parameters, R_k and Q_k, respectively, which are tabulated in literature.[21] Different approaches are suggested for other types of particles. In this paper, DESs are treated as qua-

si-components and the approach of *Domańska*[22] is applied. By that correlation, r_i and q_i parameters can be related to experimental values of molar volumes of components or, in this case, quasi-components:

$$r_i = 0.029281 v_i \qquad (10)$$

$$q_i = (z-2)r_i/z + 2(1-l_i)/z \qquad (11)$$

Molar volumes are easily calculated from measured system density and the molar mass of the quasi-component. l_i is the so-called bulk factor, and here it is assumed to take the value of 0. z is the lattice coordination number and it usually amounts to 10, both in the expression for q_i and in equation for $g^{ex,C}$. The UNIQUAC model parameters used in this paper are listed in Table 5. Interaction parameters τ_{ij} and τ_{ji} are determined by regression from experimental tie line data.

Table 5 – UNIQUAC model structure parameters
Tablica 5 – Strukturni parametri modela UNIQUAC

Component Komponenta	r	q
n-hexane	4.4998	3.856
n-heptane	5.1742	4.3960
i-octane	5.8463	5.0080
toluene	3.9228	2.968
thiophene	2.8569	2.140
pyridine	2.9993	2.113
ChCl-EG 1 :2	6.859	5.687
ChCl-EG 1:3	8.487	6.990
ChCl-EG 1:3.5	9.304	7.643
ChCl-Gly 1:1.5	6.841	5.673
ChCl-Gly 1:2	7.897	6.518
ChCl-Gly 1:3	10.079	8.263

3.3 Interaction parameters in quasi-three component systems with pyridine

The regression procedure for both models in this part is virtually identical to that described in our previous works.[19,20] A modified Sørensen-Arlt procedure is used; in the first step, the minimum of the following function is searched for:

$$OF_1 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \left[\left(x_i^R \gamma_i^R - x_i^E \gamma_i^E\right) \middle/ \left(x_i^R \gamma_i^R + x_i^E \gamma_i^E\right)\right]_j^2 + \\ + Q\left(\tau_{12}^2 + \tau_{21}^2 + \tau_{13}^2 + \tau_{31}^2 + \tau_{23}^2 + \tau_{32}^2\right) \qquad (12)$$

with respect to six interaction parameters τ_{ij} using fixed values of nonrandomness parameters $\alpha_{ij} = 0.3$. γ_i are the activity coefficients; the expressions for γ_i are obtained by differentiating the appropriate expressions for the excess Gibbs energy and can be found elsewhere.[23] $n_c = 3$ is the number of components and quasi-components, and n_d is the number of experimental tie lines. The so-called penalty function is set to $Q = 1 \times 10^{-6}$ for both models[10] and

serves to reject unrealistically large τ-values which might produce local minima of OF_1.

Calculated interaction parameters serve as an initiation for the second step, where the minimum of the following function is searched for:

$$OF_2 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \sum_{p=R,E} \left[\left(w_i^p\right)_{\text{exp}} - \left(w_i^p\right)_{\text{mod}} \right]_j^2 + {} \atop {} + Q\left(\tau_{12}^2 + \tau_{21}^2 + \tau_{13}^2 + \tau_{31}^2 + \tau_{23}^2 + \tau_{32}^2\right) \tag{13}$$

aiming at producing the best possible match of experimental equilibrium compositions. The penalty function value here is set to $Q = 1 \times 10^{-10}$ for both models.[10] w_i are the mass fractions of the components (which is the difference compared to the original Sørensen-Arlt method that defines the function over molar ratios). $p = R$ and $p = E$ denote raffinate and extract phase, respectively.

The optimal model parameters are shown in Table 6, together with the average absolute prediction errors of equilibrium mass fractions as calculated by:

$$A = {} \atop \sqrt{\left[OF_2 - Q\left(\tau_{12}^2 + \tau_{21}^2 + \tau_{13}^2 + \tau_{31}^2 + \tau_{23}^2 + \tau_{32}^2\right)\right]\Big/\left(n_d \cdot n_c \cdot 2\right)} \tag{14}$$

Equilibrium compositions calculated using the models are compared to experimental ones and they are shown for selected systems in Figs. 1–4. The agreement can be considered rather good, based on low A-values obtained. By comparing interaction parameters of individual systems, certain regularities were observed that would be taken into account later when extrapolating data to other systems. The calculated equilibrium compositions for all systems are available only on request as supplemental information, due to their extensiveness.

Table 6   – Optimal NRTL and UNIQUAC model interaction parameters and average absolute prediction errors for the pyridine-containing systems studied
Tablica 6 – Optimalni interakcijski parametri modela NRTL i UNIQUAC i srednja kvadratna odstupanja od predviđanja za istraživane sustave s piridinom

NRTL α_{12}; α_{13}; α_{23} = 0.3; 0.3; 0.3	τ_{12}	τ_{13}	τ_{21}	τ_{23}	τ_{31}	τ_{32}	A
n-hexane (1) – pyridine (2) – ChCl-EG 1:2 (3)	1.4938	12.4133	8.9182	13.5841	9.8920	0.8335	0.0054
n-heptane (1) – pyridine (2) – ChCl-EG 1:2 (3)	0.0297*	19.3031	7.8438	19.3636	9.1566	−0.7028*	0.0052
i-octane (1) – pyridine (2) – ChCl-EG 1:2 (3)	0.7280	15.0908	6.3910	14.8661	13.6420	1.3190	0.0029
toluene (1) – pyridine (2) – ChCl-EG 1:2 (3)	0.1445*	11.0991	5.8003	16.5042	9.4131	1.1202	0.0071
n-hexane (1) – pyridine (2) – ChCl-EG 1:3 (3)	1.7119	18.7921	10.3059	18.6398	7.0916	0.4363	0.0027
n-heptane (1) – pyridine (2) – ChCl-EG 1:3 (3)	1.0741	14.2729	7.9995	15.9081	5.2913	−0.2533*	0.0054
i-octane (1) – pyridine (2) – ChCl-EG 1:3 (3)	1.2821	21.6590	8.5159	19.2138	7.9995	1.0606	0.0049
toluene (1) – pyridine (2) – ChCl-EG 1:3 (3)	1.3687*	14.0906	5.1349	8.7051	15.5565	0.2939*	0.0057
n-hexane (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	2.0993	19.3546	8.2701	11.5739	5.4768	1.0061	0.0036
n-heptane (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	1.5488	18.2480	7.8869	12.9789	11.1737	14.9702*	0.0040
i-octane (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	1.5483	24.7799	8.9062	18.1421	6.9045	1.2557	0.0057
toluene (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	1.3075*	13.8464	5.0101	8.7253	15.4801	1.6839	0.0067
n-hexane (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	2.2566	14.9139	12.0938	13.3919	12.3707	2.2505	0.0099
n-heptane (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	1.9382	14.5587	12.0775	13.6596	12.3867	0.7656	0.0096
i-octane (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	1.1168	15.5462	11.2275	15.0223	11.8542	1.4458	0.0028
toluene (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	11.9978	19.7290	8.7013	15.9875	32.6193	1.0081	0.0107
n-hexane (1) – pyridine (2) – ChCl-Gly 1:2 (3)	2.1774	8.1347	9.8881	11.6690	12.9617	1.7835	0.0037
n-heptane (1) – pyridine (2) – ChCl-Gly 1:2 (3)	2.0920	8.2722	10.0840	11.7431	13.2568	1.4582	0.0089
i-octane (1) – pyridine (2) – ChCl-Gly 1:2 (3)	1.9229	14.4350	10.6853	13.8492	12.6237	2.1945	0.0030
toluene (1) – pyridine (2) – ChCl-Gly 1:2 (3)	12.3460	20.1972	11.3394	14.8723	32.4246	−0.4306*	0.0084
n-hexane (1) – pyridine (2) – ChCl-Gly 1:3 (3)	0.7578	5.2734	2.5079*	11.7239	6.5733	−1.2651*	0.0091
n-heptane (1) – pyridine (2) – ChCl-Gly 1:3 (3)	0.9317	5.4217	1.8711*	15.7645	7.7945	0.8885	0.0124
i-octane (1) – pyridine (2) – ChCl-Gly 1:3 (3)	−0.0685*	4.5201	2.7072*	17.8930	5.9000	−1.5744*	0.0108
toluene (1) – pyridine (2) – ChCl-Gly 1:3 (3)	13.3033	18.4480	11.2062	16.9567	33.8312	−0.6163*	0.0104

Table 6 – (continued)
Tablica 6 – (nastavak)

UNIQUAC	τ_{12}	τ_{13}	τ_{21}	τ_{23}	τ_{31}	τ_{32}	A
n-hexane (1) – pyridine (2) – ChCl-EG 1:2 (3)	1.6374	0.2165	0.0755	0.0093	0.0632	3.0117	0.0058
n-heptane (1) – pyridine (2) – ChCl-EG 1:2 (3)	1.0171	0.0650*	0.2688	0.0011	0.0121*	2.1551	0.0035
i-octane (1) – pyridine (2) – ChCl-EG 1:2 (3)	1.6856	0.7864	0.0061*	0.6457*	0.2730	1.3489	0.0082
toluene (1) – pyridine (2) – ChCl-EG 1:2 (3)	1.2933	0.1855	0.0140	0.7069*	0.0058	0.7201	0.0025
n-hexane (1) – pyridine (2) – ChCl-EG 1:3 (3)	2.3526*	0.0547*	0.0285	0.7191*	0.4595*	2.4625	0.0033
n-heptane (1) – pyridine (2) – ChCl-EG 1:3 (3)	0.9787	0.0128*	0.3898	0.0859	0.7068*	2.6309	0.0052
i-octane (1) – pyridine (2) – ChCl-EG 1:3 (3)	1.6759	0.4115	0.0184	0.5819*	0.1698	1.7041	0.0060
toluene (1) – pyridine (2) – ChCl-EG 1:3 (3)	0.6160	0.0184	0.2603	0.0418	0.1876	1.5621	0.0054
n-hexane (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	1.5667	0.6317	0.1577	3.6030*	0.0840	0.0022*	1.5667
n-heptane (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	0.5267	0.0331*	0.6659	0.0078	0.1418	2.2502	0.5267
i-octane (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	1.7022	0.3966	0.0341	0.3622*	0.1327	2.3550	1.7022
toluene (1) – pyridine (2) – ChCl-EG 1:3.5 (3)	1.1534	0.0711	0.2098	1.8057*	0.0656	0.2228*	1.1534
n-hexane (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	0.8788	0.0668	0.1234	0.0147	0.0380	1.2029	0.0102
n-heptane (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	0.5833	0.0697	0.7473	0.0377	0.0523	1.9962	0.0037
i-octane (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	0.5256	0.0025	1.1915	1.7811*	0.0329	0.2580*	0.0024
toluene (1) – pyridine (2) – ChCl-Gly 1:1.5 (3)	1.7363	0.0008	0.0008*	0.5214*	0.0009*	1.0372	0.0131
n-hexane (1) – pyridine (2) – ChCl-Gly 1:2 (3)	0.6886	0.4331	0.3674	0.0120	0.0580	1.5316	0.0036
n-heptane (1) – pyridine (2) – ChCl-Gly 1:2 (3)	0.7430	0.5701	0.5097	0.0362	0.0700	1.8564	0.0017
i-octane (1) – pyridine (2) – ChCl-Gly 1:2 (3)	0.8054	0.7658	0.4650	0.0719	0.1804	1.7658	**
toluene (1) – pyridine (2) – ChCl-Gly 1:2 (3)	1.0249	0.2680	0.0042	0.0925	0.0730	1.1876	0.0121
n-hexane (1) – pyridine (2) – ChCl-Gly 1:3 (3)	0.5560	0.1037	0.8760	0.0034	0.0129	3.1512	0.0061
n-heptane (1) – pyridine (2) – ChCl-Gly 1:3 (3)	0.6098	0.0786	0.7058	0.0029	0.0136	2.5666	0.0061
i-octane (1) – pyridine (2) – ChCl-Gly 1:3 (3)	0.9298	0.0309	0.7329	0.0245	0.2601	3.9091	0.0068
toluene (1) – pyridine (2) – ChCl-Gly 1:3 (3)	1.9656	0.6037	0.0313	0.1128	0.0557	2.1961	0.0116

* outlying values not used for subsequent averaging / stršeće vrijednosti koje nisu primijenjene za naknadno uprosječivanje
** for this system, the second best set of parameters was used due to a better accordance with other systems / za ovaj je sustav odabran drugi najbolji skup parametara zbog boljega slaganja s ostalim sustavima

3.4 Interaction parameters in quasi-three component systems with thiophene

As already mentioned, using the described experimental procedure a thermodynamically consistent set of tie lines could not be obtained, from which the interaction parameters would be determined. Nevertheless, the literature describes the possibilities of determining interaction parameters based on a limited set of experimental data, with the extrapolation of part of information from other systems, or other models. Thus, ChemCAD chemical-engineering simulation software by Chemstations™ offers an estimation of the interaction parameters of the NRTL and UNIQUAC models based on the Gibbs energy vs. composition dependence simulated by the UNIFAC model. This option is default in two-component systems in which there are no corresponding experimental data on vapour-liquid equilib-

rium. This *de facto* means that data from related systems are extrapolated to the one currently under consideration.

Following this idea, an extrapolation procedure for determining the interaction parameters in the thiophene system was constructed. Three assumptions were taken into consideration. The first is that the interaction parameters already determined from the experimental data in the pyridine systems could be carried over to the thiophene systems, which both NRTL and UNIQUAC models provide in principle. Prior to transferring, the interaction parameters (from Table 6) were averaged wherever possible, rejecting the outlying values (marked with an asterisk in Table 6). Secondly, it was assumed that the interaction parameters of all three aliphatic hydrocarbons to other components of the system (ionic liquid or pyridine) are equal, which is the "natural" assumption of the UNIQUAC mod-

el; in the NRTL model it is not a "natural" assumption, but merely the regularity observed in the previous calculations (see Table 6) is taken into account. Here, only the parameters of the interaction of hydrocarbons with ionic liquid are relevant for transferring into thiophene systems; those describing hydrocarbon/pyridine interactions will be important later when transferring to quasi-seven-component systems. Thirdly, the previous experiments confirmed the complete immiscibility of the investigated DESs with all the hydrocarbons; additional experiments determined the mutual solubility of thiophene and all explored DESs. Therefrom it was possible to generate a set of extract phase compositions equidistantly distributed between the point of pure DES and the point of maximum thiophene solubility in DES (in the triangular diagram). Because of the low solubility of thiophene in all explored DESs, the extract phase compositions thus generated could not differ significantly from the true compositions of the extract phase. In other words, they could very probably be within the experimental error of some better method for the equilibrium composition determination, e.g. ¹H NMR as described in the literature.[16] Further on, a set of tie lines linking the actual, experimentally determined raffinate phase compositions and generated extract phase compositions could be formed.

After generating a set of tie lines, the interaction parameters were determined in a manner analogous to that described in the previous section. Since the parameters related to the hydrocarbon/DES interactions, τ_{13} and τ_{31} were fixed based on previous calculations, the remaining four parameters were optimized, and the objective functions in the first and second step of the modified Sørensen-Arlt procedure were:

$$OF_3 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \left[\left(x_i^R \gamma_i^R - x_i^E \gamma_i^E \right) / \left(x_i^R \gamma_i^R + x_i^E \gamma_i^E \right) \right]_j^2 + \\ + Q \left(\tau_{12}^2 + \tau_{21}^2 + \tau_{23}^2 + \tau_{32}^2 \right)$$ (15)

$$OF_4 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \sum_{p=R,E} \left[\left(w_i^p \right)_{\text{exp}} - \left(w_i^p \right)_{\text{mod}} \right]_j^2 + \\ + Q \left(\tau_{12}^2 + \tau_{21}^2 + \tau_{23}^2 + \tau_{32}^2 \right)$$ (16)

Since the tie lines obtained by the model were not compared with the experimental ones but rather with those generated on the basis of the several assumptions described, it made no sense to define average absolute prediction errors in the manner described in Eq. (14).

The optimum model parameters are shown in Table 7. The tie lines calculated using the model are compared to the experimental findings in selected systems, as shown in Figs. 5–8. Comparison of the interaction parameters between individual systems also shows certain regularities that will be taken into account when extrapolating the data to other systems. The calculated equilibrium compositions for all systems are available only on request as supplementary information, due to their extensiveness.

Table 7 – Optimal NRTL and UNIQUAC model interaction parameters
Tablica 7 – Optimalni interakcijski parametri modela NRTL i UNIQUAC

NRTL α_{12}; α_{13}; $\alpha_{23} = 0.3$; 0.3; 0.3	τ_{12}	τ_{13}^*	τ_{21}	τ_{23}	τ_{31}^*	τ_{32}
n-hexane (1) – thiophene (2) – ChCl-EG 1:2 (3)	14.7027	15.6024	18.3542	5.7708	10.8969	0.8495
n-heptane (1) – thiophene (2) – ChCl-EG 1:2 (3)	14.5569	15.6024	18.2657	5.9139	10.8969	1.0641
i-octane (1) – thiophene (2) – ChCl-EG 1:2 (3)	14.5583	15.6024	18.2083	5.8257	10.8969	0.9597
toluene (1) – thiophene (2) – ChCl-EG 1:2 (3)	14.5816	14.0906	18.1939	5.7809	9.4131	0.8685
n-hexane (1) – thiophene (2) – ChCl-EG 1:3 (3)	12.3085	18.2413	15.2669	5.8084	6.7942	0.6283
n-heptane (1) – thiophene (2) – ChCl-EG 1:3 (3)	14.5842	18.2413	18.2904	5.7469	6.7942	0.6057
i-octane (1) – thiophene (2) – ChCl-EG 1:3 (3)	13.2086	18.2413	23.8682	5.8753	6.7942	0.6410
toluene (1) – thiophene (2) – ChCl-EG 1:3 (3)	14.6474	11.0991	18.2144	5.7991	15.5565	0.6563
n-hexane (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	14.6657	20.7942	18.2990	6.3105	7.8517	0.4754
n-heptane (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	14.6638	20.7942	18.1966	6.1026	7.8517	0.6398
i-octane (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	14.8939	20.7942	24.0836	6.1000	7.8517	0.5731
toluene (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	14.5782	13.8464	18.1906	6.0580	15.4801	0.4949
n-hexane (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	0.7461	15.0063	14.7423	6.3765	12.2039	1.5503
n-heptane (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	0.0958	15.0063	14.9081	7.2515	12.2039	1.8053
i-octane (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	0.3501	15.0063	14.7983	6.3174	12.2039	1.6961
toluene (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	0.7247	19.7290	13.4731	7.0417	32.6193	1.7603

Table 7 – (continued)
Tablica 7 – (nastavak)

NRTL α_{12}; α_{13}; α_{23} = 0.3; 0.3; 0.3	τ_{12}	$\tau_{13}{}^{*}$	τ_{21}	τ_{23}	$\tau_{31}{}^{*}$	τ_{32}
n-hexane (1) – thiophene (2) – ChCl-Gly 1:2 (3)	0.8256	10.2806	14.8034	6.3475	12.9474	1.5913
n-heptane (1) – thiophene (2) – ChCl-Gly 1:2 (3)	0.5778	10.2806	14.5707	6.1912	12.9474	1.4147
i-octane (1) – thiophene (2) – ChCl-Gly 1:2 (3)	0.4962	10.2806	15.3825	6.7704	12.9474	1.6624
toluene (1) – thiophene (2) – ChCl-Gly 1:2 (3)	0.7574	20.1972	13.4993	7.0997	32.4246	1.6525
n-hexane (1) – thiophene (2) – ChCl-Gly 1:3 (3)	1.0107	5.0717	15.9117	6.9515	6.7559	1.7216
n-heptane (1) – thiophene (2) – ChCl-Gly 1:3 (3)	0.4921	5.0717	16.0278	7.5559	6.7559	1.9789
i-octane (1) – thiophene (2) – ChCl-Gly 1:3 (3)	0.6477	5.0717	15.3116	8.1445	6.7559	2.0653
toluene (1) – thiophene (2) – ChCl-Gly 1:3 (3)	0.7167	18.4480	13.6023	7.0666	33.8312	1.7879
UNIQUAC	τ_{12}	τ_{13}	τ_{21}	τ_{23}	τ_{31}	τ_{32}
n-hexane (1) – thiophene (2) – ChCl-EG 1:2 (3)	2.1182	0.5015	0.2417	0.0259	0.1681	1.1720
n-heptane (1) – thiophene (2) – ChCl-EG 1:2 (3)	2.3845	0.5015	0.2729	0.0333	0.1681	1.1613
i-octane (1) – thiophene (2) – ChCl-EG 1:2 (3)	2.6330	0.5015	0.1242	0.0403	0.1681	1.1423
toluene (1) – thiophene (2) – ChCl-EG 1:2 (3)	2.3133	0.1855	0.1670	0.0867	0.0058	1.0833
n-hexane (1) – thiophene (2) – ChCl-EG 1:3 (3)	2.2831	0.4115	0.1769	0.0457	0.1698	1.2340
n-heptane (1) – thiophene (2) – ChCl-EG 1:3 (3)	1.9542	0.4115	0.3132	0.0995	0.1698	1.1472
i-octane (1) – thiophene (2) – ChCl-EG 1:3 (3)	0.3472*	0.4115	2.0102*	0.0847	0.1698	1.1702
toluene (1) – thiophene (2) – ChCl-EG 1:3 (3)	2.2937	0.0184	0.1872	0.0446	0.1876	1.1844
n-hexane (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	2.0358	0.5142	0.2567	0.1111	0.1195	1.1711
n-heptane (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	2.3546	0.5142	0.2517	0.1317	0.1195	1.1426
i-octane (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	1.3551	0.5142	0.7296	0.2198	0.1195	1.0214
toluene (1) – thiophene (2) – ChCl-EG 1:3.5 (3)	1.8410	0.0711	0.3755	0.0395	0.0656	1.2851
n-hexane (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	2.1668	0.0463	0.2143	0.0754	0.0411	0.9304
n-heptane (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	3.3305	0.0463	0.0141	0.1570	0.0411	0.8455
i-octane (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	2.8232	0.0463	0.0861	0.1358	0.0411	0.8430
toluene (1) – thiophene (2) – ChCl-Gly 1:1.5 (3)	2.5909	0.0008	0.0803	0.0301	0.0009	0.9794
n-hexane (1) – thiophene (2) – ChCl-Gly 1:2 (3)	2.3193	0.5896	0.1822	0.0184	0.1028	0.9592
n-heptane (1) – thiophene (2) – ChCl-Gly 1:2 (3)	2.5264	0.5896	0.0391	0.1016	0.1028	0.8618
i-octane (1) – thiophene (2) – ChCl-Gly 1:2 (3)	2.9453	0.5896	0.0482	0.0909	0.1028	0.8868
toluene (1) – thiophene (2) – ChCl-Gly 1:2 (3)	2.5994	0.2680	0.0620	0.0353	0.0730	0.9922
n-hexane (1) – thiophene (2) – ChCl-Gly 1:3 (3)	2.1066	0.0711	0.2979	0.1367	0.0955	0.7965
n-heptane (1) – thiophene (2) – ChCl-Gly 1:3 (3)	0.0801*	0.0711	3.1883*	0.2152*	0.0955	0.7237*
i-octane (1) – thiophene (2) – ChCl-Gly 1:3 (3)	3.1802	0.0711	0.0392	0.1394	0.0955	0.7892
toluene (1) – thiophene (2) – ChCl-Gly 1:3 (3)	2.7467	0.6037	0.0492	0.0250	0.0557	0.8774

* fixed values averaged from the pyridine-containing systems
* fiksne vrijednosti dobivene uprosječivanjem iz sustava s piridinom

3.5 Extraction experiments in quasi-seven-component systems

The quasi-seven-component systems are obtained by mixing pre-prepared samples of model FCC-gasoline with DESs in different ratios. Components of the solutions were enumerated as: *n*-hexane – 1, *n*-heptane – 2, *i*-octane – 3, toluene – 4, thiophene – 5, pyridine – 6, DES – 7. The solution compositions were determined by weighing and the measurement uncertainty was estimated at $u(w) \leq 0.001$. The raffinate phase compositions were determined by the gas-chromatographic method, and the measurement uncertainty was estimated at $u(w) \leq 0.01$. The presence of DES in the raffinate phase was not observed, so the mass fraction was set to a low value, $w_7^R \leq 1 \times 10^{-6}$. Compositions of the extract phase were calculated from the mass balance as follows. It was assumed that the extract phase contained practically all DES and no aliphatic hydrocarbons, *i.e.* the mass fraction of aliphatic hydrocarbons in the extract stage was set at $w_i^E = 1 \times 10^{-6}$. The mass fraction of the raffinate phase, Ψ^R, was calculated according to:

$$\Psi^R = \left(w_i^F - w_i^E\right)\Big/\left(w_i^R - w_i^E\right) \qquad (17)$$

where *i* denotes the component, and the superscripts F, E, R denote the total mixture, the extract phase and the refractive phase, respectively. For each hydrocarbon, a distinct value of Ψ^R was obtained; the appropriate value for the whole system was calculated as the average of the three specific individual values. Subsequently, the mass fractions of the extractable components (toluene, thiophene and pyridine) and DES were calculated according to:

$$w_i^E = \left(w_i^F - \Psi^R w_i^R\right)\Big/\left(1 - \Psi^R\right) \qquad (18)$$

Mass fractions in both phases were then normalized to the sum of 1. The procedure was repeated for all six investigated DESs and for each of the four different mass ratios of DES / model fuel. Because of their extensiveness, the results are presented in tables as supplemental information. The graphs are included here only to compare the experimental values to those obtained from the NRTL and UNIQUAC models, Figs. 9–12, as an illustration of the possibilities and limitations in the description of the investigated systems by thermodynamic models. The discussion of the quality of the DESs as extraction media will be the subject of future publications.

3.6 Extraction experiments in quasi-seven-component systems

The approach described in our previous papers[19,20] showed that it is possible, not only in principle, to transfer the parameters from three-component systems into seven-component systems, and that it is possible to obtain a satisfactory quantitative description of the separation of an unstable system into two stable equilibrium phases in the thermodynamic equilibrium in the case of extraction of nitrogen-containing, sulphur-containing and aromatic components from model solutions mimicking FCC-gasoline.

A similar procedure was used in this paper in order to transfer the parameters determined in quasi-three-component systems into quasi-seven-component ones, by generating tables of parameters such as that shown in Table 8. Thereby, binary parameters describing interaction of low molecular components that were not determined by experiments in quasi-three-component systems (aliphatic/aliphatic, aliphatic/toluene and thiophene/pyridine binaries) were taken from our previous papers,[20] *i.e.* they were estimated as described therein.

The attempt to calculate the extraction separation by means of the given set of parameters yielded, however, the compositions of two equilibrium phases, which did not correspond to the experimental observation. Thus, for the system with ChCl-EG 1:2 , with the ratio DES / model gasoline of 0.25 kg kg^{-1} and with the NRTL model, the raffinate phase composition (in mass fractions) of $w^R = \{0.2477, 0.2594, 0.2455, 0.1015, 0.0744, 0.0715, 0.0000\}$ was obtained; the corresponding extract phase composition $w^E = \{0.1819, 0.1904, 0.1802, 0.0691, 0.0120, 0.0292, 0.3371\}$ was calculated. The result points to the extraction of excessive amounts of aliphatic components. For the same system, using the UNIQUAC model, the raffinate phase composition was $w^R = \{0.2631, 0.2756, 0.2608, 0.1038, 0.0462, 0.0502, 0.0003\}$ and the extract phase composition was $w^E = \{0.0000, 0.0000, 0.0000, 0.0000, 0.0037, 0.0320, 0.9642\}$. In the raffinate phase, a too large mass fraction of DES was calculated and in the extract phase the amount of extracted substances was too low, with the mass fraction of extracted toluene being three orders of magnitude smaller ($w \approx 10^{-9}$) than the mass fraction of extracted aliphatic hydrocarbons ($w \approx 10^{-6}$). Since such a procedure of direct transfer of parameters appears to be a dead end, parameters for other systems are available only on request, as supplemental information.

It is interesting to try to explain the possible causes of the observed deviations here. One has to assume that the binary interaction parameters determined in quasi-three-component systems carry the wrong or too little experimental information. For example, it was not possible to determine the mass fraction of DES in the raffinate phase by the described experiment or the mass fraction of hydrocarbons in the extract phase, because they were below the detection limit of the method. Therefore, they were assumed to be zero, or for the purpose of computation, they were assigned an arbitrary low value of ~10^{-6}. Quasi-three-component systems were successfully described by the models, but the resulting interaction parameters did not contain true experimental but mere arbitrary information. This problem could only be solved by a different experiment. For systems with a small but measurable hydrocarbon solubility in DES, an alternative experimental method for determining the equilibrium phase composition is, for example, ^{1}H NMR[16]. For systems with extreme insolubility, gas chromatography on a stationary phase impregnated with a non-volatile liquid extraction medium can also be applied, which is in fact a description of gas-liquid chromatography (GLC). The method was experimentally applied for ionic

Table 8 – Example of a complete NRTL and UNIQUAC model interaction parameter set obtained by simple transfer of parameters from quasi-three-component to quasi-seven-component systems. All α-parameters of NRTL model are set to 0.3.
Tablica 8 – Primjer potpunoga skupa interakcijskih parametara modela NRTL i UNIQUAC dobivenoga jednostavnim prijenosom parametara iz kvazi-trokomponentnih u kvazi-sedmerokomponentne sustave. Svi α-parametri modela NRTL postavljeni su na 0.3.

NRTL	*n*-hexane	*n*-heptane	*i*-octane	toluene	thiophene	pyridine	ChCl-EG 1:2
n-hexane	0	0.1398	0.2700	0.8425	14.2343	1.4969	15.6024
n-heptane	−0.1428	0	0.1206	0.9016	14.2343	1.4969	15.6024
i-octane	−0.2814	−0.1228	0	0.8795	14.2343	1.4969	15.6024
toluene	−0.5900	−0.6595	−0.6579	0	14.6024	12.5490	14.0906
thiophene	19.2008	19.2008	19.2008	18.1996	0	1.2960	5.8228
pyridine	9.2895	9.2895	9.2895	7.8654	−0.8452	0	16.0795
ChCl-EG 1:2	10.8969	10.8969	10.8969	9.4131	0.9355	1.0909	0
UNIQUAC	*n*-hexane	*n*-heptane	*i*-octane	toluene	thiophene	pyridine	ChCl-EG 1:2
n-hexane	1	1	1	0.5184	2.3734	0.9880	0.5015
n-heptane	1	1	1	0.5237	2.3734	0.9880	0.5015
i-octane	1	1	1	0.5288	2.3734	0.9880	0.5015
toluene	1.6470	1.6380	1.6290	1	2.3975	1.2982	0.1855
thiophene	0.2005	0.2005	0.2005	0.1535	1	0.4197	0.0767
pyridine	0.4642	0.4642	0.4642	0.0867	1.7690	1	0.0052
ChCl-EG 1:2	0.1681	0.1681	0.1681	0.0058	1.1397	1.8090	1

liquids[18,24–27] and DESs.[28] The method provides the activity coefficients at infinite dilution which bear the key experimental information.

Without measurable levels of DES in the raffinate phase, it was not possible to evaluate quantitatively the interaction of hydrocarbons with pyridine or thiophene. Namely, pyridine and thiophene are completely miscible with all the investigated hydrocarbons. Parameters of interaction of fully miscible components can be estimated, *e.g.*, from experimental data on vapour-liquid equilibrium, but the application of those parameters to the liquid-liquid equilibrium is unreliable in principle. This is a well-known fact, and that is why the interaction parameters of the UNIFAC model for vapour-liquid equilibrium differ from those for liquid-liquid equilibrium modelling, *i.e.* there exist different versions of the parameter tables.[21,29,30] Ideally, the interaction parameters of miscible component pairs can be transferred from another, similar system, containing an extraction agent significantly more soluble in pyridine/hydrocarbon or thiophene/hydrocarbon mixtures. Fortunately, here it was possible to use data from previous research in similar systems, with ionic liquid as an extraction medium.[20]

Therefore, a procedure for determining unknown interaction parameters for DES/low molecular weight component pairs was designed using directly the liquid-liquid

equilibria measurements in quasi-seven-component systems. Firstly, all interaction parameters for low molecular component pairs were taken from the literature.[20] Further, based on the mutual similarity of the phase diagrams in quasi-three-components systems with aliphatic hydrocarbons it is assumed that the aliphatic/DES pair interaction can be described by a unique pair of parameters: $\{\tau_{A7} = \tau_{17} = \tau_{27} = \tau_{37}, \tau_{7A} = \tau_{71} = \tau_{72} = \tau_{73}\}$. In this way, the problem is reduced to the simultaneous determination of eight interaction parameters: $\tau_{A7}, \tau_{47}, \tau_{57}, \tau_{67}, \tau_{7A}, \tau_{74}, \tau_{75}$ and τ_{76}. The modified two-step Sørensen-Arlt procedure was performed according to the expressions:

$$OF_5 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \left(\frac{x_i^R \gamma_i^R - x_i^E \gamma_i^E}{x_i^R \gamma_i^R + x_i^E \gamma_i^E} \right)_j^2 + $$
$$+ Q\left(\tau_{A7}^2 + \tau_{47}^2 + \tau_{57}^2 + \tau_{67}^2 + \tau_{7A}^2 + \tau_{74}^2 + \tau_{75}^2 + \tau_{76}^2 \right) \quad (19)$$

$$OF_6 = \sum_{j=1}^{n_d} \sum_{i=1}^{n_c} \sum_{p=R,E} \left[\left(w_i^p\right)_{exp} - \left(w_i^p\right)_{mod} \right]_j^2 + $$
$$+ Q\left(\tau_{A7}^2 + \tau_{47}^2 + \tau_{57}^2 + \tau_{67}^2 + \tau_{7A}^2 + \tau_{74}^2 + \tau_{75}^2 + \tau_{76}^2 \right) \quad (20)$$

The optimal model parameters are shown in Table 9, which gives all interaction parameters for the DES system with ChCl-EG 1:2 as an example. Tables 10 and 11 provide all the interaction parameters determined in this paper.

Table 9 – Example of a complete NRTL and UNIQUAC model interaction parameter set obtained by 1) transferring parameters for low molecular weight component pairs from literature data on seven-component systems[20] and 2) optimization of DES-related interaction parameters with respect to experimental data in quasi-seven-component systems (this work). All α-parameters of NRTL model are set to 0.3.

Tablica 9 – Primjer potpunoga skupa interakcijskih parametara modela NRTL i UNIQUAC dobivenoga 1) prijenosom parametara za parove niskomolekulskih komponenata iz literaturnih podataka o sedmerokomponentnim sustavima[20] i 2) optimiranjem parametara povezanim s DES-ovima prema eksperimentalnim podatcima u kvazi-sedmerokomponentnim sustavima iz ovoga rada. Svi α-parametri modela NRTL postavljeni su na 0.3.

NRTL	*n*-hexane	*n*-heptane	*i*-octane	toluene	thiophene	pyridine	ChCl-EG 1:2
n-hexane	0	0.1398	0.2700	0.8425	−0.0629	1.2504	5.8506
n-heptane	−0.1428	0	0.1206	0.9016	−1.0997	1.0673	5.8506
i-octane	−0.2814	−0.1228	0	0.8795	−0.3767	1.1947	5.8506
toluene	−0.5900	−0.6595	−0.6579	0	−0.5990	1.8554	2.5965
thiophene	0.6560	1.0528	0.9689	−0.4575	0	1.2960	11.8095
pyridine	0.9255	1.1736	1.2711	1.1988	−0.8452	0	1.8695
ChCl-EG 1:2	5.9858	5.9858	5.9858	−1.3317	−0.4157	−0.3100	0
UNIQUAC	*n*-hexane	*n*-heptane	*i*-octane	toluene	thiophene	pyridine	ChCl-EG 1:2
n-hexane	1	1	1	0.5184	0.3659	0.5109	0.0254
n-heptane	1	1	1	0.5237	0.2711	0.6907	0.0254
i-octane	1	1	1	0.5288	0.7013	0.4855	0.0254
toluene	1.6470	1.6380	1.6290	1	1.6860	1.3556	1.8899
thiophene	1.2831	1.9127	0.9839	0.5306	1	0.4197	2.1670
pyridine	1.1539	0.9648	1.1954	2.3717	1.7690	1	0.0152
ChCl-EG 1:2	0.0221	0.0221	0.0221	0.1331	0.1166	3.7256	1

Table 10 – NRTL and UNIQUAC model interaction parameters calculated in this work – Part 1. Only parameters that vary with the choice of DES are shown. All α-parameters of NRTL model are set to 0.3.

Tablica 10 – Interakcijski parametri modela NRTL i UNIQUAC izračunati u ovom radu – prvi dio. Prikazani su samo parametri koji se mijenjaju s izborom DES-a. Svi α-parametri modela NRTL postavljeni su na 0.3.

NRTL	ChCl-EG 1:2	ChCl-EG 1:3	ChCl-EG 1:3.5	ChCl-Gly 1:1.5	ChCl-Gly 1:2	ChCl-Gly 1:3
aliphatic	5.8506	5.6490	6.3964	7.7397	5.9927	7.0309
toluene	2.5965	2.2527	2.0252	14.2636	14.6326	18.2285
thiophene	11.8095	17.6728	16.9290	16.7038	22.1281	23.3944
pyridine	1.8695	1.0786	2.9120	0.5040	0.0414	−0.2980
UNIQUAC	ChCl-EG 1:2	ChCl-EG 1:3	ChCl-EG 1:3.5	ChCl-Gly 1:1.5	ChCl-Gly 1:2	ChCl-Gly 1:3
aliphatic	0.0254	0.0398	0.0525	0.4298	0.0202	0.0445
toluene	1.8899	1.6570	1.6145	1.5952	0.9282	1.4692
thiophene	2.1670	0.9414	1.3751	2.2217	1.9440	2.1001
pyridine	0.0152	0.0475	0.0338	0.1591	0.1936	0.2459

Table 11 – NRTL and UNIQUAC model interaction parameters calculated in this work – Part 2. Only parameters that vary with the choice of DES are shown. All α-parameters of NRTL model are set to 0.3.

Tablica 11 – Interakcijski parametri modela NRTL i UNIQUAC izračunati u ovom radu – drugi dio. Prikazani su samo parametri koji se mijenjaju s izborom DES-a. Svi α-parametri modela NRTL postavljeni su na 0.3.

NRTL	aliphatic	toluene	thiophene	pyridine
ChCl-EG 1:2	5.9858	−1.3317	−0.4157	−0.3100
ChCl-EG 1:3	5.6168	−1.2924	−0.7613	−0.6830
ChCl-EG 1:3.5	5.3803	−1.3533	−0.7176	−1.8444
ChCl-Gly 1:1.5	4.5033	17.7687	25.8397	22.6089
ChCl-Gly 1:2	3.6891	20.7472	23.1096	20.9226
ChCl-Gly 1:3	5.0203	18.6298	25.9942	22.7379
UNIQUAC	aliphatic	toluene	thiophene	pyridine
ChCl-EG 1:2	0.0221	0.1331	0.1166	3.7256
ChCl-EG 1:3	0.0136	0.4463	0.5176	3.0445
ChCl-EG 1:3.5	0.0129	0.3113	0.4224	4.5538
ChCl-Gly 1:1.5	0.0437	0.2246	0.0052	7.8535
ChCl-Gly 1:2	0.0209	0.6952	0.0345	13.5865
ChCl-Gly 1:3	0.0336	0.5110	0.0137	2.8563

Based on the obtained parameters, the equilibrium compositions of both phases were calculated. The results are numerically shown in the tables, as compared to the experimental values; the tables are given in the supplemental
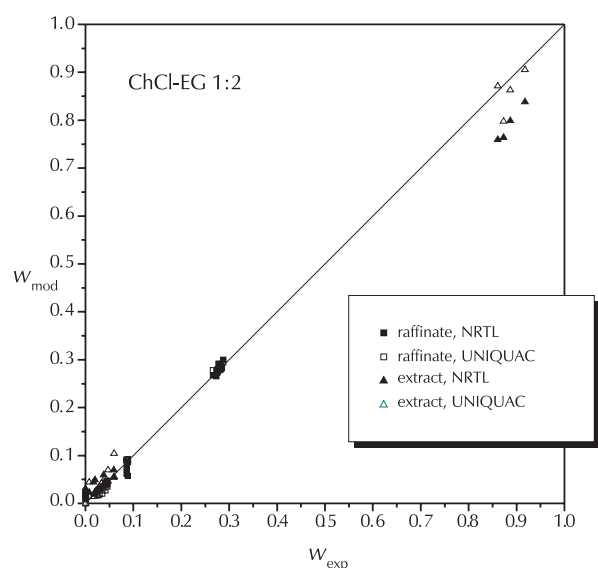
information, due to their extensiveness. The same comparison is presented graphically for a selected system in Figs. 9–12.

As an illustration, for the system with ChCl-EG 1:2, with DES / model gasoline ratio of 0.25 kg kg^{-1} and with the NRTL model, the calculated composition of the raffinate phase (in mass fractions) was w^R = {0.2674, 0.2802, 0.2654, 0.0864, 0.0422, 0.0434, 0.0149} and the composition of the extract phase was w^E = {0.0296, 0, 0304, 0.0283, 0.0698, 0.0228, 0.0556, 0.7634}. For the same system, using the UNIQUAC model, the composition of the raffinate phase was w^R = {0.2784, 0.2916, 0.2760, 0.0917, 0.0351, 0.0273, 0.0000} and the composition of the extract phase was w^E = {0.0001, 0.0000, 0.0000, 0.0541, 0.0444, 0.1037, 0.7977}. At a first glance, it seems that the results for both models are quite satisfactory; in Fig. 9, experimental *vs.* model mass fractions are nicely distributed around the diagonal. Yet, certain characteristic deviations can be recognized. A preferred extraction of pyridine, toluene and thiophene with respect to aliphatic hydrocarbons is described by both models. Pyridine is the best extracted component, followed by toluene and thiophene, see Fig. 10. However, the NRTL model predicts significant extracted amounts of aliphatic compounds, not confirmed by the experiments, as seen by a group of data points within the shaded elliptic region of Fig. 10. On the other hand, the UNIQUAC model does not predict the occurrence of aliphatic hydrocarbons in the extract phase; see data points within the shaded circle encompassing the origin of the diagram in Fig. 10. Fig. 11 shows the medium concentration range, *i.e.* mass fractions of aliphatic hydrocarbons in the raffinate phase. Both models produce similar results and the dispersion of data may serve to as-
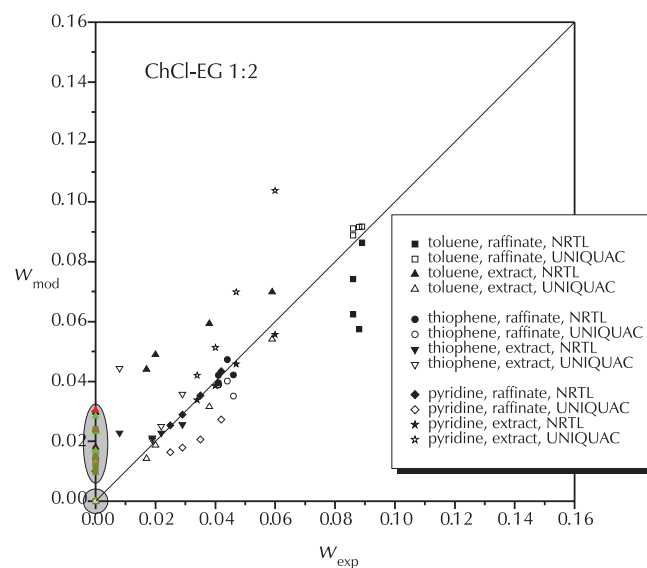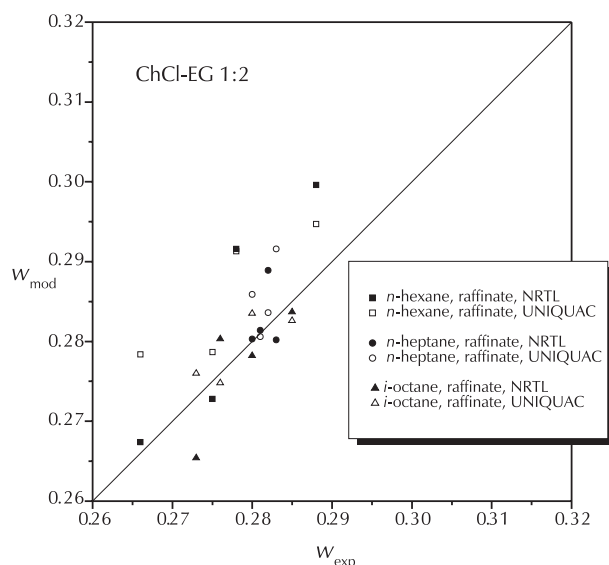

Fig. 9 – Comparison of experimental and calculated component distributions (mass fractions) for quasi-seven-component systems with DES / model gasoline ratio of 0.25 kg kg^{-1} – whole composition range

Slika 9 – Usporedba eksperimentalnih i izračunatih raspodjela komponenata (masenih udjela) za kvazi-sedmerokomponentne sustave s omjerom DES / modelno gorivo od 0,25 kg kg^{-1} – cijelo područje sastava

Fig. 10 – Comparison of experimental and calculated component distributions (mass fractions) for quasi-seven-component systems with DES / model gasoline ratio of 0.25 kg kg^{-1} – lower mass fraction range

Slika 10 – Usporedba eksperimentalnih i izračunatih raspodjela komponenata (masenih udjela) za kvazi-sedmerokomponentne sustave s omjerom DES / modelno gorivo od 0,25 kg kg^{-1} – područje manjih masenih udjela

Fig. 11 – Comparison of experimental and calculated component distributions (mass fractions) for quasi-seven-component systems with DES / model gasoline ratio of 0.25 kg kg⁻¹ – middle mass fraction range

Slika 11 – Usporedba eksperimentalnih i izračunatih raspodjela komponenata (masenih udjela) za kvazi-sedmerokomponentne sustave s omjerom DES / modelno gorivo od 0,25 kg kg⁻¹ – područje srednjih masenih udjela
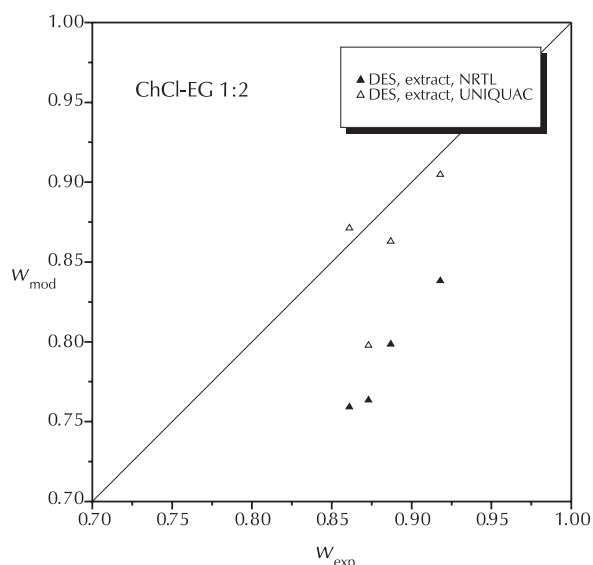
Fig. 12 – Comparison of experimental and calculated component distributions (mass fractions) for quasi-seven-component systems with DES / model gasoline ratio of 0.25 kg kg⁻¹ – higher mass fraction range

Slika 12 – Usporedba eksperimentalnih i izračunatih raspodjela komponenata (masenih udjela) za kvazi-sedmerokomponentne sustave s omjerom DES / modelno gorivo od 0,25 kg kg⁻¹ – područje viših masenih udjela

sess the measurement uncertainty of the method used to determine equilibrium compositions. In Fig. 12, the higher concentration range is shown. Here, one can observe only the data points corresponding to the DESs concentrations in the extract phase. A better agreement with experimental data is obtained by the UNIQUAC model. Namely, the NRTL model with the given set of parameters produces a rather large solubility of DESs in the raffinate phase; see other data points within the shaded elliptic region of Fig. 10. The amount of DES dissolved in raffinate is therefore missing in the extract phase.

Generally speaking, the results obtained by both models using the second set of interaction parameters (where a part of parameters is transferred from the closely related seven-component systems with the ionic liquid, and the other part is obtained by optimization from the experimental findings in the quasi-seven-component systems with the corresponding DESs) are better than those calculated with the first set of parameters (where all the parameters are transferred from the matching quasi-three-component systems with no additional optimization). This is particularly evident in the toluene solubility in DESs. The experiments in quasi-three-component systems point to negligible solubility of toluene in all DESs; yet the corresponding solubility in quasi-seven-component systems is clearly expressed. Obviously, the simple transfer of parameters from the three-component-systems cannot give good results there. In addition, it is quite apparent that the UNIQUAC model proved to perform better than the NRTL model, particularly in correlating the insolubility of DESs in the raffinate phase, as well the insolubility of aliphatics in the extract phase.

4 Conclusions

As part of a wider research into the possibilities of extracting sulphur and nitrogen compounds from hydrocarbon fuels using deep eutectic solvents, this paper describes the determination of the liquid-liquid phase equilibria in a series of quasi-three-component systems with aliphatic or aromatic hydrocarbons as the first component, thiophene or pyridine as the second component, and selected DESs based on choline chloride and ethylene glycol, or choline chloride and glycerol in different proportions as the third component. Based on the assumption that DESs could be regarded as quasi-components, the interaction parameters of the NRTL and UNIQUAC models have been determined to describe the obtained experimental equilibria. On the basis of previous positive experiences in systems with ionic liquids as extraction media, an attempt was made to simply transfer parameters from quasi-three-component to quasi-seven-component systems that are much closer to the expected real industrial situation. However, the expected agreement with experimental results was not obtained. Therefore, a new computational procedure was designed in which a part of the models' interaction parameters was transmitted from existing literature data, and a part was determined by optimizing directly from the experimental data on the liquid-liquid equilibria in quasi-seven-component systems. This approach has proven to be significantly better. A fairly good agreement between the experimental and the model data was obtained, especially with the UNIQUAC model, and the limitations of the models were discussed. It is assumed that the set of interaction parameters obtained in this paper could be applied to the description of similar experiments in the same systems or that the ap-

proach described here could be applied to other, related systems during future research.

List of abbreviations and symbols
Popis kratica i simbola

Symbols
Simboli

A – average absolute deviation of experimental and calculated mass fractions, 1
– srednje kvadratno odstupanje eksperimentalnih i izračunatih masenih udjela, 1

A,B,C,D – parameters of empirical correlation of composition *vs.* refractive index
– parametri empirijske korelacije sastava i indeksa loma

exp – subscript denoting experimental value
– indeks što označava eksperimentalnu vrijednost

E – (in subscript) extract phase
– (u indeksu) ekstraktna faza

g^{ex} – molar excess Gibbs energy, J mol^{-1}
– molarna ekses Gibbsova energija, J mol^{-1}

$g^{ex,C}$ – combinatorial part of molar excess Gibbs energy in UNIQUAC model, J mol^{-1}
– kombinatorni doprinos molarnoj ekses Gibbsovoj energiji u modelu UNIQUAC, J mol^{-1}

$g^{ex,R}$ – residual part of molar excess Gibbs energy in UNIQUAC model, J mol^{-1}
– rezidualni doprinos molarnoj ekses Gibbsovoj energiji u modelu UNIQUAC, J mol^{-1}

G_{ij} – symbol appearing in NRTL model, exponential function of model parameters, 1
– simbol koji se pojavljuje u modelu NRTL, eksponencijalna funkcija parametara modela, 1

l_i – bulk factor of correlation by Domańska
– volumni faktor korelacije Domańske

mod – subscript denoting model or calculated value
– indeks koji označava modelnu ili računsku vrijednost

n_c – number of components
– brojnost komponenata

n_d – number of tie line experimental data points
– brojnost eksperimentalnih veznih linija

$n_{D,25}$ – refractive index measured at 25 °C and using sodium D-lines
– indeks loma mjeren pri 25 °C te pri svjetlosti natrijevih D-linija

n_g – number of structural groups in component
– brojnost strukturnih grupa u komponenti

$OF_{1–6}$ – objective function to be minimized, 1
– funkcija cilja koju se minimizira, 1

Q – penalization factor, 1
– kaznena funkcija, 1

q_i – surface parameter of component i in UNIQUAC model, 1
– površinski parametar komponente i u modelu UNIQUAC, 1

Q_k – surface parameter of structural group k, 1
– površinski parametar strukturne grupe k, 1

R – gas constant, J K^{-1} mol^{-1}
– opća plinska konstanta, J K^{-1} mol^{-1}

R – (in subscript) raffinate phase
– (u indeksu) rafinatna faza

r_i – volume parameter of component i in UNIQUAC model, 1
– volumni parametar komponente i u modelu UNIQUAC, 1

R_k – volume parameter of structural group k
– volumni parametar strukturne grupe k

T – temperature, K
– temperatura, K

u – standard uncertainty, 1
– standardna mjerna nesigurnost, 1

v_i – molar volume of component i, m^3 mol^{-1}
– molarni volumen komponente i, m^3 mol^{-1}

w_i – mass fraction of component i, 1
– maseni udjel komponente i, 1

x_i – molar fraction of component i, 1
– molarni udjel komponente i, 1

z – lattice coordination number
– koordinacijski broj rešetke

α_{ij} – nonrandomness parameter of NRTL model, 1
– parametar neslučajnosti modela NRTL, 1

γ_i – activity coefficient of component i, 1
– koeficijent aktivnosti komponente i, 1

Θ_i – surface fraction of component i, 1
– površinski udjel komponente i, 1

τ_{ij} – interaction parameter of NRTL or UNIQUAC models, 1
– interakcijski parametar modela koeficijenta aktivnosti NRTL i UNIQUAC, 1

Φ_i – volume fraction of component i, 1
– volumni udjel komponente i, 1

Ψ – mass fraction of a particular liquid phase
– maseni udjel pojedine kapljevite faze

Abbreviations
Kratice

CAD – Computer Aided Design
– računalom potpomognuto projektiranje

ChCl – choline chloride
– kolin-klorid

COSMO-RS – COnductor like Screening MOdel for Real Solvents – a thermodynamic model for liquid solutions based on quantum chemistry calculations
– termodinamički model za kapljevite otopine zasnovan na kvantno-kemijskim proračunima

DES – Deep Eutectic Solvent
– niskotemperaturno eutektičko otapalo

EDS – extractive desulphurization
– ekstrakcijska desulfurizacija

EG – ethylene glycol
– etilen-glikol

FCC – Fluid Catalytic Cracking
– katalitičko krekiranje u fluidiziranom (uzvitlanom) sloju katalizatora

FID	– Flame Ionization Detector	
	– plameno-ionizacijski detektor	
GC	– Gas Chromatography	
	– plinska kromatografija	
Gly	– glycerol	
	– glicerol	
HDS	– hydrodesulphurization	
	– hidrodesulfurizacija	
IL	– Ionic Liquid	
	– ionska kapljevina	
NMR	– Nuclear Magnetic Resonance	
	– nuklearna magnetska rezonancija	
NRTL	– Non-Random Two-Liquid – a correlative thermodynamic model for liquid solutions, 1	
	– korelativni termodinamički model za kapljevite otopine, 1	
UNIFAC	– UNIquac Functional group Activity Coefficients – a predictive thermodynamic model for liquid solutions	
	– prediktivni termodinamički model za kapljevite otopine	
UNIQUAC	– UNIversal QUAsiChemical – a correlative thermodynamic model for liquid solutions, 1	
	– korelativni termodinamički model za kapljevite otopine, 1	

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SAŽETAK

Modeliranje ravnoteže kapljevina-kapljevina u kvazi-sedmerokomponentnim sustavima s niskotemperaturnim eutektičkim otapalima kao ekstrakcijskim sredstvima

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Eksperimentalno su istražene ravnoteže kapljevina-kapljevina u sustavima u kojem je prva komponenta alifatski (*n*-heksan, *n*-heptan odnosno *i*-oktan) ili aromatski ugljikovodik (toluen), druga komponenta je piridin ili tiofen, a treća kvazi-komponenta je DES koji se sastoji od kolin klorida i glicerola, odnosno kolin klorida i etilen-glikola, pri 25 °C i atmosferskom tlaku. Ravnoteže su uspješno opisane modelima NRTL i UNIQUAC. Isti su modeli uspješno primijenjeni i za opis ravnoteža kapljevina-kapljevina i u kvazi-sedmerokomponentnim sustavima koji uključuju sve navedene niskomolekulske komponente i jedan DES. Raspravljena su ograničenja modela; čini se da se prednost može dati modelu UNIQUAC.

Ključne riječi
Niskotemperaturna eutektička otapala, NRTL, UNIQUAC, modelno gorivo,
ravnoteža kapljevina-kapljevina

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