Application of NEAT for the simulation of liquid–liquid extraction processes with poorly specified feeds

Fabian Jirasek1 | Jakob Burger2 | Hans Hasse1

1Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern, Kaiserslautern, Germany
2Chair of Chemical Process Engineering, Technical University of Munich, Campus Straubing for Biotechnology and Sustainability, Straubing, Germany

Correspondence
Fabian Jirasek, Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern, Erwin-Schrödinger-Str. 44, 67663 Kaiserslautern, Germany.
Email: fabian.jirasek@mv.uni-kl.de

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Abstract
The conceptual design of fluid separation processes is particularly challenging if the considered mixtures are poorly specified, since classical thermodynamic models cannot be applied when the composition is unknown. We have recently developed a method (NEAT) to predict activity coefficients in such mixtures. It combines the thermodynamic group contribution concept with the ability of NMR spectroscopy to quantify chemical groups. In the present work, we describe how NEAT can be applied to equilibrium stage simulations of liquid–liquid extraction processes with poorly specified feeds. Only a single $^{13}$C NMR spectrum of the feed is needed for predicting the distribution of a target component for different process parameters, such as temperature or extracting agent. The predictions from several test cases are compared to results that are obtained using the full knowledge on the composition of the feed and surprisingly good agreement is found.

KEYWORDS
equilibrium stage simulation, liquid–liquid equilibrium, NMR spectroscopy, poor specification

1 | INTRODUCTION

Poorly specified mixtures, that is, mixtures that contain components of which the nature or concentration is unknown, are common in many fields of process engineering, such as bioprocess engineering. Designing processes with such mixtures is challenging as their composition is not known and therefore common thermodynamic models cannot be applied to describe their properties. The separation of a target component from a liquid mixture is a common task in downstream processing and fluid separation processes, such as liquid–liquid extraction, distillation, absorption, and crystallization, are established methods for this purpose. The separating effect of such processes is based on concentration differences between the coexisting phases and their design is often based on the equilibrium stage concept, for which information on the phase equilibria is needed. The most common approaches to describe phase equilibria of mixtures are models of the Gibs excess energy ($G^E$ models) and equations of state (EoS). However, these approaches can only be applied if the considered mixtures are fully specified, that is, if all components and their concentrations are known.

Different ways for describing phase equilibria of poorly specified mixtures have been described in the literature: in petrochemistry, fraction-wise characterization of the mixtures is common, see, for example, References 1-8, and continuous thermodynamics has been applied for describing polymer systems, see, for example, References 9-15. In this work, we present a generic approach to tackle the problem of poorly specified mixtures in process design. The approach is based on the method NEAT (NMR spectroscopy for the Estimation of Activity coefficients of Target components in poorly specified mixtures), which we have introduced recently.\textsuperscript{16,17} NEAT is based on a combination of NMR spectroscopy to estimate the chemical groups of the unknown components in poorly specified mixtures and thermodynamic group contribution methods for calculating activity coefficients. Obtaining information on chemical groups in poorly specified mixtures from NMR analysis is much easier than the identification and quantification of all components in a mixture. For applying NEAT, the concentration of the target component must be known, but no information on the rest of the mixture is needed. The activity coefficient of the target component is then determined from a single $^2$H or $^{13}$C NMR
spectrum of the mixture that yields the information on the groups, which is then used in the thermodynamic group contribution method modified UNIFAC (Dortmund).\textsuperscript{18,19} In previous work, NEAT was applied for predicting the activity coefficients of target components in a variety of aqueous and nonaqueous poorly specified mixtures.\textsuperscript{16,17} Test cases were studied, in which parts of the information on the speciation was deliberately ignored in NEAT. The agreement between the predictions with NEAT and results that were obtained using the full knowledge of the speciation was found to be very good.

Typical systems to which NEAT is applied are of the type (target component $T +$ solvent $S +$ unknown components $U_1...U_n$). It has recently been shown that the application of NEAT is particularly simple if the ratios of the amounts of the unknown components remain unchanged, as this is, for example, the case when the target component $T$ or the solvent $S$ are selectively removed.\textsuperscript{20} Then, only a single NMR spectrum is needed to predict the activity coefficient of the target component $T$ for arbitrary variations of the amounts of $T$ and $S$.

In the present work, we describe how NEAT can be used for the simulation of liquid–liquid extraction processes with poorly specified feeds. The applicability of NEAT for this purpose is demonstrated by considering single-stage liquid–liquid extractions with poorly specified feed mixtures of the type (target component $T +$ solvent water $W +$ unknown components $U_1...U_n$) and pure extracting agents $E$. The composition of each studied feed mixture was known from sample preparation, but this information was only used for comparison and not for the predictions with NEAT in the present work. Based on a \textsuperscript{13}C NMR spectrum of the feed and using modified UNIFAC (Dortmund), the partitioning of the target component between the extract and the raffinate phase was predicted using NEAT.

No experiments were carried out in the present work. The NMR spectra that were used for the evaluations of the present work were taken from an earlier work of our group.\textsuperscript{16} The results of the liquid–liquid equilibrium stage simulations are compared to predictions of the extraction process using modified UNIFAC (Dortmund) and the full information on the feed and good agreement is observed. The partitioning of the target component is predicted well with NEAT for different feed compositions, temperatures, extracting agents, and mass ratios of feed to extracting agent.

2 | APPLICATION OF NEAT

A comprehensive description of the NEAT method and its application for predicting activity coefficients in poorly specified mixtures is given in Reference 17. Therefore, the method itself is not described in detail here. We focus on the description of the new application of NEAT for equilibrium stage simulations. The methodology of the present work is shown in Figure 1a.

In the present work, single-stage liquid–liquid extraction processes are considered. In all cases, a poorly specified mixture is considered as feed $F$ that is mixed and equilibrated with an extracting agent $E$ in the extraction unit as schematically shown in Figure 1b.

![Figure 1](image.png)

**FIGURE 1** (a) Methodology of the present work. The chemical groups of the unknown components in the feed are identified from a $\textsuperscript{13}$C NMR spectrum of the poorly specified feed with NEAT and lumped to a single mean unknown component $\bar{U}$ here. (b) Single-stage liquid–liquid extraction process as considered in the present work. Extract and raffinate are in phase equilibrium.

All mixtures that are considered as feed in the present work are of the type $(T + W + U_1...U_n)$. Here, $T$ denotes the target component, of which the nature and mass fraction in the feed are assumed to be known. $W$ denotes the solvent water, of which the mass fraction in the feed does not have to be known as it can be obtained from NEAT using a mass balance.\textsuperscript{17} For the remaining components $U_1...U_n$, which are called unknown components here, no information on the nature and concentration is used in NEAT. Quantitative $\textsuperscript{13}$C NMR spectroscopy and modified UNIFAC (Dortmund) were used in NEAT for the determination of the nature and concentration of the chemical groups in the unknown components and the calculation of activity coefficients, respectively. The application of NEAT requires the assignment of chemical groups to chemical shift regions in an NMR spectrum. The assignment that was used in the present work is the same as the one that was used in our previous work\textsuperscript{17} for aqueous mixtures and is given in Table S.2.

To use modified UNIFAC (Dortmund) for the calculation of activity coefficients, the chemical groups of the unknown components that are identified with NMR spectroscopy have to be lumped to mean unknown components. In our previous work,\textsuperscript{16,17} all identified groups in the studied mixture were simply lumped to a single mean unknown component $\bar{U}$, to which a molar mass of $M_{\bar{U}} = 150$ g/mol was assigned. It was shown that this arbitrary assignment of the molar mass is not critical for the prediction of the activity coefficients of the target components in many cases. Hence, each poorly specified feed $F$ was considered as pseudo-ternary mixture of the components $T$, $W$, $\bar{U}$, and a thermodynamic model of the pseudo-ternary mixture was obtained from NEAT. The model can be straightforwardly extended by adding further known components, in our case the extracting agent $E$. Since only aqueous feeds were studied, the extracting agents were selected such as to exhibit a miscibility gap with water, compare Table 1.

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**TABLE 1**

| Component | Mass Fraction |
|-----------|---------------|
| $T$       | 0.5           |
| $W$       | 0.3           |
| $\bar{U}$| 0.2           |

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**Figure 1 Notes**

(a) Feed $F$ (poorly specified) is mixed and equilibrated with extracting agent $E$. The extract and raffinate are in phase equilibrium.

(b) Extracting agent $E$ is mixed with feed $F$ (modeled with NEAT) and the resulting mixture is subjected to liquid–liquid extraction. The extract and raffinate are in phase equilibrium.

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**Figure 1 Diagram**

- **Feed $F$**: Mixed with extracting agent $E$.
- **Extract $E$**: Produced from the liquid–liquid extraction.
- **Raffinate $E$**: Produced from the liquid–liquid extraction.
- **Mixtures $T$, $W$, $U$**: Represent the feed mixture.
- **Equilibrium simulation**: Represents the thermodynamic calculation of the equilibrium phase compositions.

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**Figure 1 legends**

1. **NEAT**: Near Equilibrium Activity Theory
2. **UNIFAC**: Universal Functional Group Activity Coefficient model
3. **$\textsuperscript{13}$C NMR**: Carbon-13 Nuclear Magnetic Resonance
4. **Pseudo-ternary mixture**: Model for mixtures with two known components and one unknown component
5. **Pseudo-quaternary mixture**: Model for mixtures with three known components and one unknown component

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**Figure 1 References**

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Lumping all unknown components into a single mean unknown component constrains the partitioning if more than one unknown component is present in the feed. This can lead to poor predictions with NEAT, especially if the unknown components in the studied mixture differ significantly in their nature, such that they are expected to partition differently on the coexisting phases in liquid–liquid equilibrium. That constraint can be relaxed by introducing more than one mean unknown component. This option is discussed briefly in Section 3 of the present paper. For simplicity, only the case with a single mean unknown component is described in the present section.

Once the thermodynamic model of the pseudo mixture is available, process simulations can be done with ease. Here, the liquid–liquid extraction process is simulated. The distribution of the (pseudo) components T, W, U, and E on the coexisting phases in liquid–liquid equilibrium at constant temperature T was calculated from the isoactivity relations:

\[
x_i^{(n)}y_i' = x_i^{(n)''}y_i'', \quad i = T, W, U, E
\]

where \(x_i^{(n)}\) and \(y_i\) are the mole fractions and the activity coefficients normalized according to Raoult's law of the components \(i\) in the coexisting phases labeled with ′ and ″, respectively. The equilibrium composition of the raffinate and the extract in the pseudo-quaternary system \((T + W + U + E)\) was obtained, compare Figure 1b. From the equilibrium composition of the coexisting phases, the molality-based liquid–liquid partition coefficient \(K_T\) and the liquid–liquid extraction yield \(Y_T\) of the target component T were computed:

\[
K_T = \frac{y_T''}{y_T'} \quad (2)
\]

\[
Y_T = \frac{n_T''}{n_T'} \quad (3)
\]

TABLE 1 Overview of the single-stage liquid–liquid extraction processes that were studied in the present work

| System | Target T | Unknown U | Extracting Agent E | Process parameters |
|--------|----------|-----------|-------------------|-------------------|
| I      | Ethanol  | 2-Butanone| 1-Octanol         | 298               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
| II     | Ethanol  | Methyl acetate | 1-Octanol       | 298               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
| III    | Ethanol  | Acetic acid | 1-Octanol        | 298               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
| IV     | Ethanol  | Glucose   | 1-Octanol        | 298               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
| V      | Citric acid | Glucose | 1-Octanol         | 298               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |
| VI     | 1,4-Butanediol | Cyclohexanone | Acetonitrile  | 1-Octanol        | 298               |
|        |          |           | Acetonitrile      | 1-Octanol         | 1:1               |
|        |          |           | Methyl acetate    | 1-Octanol         | 1:1               |
| VII    | Acetone  | Xylose    | 1-Octanol        | 298               |
|        |          |           | 1-Octanol         | 1:1               |
|        |          |           | 1-Octanol         | 1:1               |

Note: Besides the target component T and the unknown components U, water W was always present in the feed. The mass ratio of T:W in the feed F is always 1:9. In Systems VI and VII, the mass ratios of U1:U2:U3 in F are always 1:1:1. No information on U was used for the predictions with NEAT.

Abbreviation: NMR spectroscopy for the Estimation of Activity coefficients of Target components in poorly specified mixtures.
where \( b_T \) and \( b_T' \) denote the molality of \( T \) in the raffinate \( \cdot' \) and in the extract \( \cdot'' \), respectively, and \( n_T \) and \( n_T' \) denote the mole number of \( T \) in the extract \( \cdot'' \) and in the feed \( F \), respectively. The molalities \( b_T \) in both phases were calculated referring to the mixed solvent \( (W + E) \):

\[
b_T = \frac{n_T}{m_W + m_E}
\]

where \( m_W \) and \( m_E \) denote the mass of water \( W \) and extracting agent \( E \), respectively.

The predictions for \( K_T \) and \( Y_T \) obtained with NEAT for the poorly specified feed are compared to results that were obtained in the same way but using information on the full speciation of the feed. To obtain these results for the fully specified mixtures, also modified UNIFAC (Dortmund) was used for calculating the activity coefficients. It is not the intention of the present work to evaluate the suitability of modified UNIFAC (Dortmund) for calculating the activity coefficients in the studied systems. It is obvious that if modified UNIFAC (Dortmund) gives poor results for the activity coefficients in the studied systems, the predictions with NEAT based on modified UNIFAC (Dortmund) will also be poor. The same holds for subsequent predictions of phase equilibria. However, for the predictions with NEAT, also any other group contribution method can be used.

3 | OVERVIEW OF THE PRESENT STUDY

Table 1 gives an overview of the studied feed systems, extracting agents, and the parameters that were varied in the equilibrium stage simulations, which were the temperature \( T \) and the mass ratio of extracting agent to feed \( m_E:\text{m}_F \). For each feed system and the selected process parameters, compare Table 1, five mixtures with constant ratio of target component to water and different amounts of unknown components were considered. For the predictions with NEAT, the feed \( F \) was always considered as poorly specified mixture and characterized using a single \(^{13}\text{C} \) NMR analysis, whereas the extracting agent \( E \) was always assumed to be known. In the present work, only pure extracting agents were considered.

4 | RESULTS AND DISCUSSION

In the following diagrams, results for the partition coefficient \( K_T \) and the extraction yield \( Y_T \) of the target component \( T \) for the single-stage liquid–liquid extraction processes are shown. The results are always depicted as a function of the concentration of the unknown components \( U \) in the feed \( F \). Furthermore, in each diagram, an additional parameter was varied. The varied parameters are: the nature of the unknown components \( U \) in the feed, the extraction temperature \( T \), the extracting agent \( E \), and the mass ratio of extracting agent to feed \( m_E:\text{m}_F \).

In Figure 2, results of simulations are shown, in which the nature of the unknown components was varied. The feed mixtures are from the Systems I (ethanol + water + 2-butanone), II (ethanol + water + methyl acetate), III (ethanol + water + acetic acid), and IV (ethanol + water + glucose). The target component is \( T = \text{ethanol} \), the extracting agent is \( E = \text{1-octanol} \), the temperature is 298 K, and the mass ratio of extracting agent \( E \) to feed \( F \) is \( m_E:\text{m}_F = 1:1 \) in all cases. The results for the fully specified feeds, which were calculated using modified UNIFAC (Dortmund), are depicted as lines, the symbols are the predictions with NEAT. The predictions were obtained based only on information on \( T \) and \( E \) and a \(^{13}\text{C} \) NMR spectrum of the feed.

Since the mass ratio of the target component to water in the feed is the same in all cases, all lines coincide for \( x_U = 0 \text{ g/g} \) in the octanol–water partition coefficient of pure ethanol. Adding the different unknown components \( U \) has a different influence on the partition coefficient \( K_T \) of the target component \( T \). Adding 2-butanone or methyl acetate leads to an increase of \( K_T \), whereas the addition of acetic acid or glucose leads to a decrease, compare Figure 2a. The
extraction yield $Y_T$ shows an increasing trend for increasing mass fractions of the unknown component U in the feed in all cases, compare Figure 2b. All trends are represented well by the predictions with NEAT, except for the influence of glucose on $Y_T$. The reasons for the observed deviations are diverse. First, there is an inherent uncertainty of the NMR analysis. For the examples shown here, we estimate the relative error of the quantification of the peak areas in the NMR spectra to be less than 5%. Second, there is uncertainty in the identification of chemical groups, which mainly depends on the assignment of modified UNIFAC (Dortmund) groups to chemical shift regions in the NMR spectrum but can also be caused by peaks that shift depending on the composition of the mixture. For a more comprehensive discussion of the uncertainties, the reader is referred to our previous work. However, the results point out that NEAT can be applied to predict the temperature dependence based on a single NMR analysis.

In Figure 3, results of simulations are shown, in which the extracting agent E was varied (E = 1-octanol, 1-pentanol, chloroform, diethyl ether, or toluene). The feeds are from System I (ethanol + water + 2-butanone) and System V (citric acid + water + glucose). The target component is either (T = ethanol) or (T = citric acid). The temperature is always 298 K and the mass ratio $m_E:m_F$ is always 1:1. The predictions with NEAT are based on one NMR spectrum of the respective feeds and independent of the studied extracting agent. The presentation is the same as in the previous diagrams. Again, very good agreement of the predictions of NEAT with the results for the fully specified feeds is observed. For both systems, higher temperatures lead to higher partition coefficients of T. This is correctly predicted by NEAT. Since the accuracy of the predictions with NEAT depends mainly on the estimation of the chemical groups of the unknown components in the feed, which is unrelated to the temperature, it is not surprising that NEAT predicts the influence of the temperature well. However, the results point out that NEAT can be applied to predict the temperature dependence based on a single NMR analysis.

Figure 4 shows results of simulations, in which the extracting agent E was varied (E = 1-octanol, 1-pentanol, chloroform, diethyl ether, or toluene). The feeds are from System I (ethanol + water + 2-butanone) and System V (citric acid + water + glucose). The target component is either (T = ethanol) or (T = citric acid). The temperature is always 298 K and the mass ratio $m_E:m_F$ is always 1:1. The predictions with NEAT are based on one NMR spectrum of the respective feeds and independent of the studied extracting agent. The presentation is the same as in the previous diagrams. Again, only the results for the partition coefficient $K_T$ are shown. The respective results for the extraction yield $Y_T$ are given in Figure S.2 and show analogous agreement.

For both studied systems, the results show a strong influence of the extracting agent on the partition coefficient of T, with the largest numbers for 1-pentanol and the lowest numbers for toluene. For all considered extracting agents, the predictions with NEAT are in excellent agreement with the results for the fully specified feeds. Hence, based on a single NMR spectrum of a poorly specified feed, the distribution of the target component between raffinate and extract can be predicted well with NEAT for different extracting agents. This shows that NEAT can be applied for the selection of extracting agents for the liquid–liquid extraction of target components from poorly specified mixtures.
In Figures 5, results of simulations are shown, in which the influence of the mass ratio of extracting agent to feed \( m_E/m_F \) on the extraction process is studied. The considered feeds are from System V (citric acid + water + glucose), in which the target component is \( T = \text{citric acid} \). The extracting agent is always \( E = \text{1-octanol} \) and the temperature is always 298 K. The presentation is again the same as in the previous diagrams, only the results for the extraction yield \( Y_T \) are shown here. The respective results for the partition coefficient \( K_T \), for which a significantly smaller influence of \( m_E/m_F \) is found, are reported in Figure S.3.

As expected, the results show an increasing extraction yield with increasing ratios of extracting agent to feed. For all ratios, the agreement of the predictions with NEAT with the results calculated using the full knowledge on the speciation of the feed is very good. This demonstrates that NEAT can be used to predict the amount of an extracting agent that is required for extracting the target component from a poorly specified feed with a specific extraction yield based on a single NMR spectrum of the feed.

In Figures 2–5, only results for ternary feeds that contain a single unknown component U are shown. For such feeds, lumping all identified groups of U into a single mean unknown component \( \bar{U} \), as is was done for the predictions with NEAT in all previous examples, is obviously adequate. In practice, more than one unknown component may be present and lumping them together into a single mean unknown component in NEAT might cause problems. In the following, an approach to relax this constraint by introducing more than one mean unknown component is presented and tested using five-component feed mixtures from System VI (1,4-butanediol + water + cyclohexanone + acetonitrile + methyl acetate) and System VII (acetone + water + xylose + acetic acid + methyl acetate), where the target component is either \( T = \text{1,4-butanediol} \) or \( T = \text{acetone} \). The extracting agent is \( E = \text{1-octanol} \), the temperature is 298 K, and the mass ratio of extracting agent to feed \( m_E/m_F = 1:1 \) in all cases.

First, the results for the case that all unknown components are lumped together into a single mean unknown component are discussed. They are shown in Figure 6 as open symbols. The plot in Figure 6 is the same as in the previous figures. The results that were obtained with NEAT are good. For both systems, a fair agreement with the results based on the full specification of the feed is obtained both for the partition coefficient \( K_T \) and the extraction yield \( Y_T \) of the target component T.

Figure 6 also contains results that were obtained with NEAT when instead of a single mean unknown component, two such components are used. These results are represented by the filled symbols. The idea behind using two different mean unknown components here is simple. It was assumed that one of them is polar \( (\bar{U}_P) \) and the other is unpolar...
In principle, simply all polar groups of U identified by NEAT could be assigned to \(~U\) and all unpolar groups to \(~U_{up}\). As it is more realistic to assume that a given molecule contains a mixture of both polar and unpolar groups, it was assumed here that \(~U\) contains 80% of the polar groups and 20% of the unpolar groups of U, whereas \(~U_{up}\) contains 20% of the polar groups and 80% of the unpolar groups of U in the mixture. Different choices of this type are possible. The results shown in Figure 6 indicate that they are not crucial as the differences compared to using only a single mean unknown component are small. However, in all studied cases, improvements by introducing the second mean unknown component were observed. The simple modification of NEAT discussed here requires no additional information on the unknown components. If at least some additional information on the nature of the unknown components is available, it can be incorporated in the method. That is, it could help in the assignment of chemical groups to different mean unknown components, which is expected to improve the predictions with NEAT. More information on the definition of several mean unknown components are given in the Supporting Information.

5 | CONCLUSIONS

The NEAT method, which was introduced recently by our group, enables calculating activity coefficients of target components in poorly specified mixtures. It is based on an NMR analysis of the mixture that yields quantitative information on the chemical groups in the mixture, which is then used in the thermodynamic group contribution method modified UNIFAC (Dortmund). In the present work, it is shown how NEAT can be applied to the simulation of liquid–liquid extraction processes with poorly specified feeds. For simplicity, only single-stage extraction processes are discussed, but the approach can be extended to multi-stage processes in a straightforward manner. Different examples are discussed. The parameters that are varied include the nature and concentration of the target components and the unknown components in the feed, the type of the extracting agent and its amount, and the extraction temperature. Throughout this work, the reference is the result that modified UNIFAC (Dortmund) yields for the fully specified feed. The partition coefficient of the target component and its yield in the extraction are well predicted by NEAT in all cases: the differences between the results from NEAT, in which no information on the unknown components is used, and the modified UNIFAC (Dortmund) results for the fully specified feeds are generally small.

The unknown components can be handled in different ways. In the simplest case, they are lumped together into a single mean unknown component, but also several mean unknown components can be introduced based on the NMR results. In the examples that were studied here, the differences between the results of these two approaches were not large.

The results of this work demonstrate the potential of NEAT for the conceptual design of liquid–liquid extraction processes for systems with poorly specified mixtures, for example, regarding the selection of suitable extracting agents. The quality of the results that are obtained by NEAT is, however, limited by the quality of the underlying thermodynamic group contribution method. The NEAT approach can not only be used together with modified UNIFAC (Dortmund) but in principle together with any group contribution method. It should be possible to extend the application of NEAT also to other separation processes, such as crystallization and distillation.

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CONFLICT OF INTEREST

None.
NOMENCLATURE

Symbols

$\gamma$ activity coefficient

Sub- and Superscripts

$\gamma$ activity coefficient

Greek letters

$\gamma$ activity coefficient

Notation

EoS Equation of State

LLE Liquid–Liquid Equilibrium

NEAT NMR Spectroscopy for the Estimation of Activity coefficients of Target components in poorly specified mixtures

NMR Nuclear Magnetic Resonance

UNIFAC UNIversal quasichemical Functional group Activity Coefficients

ORCID

Fabian Jirasek https://orcid.org/0000-0002-2502-5701

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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