Application of NEAT for determining the composition dependence of activity coefficients in poorly specified mixtures

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Abstract

Poorly specified mixtures, of which the composition is only partially known, are important in many fields. In a recent work of our group, the method NEAT for estimating activity coefficients of target components in such mixtures was introduced. In the present work, it is shown that based on a single NMR analysis of a poorly specified mixture not only the activity coefficient of the target component in that mixture but also its composition dependence can be predicted with NEAT. Hence, based on a single NMR analysis, the activity coefficient of the target component in many mixtures can be predicted with NEAT. This is possible, if the unknown part of the mixture remains unchanged, which is the case e.g. when the target component is selectively removed or when a known solvent is added or removed. The approach is successfully tested using several aqueous test mixtures.

Keywords: NEAT, NMR spectroscopy, activity coefficients, unknown composition, varying composition

1. Introduction

Mixtures that contain components of unknown type or in an unknown concentration are called poorly specified mixtures here. They are common in many fields of engineering and science, such as petrochemical engineering [1–4], waste water treatment [5, 6], and biotechnology [7–9]. In process design, such mixtures are hard to handle since classical thermodynamic methods, such as NRTL [10], UNIQUAC [11, 12], UNIFAC [13–15], or COSMO-RS [16, 17], require a full specification of the mixture. In a recent work of our group, the NEAT method (NMR Spectroscopy for the Estimation of Activity Coefficients of Target Components in Poorly Specified Mixtures) was introduced, which tackles this challenge [18, 19]. NEAT is based on a combination of NMR spectroscopy and thermodynamic group contribution methods and enables the estimation of the activity coefficients of known target components in poorly specified mixtures. In NEAT, the components of a poorly

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specified mixture are divided in two classes: known and unknown components. For the known components, it is assumed that the mass fraction of the component in the mixture and its nature are known or can be obtained by established analytical methods. For the unknown components,
15 no information is needed. NMR spectroscopy is used to estimate the type and the concentration of chemical groups of the unknown components in the mixture. This information on the groups is much easier to obtain than the corresponding information regarding the components. These data are then used for calculating the activity coefficients of the target components with a thermodynamic group contribution method. The target components can be selected arbitrarily among the
20 known components. In our previous work [18, 19], modified UNIFAC (Dortmund) [15] was used as group contribution method. It was shown that based on a single ^1H or ^{13}C NMR spectrum of the poorly specified mixture, NEAT gives an excellent prediction for the activity coefficient of the target component: in tests in which the full composition of the mixtures was known but not used in NEAT, the results from NEAT agreed very well with those obtained from modified UNIFAC
25 (Dortmund) for the fully specified mixtures. However, in those studies, one NMR spectrum of each considered mixture had to be taken.

In the following, the term ‘system’ is used to summarize all mixtures that contain the same components in different compositions. In process engineering, different mixtures of the same system occur frequently, e.g. during downstream processing due to the separation of target components or
30 the solvent from a mixture or as result of a varying turnover in a reaction process. An individual NMR analysis of each mixture for the application of NEAT in these cases would be tedious.

In the present work, we study if based on the NMR analysis of a single poorly specified mixture, the activity coefficient of the target component not only in that mixture but also in other mixtures of the same system can be predicted with NEAT. Hence, we present an approach to determine the
35 composition dependence of activity coefficients of target components in poorly specified mixtures based on a single NMR analysis, which makes the application of NEAT significantly more practical in many situations.

The approach is tested using several systems of the type (known target component + known solvent water + unknown components). The data on the studied systems are taken from our previous
40 work [18] and no experiments were carried out in the present work. In contrast to our previous work, in which the activity coefficient of the target component in several mixtures of a system was predicted based on a separate NMR analysis of each mixture, we use only one single NMR spectrum of a single mixture per system to predict the activity coefficients at a wide range of compositions here. The only condition is thereby that the composition of the unknown part of the mixtures, i.e.
45 the type and the ratio between the unknown components, remains constant. The predictions are compared to results obtained in our previous work for which an NMR spectrum of each studied

mixture was used and to results that were calculated with modified UNIFAC (Dortmund) using the full knowledge on the composition of the mixtures.

2. Application of NEAT

50 A comprehensive description of the NEAT method has been given in Ref. [19]. The method itself is therefore not discussed in detail here.

All mixtures that are considered in the present work are of the type $(T + W + U_1 \dots U_N)$. Here, T is the target component of which the nature and the concentration in the mixture are known and W is a second component of which the nature is known. In all examples that are discussed here, 55 that second component is the solvent water. The concentration of W in the mixture does not have to be known as it can be obtained from NEAT using a mass balance [19]. For the other components $U_1 \dots U_N$, nothing is known – neither their nature nor their concentration, and in general not even the number N is known. These components are called unknown components. In NEAT, they are simply lumped together to a single mean unknown component $\tilde{U}$, which is in contrast to using 60 modified UNIFAC (Dortmund) or other group contribution methods, in which each component is considered explicitly. The nature and concentration of $\tilde{U}$ in the mixture is determined within NEAT from an NMR analysis as described in detail in Ref. [19].

After lumping the unknown components to $\tilde{U}$, the studied mixture can be considered as pseudo-ternary mixture of the type $(T + W + \tilde{U})$. To calculate the activity coefficient of T in NEAT, 65 an activity model based on modified UNIFAC (Dortmund) is used here. However, also other activity models can be used for this purpose. This model is completely parametrized during the application of NEAT, cf. Ref. [19]. Thus, it is available for extrapolations to other mixtures of the same pseudo-ternary system $(T + W + \tilde{U})$ and for a given poorly specified mixture, variations of the concentrations of T , W , and $\tilde{U}$ can be studied with NEAT. The only condition is thereby 70 that the pseudo component $\tilde{U}$ does not change its nature, i.e. that the ratios of the amounts of U_i ($i = 1 \dots N$) are constant. There are many practical cases in which this is a good assumption, e.g. the addition or the selective removal of the target component T or the solvent W .

If this assumption holds, only one single NMR spectrum of a single mixture has to be taken and the activity coefficients of T in all mixtures of the system $(T + W + \tilde{U})$ can be predicted with 75 NEAT. The mixture of which the NMR spectrum is taken to obtain the information on $\tilde{U}$ is called reference mixture R here. The results of NEAT for the stoichiometry of $\tilde{U}$ and the composition of the studied reference mixtures are summarized in Tables C.1 - C.3 in the Appendix. There are no restrictions of the present method regarding the choice of the reference mixture R . If doubts arise, whether the basic assumption of the present work holds in a practical application, i.e. if there is 80 reason to believe that the ratios of the U_i might vary, the following can be done: the assumption

can be tested using two or more reference mixtures and applying NEAT to each of them. If the group speciation of $\tilde{U}$ is constant in the set, the assumption is good. If not, the procedure described in Refs. [18, 19] can be applied.

3. Overview of the Present Study

85 Table 1 gives an overview of the systems that were investigated in the present work. The experimental data on the reference mixtures were taken from our previous work [18]. In each system, two reference mixtures R_1 and R_2 were used. In principle, only one reference mixture is needed. Two of them were used here only to test whether the choice of the reference mixture has an influence on the results.

Quantitative ^{13}C NMR spectra of the reference mixtures were used to obtain information on the

Table 1: Overview of the studied systems and reference mixtures. Two reference mixtures R_1 and R_2 were used for comparisons in each system. Besides the target component (T) and the unknown components (U_i), water (W) was always present in the mixtures. No information on the components U_i was used in NEAT.

System	Target component T	x_T / g/g		Unknown components U_i	x_{U_i} / g/g	
		R_1	R_2		R_1	R_2
A	ethanol	0.098	0.076	2-butanone	0.037	0.248
B	acetone	0.096	0.084	xylose	0.012	0.052
				acetic acid	0.014	0.052
				methyl acetate	0.012	0.053
C	1,4-butanediol	0.096	0.083	cyclohexanone	0.005	0.041
				acetonitrile	0.006	0.049
				methyl acetate	0.006	0.053

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chemical groups of the unknown components in the studied systems. The assignment of chemical groups to chemical shift regions in the NMR spectra that was used in the present work is the same as the one that was used in our previous work [19] for aqueous mixtures and is given in Table A.1 the Appendix. The identified chemical groups of the unknown components were lumped to a mean unknown component $\tilde{U}$, to which a molar mass of $M_{\tilde{U}} = 150$ g/mol was assigned as suggested 95 in our previous work [19], in which was demonstrated that the value of $M_{\tilde{U}}$ has only a minor influence on the predictions with NEAT, if not unreasonably small values are chosen. In principle, any mixture of the system can be chosen as reference mixture. The mass fraction of the target component T in that reference mixture was assumed to be known, that of the mean unknown component $\tilde{U}$ was obtained from NMR data of the mixture, and that of water was obtained using 100 a mass balance [19]. Hence, for each poorly specified reference mixture R, the composition in the pseudo-ternary system (T + W + $\tilde{U}$) was obtained from NEAT. Further, a modified UNIFAC (Dortmund) model to calculate activity coefficients in the pseudo-ternary system is provided by NEAT. This model is used to calculate the activity coefficient of the target component not only in

105 the reference mixture R but at any composition in the pseudo-ternary system ($T + W + \tilde{U}$). This is exemplarily shown in Figure 1 for system A.

In Figure 1, the symbol indicates the result for the activity coefficient of the target component

Figure 1: Prediction of the activity coefficient γ_T of target component ethanol (T) in mixtures of system A based on the NMR analysis of reference mixture R₂. The symbol indicates the result for R₂. No information on U_i was used in NEAT. $T = 298$ K.

(T = ethanol) in reference mixture R₂ of system A as predicted with NEAT based on the NMR analysis of R₂. The surface indicates the activity coefficient of T in all possible mixtures of the pseudo-ternary system ($T + W + \tilde{U}$) as predicted with NEAT based on the same NMR analysis of R₂.

Figure 1 shows only the predictions with NEAT for the pseudo-ternary system ($T + W + \tilde{U}$). The results for each fully specified system ($T + W + U_1 \dots U_N$) could in principle be shown in the same type of diagram, which requires summing the components U_i to $\tilde{U}$ if $i > 1$. For all studied systems, the respective surface calculated for the fully specified system was found to be very close to the surface predicted with NEAT. However, these results are not included in Figure 1 for improved illustration but shown in Figure B.1 in the Appendix together with a diagram representing the deviation between the results for the fully specified mixtures and the predictions with NEAT.

For improved illustration of the accuracy of the predictions with NEAT, only the following variations were considered and the respective results are shown in the diagrams of the present work:

starting from each reference mixture, the composition in the respective system of was varied in three ways as shown in Figure 2 in a schematic triangular diagram of the pseudo-ternary system ($T + W + \tilde{U}$). The black squares denote the compositions of two reference mixtures R_1 and R_2

Figure 2: Schematic triangular diagram of a pseudo-ternary system ($T + W + \tilde{U}$). The black squares denote the compositions of two reference mixtures R_1 and R_2 and the colored lines denote the compositions of mixtures that are obtained by the variation of the amount of T , W , or $\tilde{U}$ starting from R_1 or R_2 . The ratio of T/W is the same in both reference mixtures, cf. Table 1.

of which NMR spectra were taken. The reference mixtures were typically water-rich, cf. Table 1.

125 Starting from each reference mixture R , the amount of one of the three overall components T , W , or $\tilde{U}$ was varied whereas the ratio of the two others was held constant. This corresponds to an enrichment or a depletion of the chosen component and is indicated by the colored lines in Figure 2. The symbols indicating R_1 and R_2 lie on the red line since the ratio of T/W is the same in both reference mixtures of each system, cf. Table 1. The predictions are compared with the results
130 that were obtained with modified UNIFAC (Dortmund) using the full information on the true composition regarding the components T , W , and $U_1 \dots U_N$ and with results that were obtained in our previous work [19], in which an NMR analysis of each mixture was used. All results are shown as functions of the composition of the fully specified mixtures in the following.

4. Results and Discussion

135 In Figures 3 - 5, results for the activity coefficient of the target component ethanol in mixtures of system A (ethanol (T) + water (W) + 2-butanone (U)) are shown. The predicted activity coefficients of T in the mixtures with varying compositions based on R_1 were obtained with NEAT using only an NMR spectrum of R_1 ; the same holds for R_2 .

In Figure 3, the influence of the variation of the amount of T on the activity coefficient of T is studied. The ratio $\tilde{U}/W$ is held constant (cf. green lines in Figure 2). In all cases the predictions
140 from NEAT are in excellent agreement with the results for the fully specified mixtures. This also

Figure 3: Activity coefficient γ_T of target component ethanol (T) in ternary mixtures of T with water (W) and 2-butanone (U). The amount of T is varied as shown in Figure 2, cf. green lines. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. No information on U was used in NEAT. $T = 298$ K.

holds for the limiting activity coefficient of T.

In Figure 4, the influence of the variation of the amount of $\tilde{U}$ on the activity coefficient of T is studied. Since the mass ratio of T/W is the same in both reference mixtures R_1 and R_2 (cf. red line in Figure 2), the results from modified UNIFAC (Dortmund) for the fully specified mixtures merge in one line. The predictions from NEAT are in very good agreement with the results for the fully specified mixtures. The predictions based on the NMR analysis of R_1 and R_2 are similar – no significant influence of the choice of the reference mixture is found. Furthermore, no significant difference between the results of the present work and the results from our previous work [19] for which an NMR analysis of each studied mixture was used is found. Hence, the simplification of using only one NMR spectrum of a single mixture per system for the predictions with NEAT has basically no influence on the quality of the predictions.

In Figure 5, the influence of the variation of the amount of W on the activity coefficient of T is studied. The ratio $\tilde{U}/T$ is held constant (cf. blue lines in Figure 2). For water mass fractions approaching unity, the activity coefficient of T approaches the activity coefficient of T at infinite dilution in water since the influence of $\tilde{U}$ is vanishing. Hence, the curves merge for $x_W \rightarrow 1$ g/g. All trends are well represented by the predictions from NEAT and the agreement with the results for the fully specified mixtures is excellent.

Figure 4: Activity coefficient γ_T of target component ethanol (T) in ternary mixtures of T with water (W) and 2-butanone (U). The amount of $\tilde{U}$ is varied as shown in Figure 2, cf. red line. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. The blue triangles indicate results from our previous work [19]. No information on U was used in NEAT. $T = 298$ K.

Figures 6 - 8 show results for the activity coefficient of the target component acetone in system
 160 B (acetone (T) + water (W) + xylose (U_1) + acetic acid (U_2) + methyl acetate (U_3)). The presentation is similar to the one for system A.

In Figure 6, the influence of the variation of the amount of T on the activity coefficient of T is shown. The ratio $\tilde{U}/W$ is held constant (cf. green lines in Figure 2). The agreement of the predictions from NEAT with the results for the fully specified mixtures is excellent. Again, this
 165 also holds for the limiting activity coefficient of T.

In Figure 7, the influence of the variation of the amount of $\tilde{U}$ on the activity coefficient of T is studied. Since the mass ratio of T/W is the same in both reference mixtures R_1 and R_2 (cf. red line in Figure 2), the results from modified UNIFAC (Dortmund) for the fully specified mixtures coincide again. No significant difference between the predictions from NEAT based on the NMR
 170 analysis of R_1 or R_2 and the predictions from our previous work, for which an NMR analysis of each mixture was used, is found. In all cases, the predictions from NEAT are very good.

In Figure 8, the influence of the variation of the amount of W on the activity coefficient of T is studied. The ratio $\tilde{U}/T$ is held constant (cf. blue lines in Figure 2). For water mass fractions approaching unity, the activity coefficient of T approaches the activity coefficient of T at infinite
 175 dilution in water since the influence of $\tilde{U}$ is vanishing. Hence, the curves merge again for $x_W \rightarrow 1$ g/g. The agreement of all predictions from NEAT with the results for the fully specified mixtures is very good.

Figure 5: Activity coefficient γ_T of target component ethanol (T) in ternary mixtures of T with water (W) and 2-butanone (U). The amount of W is varied as shown in Figure 2, cf. blue lines. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. No information on U was used in NEAT. $T = 298$ K.

Figure 6: Activity coefficient γ_T of target component acetone (T) in five-component mixtures of T with water (W), xylose (U₁), acetic acid (U₂), and methyl acetate (U₃). The amount of T is varied as shown in Figure 2, cf. green lines. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. No information on U was used in NEAT. $T = 298$ K.

Figure 7: Activity coefficient γ_T of target component acetone (T) in five-component mixtures of T with water (W), xylose (U_1), acetic acid (U_2), and methyl acetate (U_3). The amount of $\tilde{U}$ is varied as shown in Figure 2, cf. red line. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. The blue triangles indicate results from our previous work [19]. No information on U was used in NEAT. $T = 298$ K.

Figure 8: Activity coefficient γ_T of target component acetone (T) in five-component mixtures of T with water (W), xylose (U_1), acetic acid (U_2), and methyl acetate (U_3). The amount of W is varied as shown in Figure 2, cf. blue lines. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures, cf. Table 1. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures. No information on U was used in NEAT. $T = 298$ K.

In Figures 9 - 11, results for the activity coefficient of the target component 1,4-butanediol in system C (1,4-butanediol (T) + water (W) + cyclohexanone (U₁) + acetonitrile (U₂) + methyl acetate (U₃)) are shown. The presentation is similar to the one for the previous examples.

Figure 9: Activity coefficient γ_T of target component 1,4-butanediol (T) in five-component mixtures of T with water (W), cyclohexanone (U₁), acetonitrile (U₂), and methyl acetate (U₃). The amount of T is varied as shown in Figure 2, cf. green lines. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. No information on U was used in NEAT. $T = 298$ K.

In Figure 9, the influence of the variation of the amount of T on the activity coefficient of T is shown. The agreement of the predictions from NEAT for the poorly specified mixtures with the results from modified UNIFAC (Dortmund) for the fully specified mixtures is almost perfect, including the predictions for the limiting activity coefficient of T.

In Figure 10, the influence of the variation of the amount of $\tilde{U}$ on the activity coefficient of T is shown. Since the mass ratio of T/W is the same in both reference mixtures R₁ and R₂ (cf. red line in Figure 2), the results from modified UNIFAC (Dortmund) for the fully specified mixtures merge again in one line. Up to a mass fraction of $x_{\tilde{U}} = 0.5$ g/g, the agreement of the predictions with NEAT with the results for the fully specified mixtures is very good. At higher mass fractions of $\tilde{U}$, the deviations increase. However, the trends are represented well throughout. Again, no significant influence of the choice of the reference mixture and similar results as in our previous work [19], in which an NMR analysis of each mixture was used, are found.

In Figure 11, the influence of the variation of the amount of W on the activity coefficient of T is shown. The ratio $\tilde{U}/T$ is held constant (cf. blue lines in Figure 2). For water mass fractions approaching unity, the activity coefficient of T approaches the activity coefficient of T at infinite dilution in water since the influence of $\tilde{U}$ is vanishing. Hence, the curves merge again for $x_W \rightarrow$

Figure 10: Activity coefficient γ_T of target component 1,4-butanediol (T) in five-component mixtures of T with water (W), cyclohexanone (U_1), acetonitrile (U_2), and methyl acetate (U_3). The amount of $\tilde{U}$ is varied as shown in Figure 2, cf. red line. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled square and circle indicate the reference mixtures, cf. Table 1. The blue triangles indicate results from our previous work [19]. No information on U was used in NEAT. $T = 298$ K.

1 g/g. The agreement of all predictions from NEAT with the results for the fully specified mixtures is almost perfect.

Figure 11: Activity coefficient γ_T of target component 1,4-butanediol (T) in five-component mixtures of T with water (W), cyclohexanone (U_1), acetonitrile (U_2), and methyl acetate (U_3). The amount of W is varied as shown in Figure 2, cf. blue lines. Lines: results from modified UNIFAC (Dortmund) for the fully specified mixtures. Symbols: predictions from NEAT. The filled symbols indicate the reference mixtures, cf. Table 1. No information on U was used in NEAT. $T = 298$ K.

In a previous work of our group, the NEAT method to predict activity coefficients of target components in poorly specified mixtures was introduced. It is based on a quantitative NMR analysis to identify the chemical groups of the unknown components in the mixture and the thermodynamic group contribution method modified UNIFAC (Dortmund). In this work, we show that, based on one NMR analysis of a single mixture, the activity coefficient of the target component in all mixtures of the same system can be predicted with NEAT as long as the ratios between the amounts of the unknown components in the mixtures remain unchanged. This is the case in many practical problems, such as the selective separation of the target component from a liquid mixture or the removal of solvent to increase the concentration of a diluted solution. The quality of the predictions that are obtained with NEAT is similar to the one that is achieved when modified UNIFAC (Dortmund) is applied to fully specified mixtures. NEAT is particularly interesting for the model-based design of processes with poorly specified mixtures. The present work shows how NEAT can be applied in a particularly simple manner to an important class of problems.

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Declarations of interest

none

Symbols

M	molar mass / g/mol
N	number of unknown components
R	reference mixture
T	target component
T	temperature / K
U	unknown component
$\tilde{U}$	mean unknown component
W	water
x	mass fraction / g/g

Greek letters

γ	activity coefficient
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Abbreviations

COSMO-RS	Conductor like Screening Model for Real Solvents
NEAT	NMR Spectroscopy for the Estimation of Activity Coefficients of Target Components in Poorly Specified Mixtures
NMR	Nuclear Magnetic Resonance
NRTL	Non-Random Two-Liquid Model
UNIFAC	Universal Quasichemical Functional Group Activity Coefficient Model
UNIQUAC	Universal Quasichemical Model

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Appendix A. Assignment of Chemical Groups to NMR Chemical Shift Regions

Table A.1 shows the assignment of chemical groups from the modified UNIFAC (Dortmund) table to ^{13}C NMR chemical shift regions that was used in the present work. The assignment is the same as the one that was used in a previous work of our group Ref. [19] to predict the activity coefficients of the target components in aqueous poorly specified mixtures. In addition to the information on the unknown components, the mass fraction of water in the poorly specified mixture is determined from the mass balance.

Table A.1: Assignment of chemical groups to chemical shift regions of ^{13}C NMR spectra used in this work. All groups are groups from the modified UNIFAC (Dortmund) table. The mass fraction of water (last row) in all reference mixtures R was calculated from the mass balance.

^{13}C NMR chemical shift region	Group assignment	UNIFAC label
0 - 60 ppm	alkyl, carbonyl	' $\underline{\text{C}}\text{H}_2$ ', ' $\underline{\text{C}}\text{H}_2\text{CO}$ '
60 - 90 ppm	alcohol	' $\underline{\text{C}}\text{H}_2$ ' + ' OH(P) '
90 - 150 ppm	alkenyl	' $\underline{\text{C}}\text{H}=\text{CH}$ '
150 - 180 ppm	carboxyl	' $\underline{\text{C}}\text{OOH}$ '
>180 ppm	carbonyl	' $\text{CH}_2\underline{\text{C}}\text{O}$ '
n.a.	water	' H_2O '

Appendix B. Results for the Fully Specified Mixtures

In Figure B.1, results for the activity coefficient γ_{T} of the target component ethanol (T) in mixtures of system A calculated with modified UNIFAC (Dortmund) for the fully specified mixtures (left) and the absolute deviations between the results for the fully specified mixtures and the predictions with NEAT, cf. Figure 1, (right) are shown. Very similar surfaces and respectively small deviations are found. The largest deviations occur for high concentrations of the unknown component (U = 2-butanone) for which no information was used in NEAT, cf. edge labeled with $\tilde{\text{U}}$.

Figure B.1: Left: activity coefficient γ_T of target component ethanol (T) in mixtures of system A calculated with modified UNIFAC (Dortmund) for the fully specified mixtures. Right: absolute deviations $\Delta\gamma_T$ between the predictions with NEAT, cf. Figure 1 in the main text, and the results for the fully specified mixtures. $\Delta\gamma_T = (\gamma_T)^{\text{UNIFAC}} - (\gamma_T)^{\text{NEAT}}$. $T = 298$ K.

Appendix C. Estimated Composition of the Reference Mixtures

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In Tables C.1 - C.3, the estimated composition of the poorly specified reference mixtures and the estimated stoichiometry of the mean unknown component $\tilde{U}$ as obtained with NEAT for the studied systems are summarized.

Table C.1: Estimated composition in the component space (target component T + water W + mean unknown component $\tilde{U}$) for the reference mixtures of system A (ethanol (T) + water (W) + 2-butanone (U)) and stoichiometry of $\tilde{U}$ for $M_{\tilde{U}} = 150$ g/mol obtained with NEAT. The labels are the identifiers for the subgroup from modified UNIFAC (Dortmund).

Mixture	x_i / g/g		Stoichiometry of $\tilde{U}$				
	x_T	$x_{\tilde{U}}$	'CH2'	'OH(P)'	'HC=CH'	'COOH'	'CH2CO'
R1	0.098	0.029	4.743	0.000	0.000	0.000	1.986
R2	0.076	0.229	4.442	0.000	0.000	0.000	2.086

Table C.2: Estimated composition in the component space (target component T + water W + mean unknown component $\tilde{U}$) for the reference mixtures of system B (acetone (T) + water (W) + xylose (U_1) + acetic acid (U_2) + methyl acetate (U_3)) and stoichiometry of $\tilde{U}$ for $M_{\tilde{U}} = 150$ g/mol obtained with NEAT. The labels are the identifiers for the subgroup from modified UNIFAC (Dortmund).

Mixture	x_i / g/g		Stoichiometry of $\tilde{U}$				
	x_T	$x_{\tilde{U}}$	'CH2'	'OH(P)'	'HC=CH'	'COOH'	'CH2CO'
R1	0.096	0.031	3.640	1.266	0.237	1.582	0.000
R2	0.084	0.133	3.772	1.378	0.164	1.541	0.000

Table C.3: Estimated composition in the component space (target component T + water W + mean unknown component $\tilde{U}$) for the reference mixtures of system C (1,4-butanediol (T) + water (W) + cyclohexanone (U_1) + acetonitrile (U_2) + methyl acetate (U_3)) and stoichiometry of $\tilde{U}$ for $M_{\tilde{U}} = 150$ g/mol obtained with NEAT. The labels are the identifiers for the subgroup from modified UNIFAC (Dortmund).

Mixture	x_i / g/g		Stoichiometry of $\tilde{U}$				
	x_T	$x_{\tilde{U}}$	'CH2'	'OH(P)'	'HC=CH'	'COOH'	'CH2CO'
R1	0.096	0.013	5.793	0.000	0.653	0.666	0.518
R2	0.083	0.121	5.414	0.000	0.675	0.775	0.514