Solvent selection for extractive distillation processes to separate close-boiling polar systems

Lisette M.J. Sprakel, Peter Kamphuis, Anna L. Nikolova, Dylan J. Keijser, Boelo Schuur*

University of Twente, Faculty of Science and Technology, Sustainable Process Technology Group, The Netherlands

Abstract

Solvent selection is key in extractive distillation process development and solvent effects are often predicted based on the activity coefficients at infinite dilution. For close-boiling polar systems with strong or specific interacting species, standard simulation tools, e.g. using UNIFAC or COSMO-RS, often predict poor as the activity coefficients at infinite dilution not always reflect the selectivity in the process. For these systems, a heuristic solvent selection method in which molecular properties such as acidity, hydrogen bonding and polarity are applied is desired as first estimate in the solvent selection. To explore the key parameters for such a first selection, solvent effects on the relative volatility (σ) were measured for three different industrially relevant polar mixtures, valeric acid – 2-methylbutyric acid, diethylmethylamine – diisopropylether, and 2-butanol – 2-butanone. For each of the cases, the potential solvent on σ was measured in an ebulliometer. For the acids, the difference in pKₐ of 0.1 was too small to separate based on acidity with a moderately basic solvent. Stronger basic solvents resulted in thermal and chemical instability. Although the solvent methyl-2-methyl butyrate is not suitable as a solvent because of reactivity, this structurally similar solvent showed selectivity, indicating also in extractive distillation the like dissolves like phenomenon can be applied to induce selectivity. A larger difference in basicity of the mixture components (amine–ether mixture) and a difference in hydrogen bonding affinity between the mixture components (ketone–alcohol mixture) allowed for increasing σ based on differences in acidity and hydrogen bonding, respectively.© 2019 Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

The climate target of the European Union for the year 2030 involves 40% cuts in greenhouse gas emissions and a 27% improvement in energy efficiency (European Council, 2014). In 2016 roughly 25% of the total energy within the EU was used for industrial purposes (Eurostat, 2018). Hence, to reach the goals for 2030, reducing the industrial energy demand has an enormous potential. Because distillation is the most widely applied separation process for homogeneous fluid separations (Smith and Jobson, 2000), including many mixtures that are difficult to separate by distillation due to pinch-points or close boiling points, energy-saving opportunities include improving these difficult distillation processes. Extractive distillation is a technology that can potentially improve the separation of close-boiling mixtures and enable separation of azeotropic mixtures (Doherty and Knapp, 2004; Graczova and Vavrusova, 2018; Kockmann, 2014). In extractive distillation a solvent is applied that interacts with a preferred affinity for one of the mixture components, by which the relative volatility of the mixture is changed or an azeotrope is "broken" (Doherty and Knapp, 2004). For a wide range of mixtures from very polar to apolar extractive distillation has been used, e.g. ethanol–water mixtures using either ethylene glycol (EG) (Kiss and Ignat, 2012) or ionic liquids as entrainers (Kulajapeng et al., 2014; Quijada-Maldonado et al., 2013), ethyl acetate–ethanol mixtures (Berg and Ratanapupech, 1986; Li et al., 2009), mixtures of monochloroacetic acid and dichloroacetic acid (Jongmans et al., 2012b), mixtures of ethylbenzene and styrene (Jongmans et al., 2012a) and mixtures of aromatics/aliphatics (Canales and Brennecke, 2016).

The choice of solvent is key for the viability of an extractive distillation process, and solvent selection can be an expensive and
time-consuming procedure. Next to manipulating the relative volatility in the extractive distillation process, it is essential that the solvent is regenerated easily to recycle the solvent back to the extractive distillation column. In apolar systems the solvent typically induces positive deviations from Raoult’s law, whereas in polar systems, such as monochloroacetic acid and dichloroacetic acid (Jongmans et al., 2012b), the solvent induces negative deviations. In this work the focus is on polar close-boiling mixtures, and solvents that have an attractive effect on the high-boiling component, thereby inducing negative deviations from Raoult’s law. The combination of being effective in the extractive distillation and being regenerable requires a certain affinity window that is unfortunately not straightforward to define. Ideally, extensive experimental screening of solvents is avoided, which might be realized by making use of known solvent scales to characterize intermolecular affinity between solvent and mixture constituents. An example is the proton affinity scale, which is a scale that describes the basicity of solvents, where the proton affinity is equal to the enthalpy that is measured during the deprotonation reaction of the base in the gas phase (Laurence and Gal, 2009). Stronger bases therefore have a larger proton affinity. For this scale, as well as for other scales applied for solvent characterization, the databases that are created list properties of the solvents based on their interactions with a (scale-)specific component. Other scales often applied for solvent characterization are the BF₃ affinity scale (Laurence and Gal, 2009; Laurence et al., 2011) and the hydrogen bond basicity scale pKₜₙₑₓₙ (Laurence and Gal, 2009; Laurence et al., 2011). For most of these scales the properties or interactions of solvents with the components need to be determined experimentally, but also parametrizations based on the linear solvation energy relationship (LSEr) (Kamlet et al., 1983; Taft et al., 1985) are applied, using solvatocromatic and/or Kamlet-Taft parameters (Bizek et al., 1993; Meyer and Maurer, 1995).

The direct prediction of the solvent effect on the relative volatility of a mixture that is to be separated can also be based on infinite dilution activity coefficients (Bastos et al., 1985; Lei et al., 2003; Seader et al., 2011). These predictions are mainly applied on apolar systems of alkanes/alkenes or alkane/ aromatics, but also acetone/methanol mixtures (Kossack et al., 2008; Schult et al., 2001) and for separation of hydrocarbons with ionic liquids (Zhu et al., 2007). Software for solvent selection and prediction of VLE behavior in extractive distillation is also widely applied in which different types of chemical calculations can be combined. Examples are COSMO-SS (Eckert and Klamt, 2001), UNIFAC (Fredenslund et al., 1975) and Computer Aided Molecular Design (CAMD) on the basis of the selectivity at infinite dilution with software packages ProCAMD, a tool that is a part of the IAS® framework (Harper and Gani, 2000). These predictive methods based on activity coefficients are successfully applied for solvent selection for separation of various mixtures, including C₈ – aromatics mixtures, C₄ mixtures, aromatics and non-aromatics, ethanol–water, ILs, acids, oxocyclics, and systems of ketone, esters and alcohols (Brignole et al., 1986; Lei et al., 2003; Lek-utaiwan et al., 2011; Pretel et al., 1994).

The consideration of thermodynamics, such as the selectivity at infinite dilution, does however not always lead to the selection of the right solvent as the selectivity at infinite dilution is not in all cases related to the selectivity at finite dilution and a comparison is problematic in case the distillate product changes (Kossack et al., 2008). The selectivity only focuses on the extractive distillation column, but for a viable process the regeneration column, e.g. the enthalpy of evaporation of the solvent, should also be included (Kossack et al., 2008). Predictions based on group contribution methods are also limited by the database they were fitted on and therefore the design of new solvents is rather straightforward. There are also other cases in which application of methods based on infinite dilution activity coefficients or group contribution methods is not straightforward, especially in the case of very strong interactions and in case of specific interactions or formation of azetropes, which are all common in close-boiling systems of polar compounds. For these polar systems the prediction of VLE behavior is challenging, although a first indication for selecting the right type of solvent for a specific separation is desired. Therefore, in this work an experimental study is described that focuses on solvent effects in extractive distillation of close-boiling polar compounds.

Three specific industrially relevant binary mixture were chosen that cover a significant part of the field of polar compounds in terms of functional groups and each show different behavior regarding their relative volatility, i.e. the mixture of A) diethylmethyamine (DEMA) and diisopropylether (DIFE), B) valeric acid (HVaL) and its isomer 2-methylbutyric acid (2MBA) and C) 2-butanol (2-BuOH) and 2-butane (2-BuO). Next to differences in functional groups, for each case there are other differences regarding boiling point, and acidity (or basicity) of the components, see Table 1. The case with HVaL and 2MBA was chosen to study on the limiting ΔPₓ, for separation based on extractive distillation, in which results were compared to the separation of monochloroacetic acid and dichloroacetic acid reported by Jongmans et al. (2012b) (ΔTₓₓₓ, of 5 °C, and ΔPₓ, of 1.6). HVaL is an important industrial building block (DOW, 2014) that is produced from 1-butene, where impurities lead to production of 2MBA (Bahrmann et al., 1997; DOW, 2014; Kubitschke et al., 2000). The components in the case with DEMA–DIFE are widely applied in industry as building blocks (Roose et al. (2015)) and as solvents (Baksh et al., 2010). DEMA and DIFE are an ether and an amine and have therefore a different acidity. This case was chosen because of the very low relative volatility of the mixture which makes distillation infeasible. The case with 2-BuOH–2-BuO (relatively large ΔTₓₓ) involves two components with different functional groups (hydrogen bond donating and accepting for 2-BuOH, and only hydrogen bond accepting for 2-BuO).

For each of these cases solvents were selected from different classes and the effect on the relative volatility was measured and related to the molecular structures, interactions and activity coefficients of the components in the mixtures. Aiming at further increasing the understanding of affinities in the systems, isothermal titration calorimetry (ITC) was applied to measure the heat of interaction and excess enthalpies of mixing.

2. Materials and methods

2.1. Chemicals

Chemicals were obtained from Sigma–Aldrich, unless mentioned otherwise, i.e. acetic acid (≥ 99.5%), Acetone Lichrosolv® (≥ 98.8, Merck KGaA), beta-cyclodextrin (≥ 98%, Acros Organics), 1,8-bis(dimethylamino)naphthalene (99%, Proton Sponge®), butanoic acid (99%, HBU), 2-butanol (≥ 99.5%, 2-BuOH), 2-butane (≥ 99.5%, 2-BuO), m-cresol (≥ 98%), 18-crown-6 (TCI-GR), cyclohexanol (≥ 99%), cyrene (99.0%), dibutylamine (≥ 99.5%, DBA), dibutyl ether (≥ 93.3%, DBE), diethylene glycol (≥ 100%, Merck KGaA, DEG), diethylene glycol dibutyl ether (≥ 99%, DEGBE), diethylene glycol dimethyl ether (≥ 95.9%, diglyme), N,N-diethylmethyamine (≥ 98%, Acros Organics and TCI-GR, DEMA), diisopropyl ether (≥ 99%, DIFE), DMSO (99.9%), dodecane (≥ 99%), ethylbenzene (Fluka, 98%), ethylene glycol (≥ 98.8%, EG), glycerol (99.0%), n-heptane anhydrous (99 +%, Alfa Aesar), isovaleric acid (99%, ISOHVal), itaconic acid (≥ 99%), 2MBA (≥ 98%), 5-methyl-2-hexanone (5-ment-2-one, 98.0%), methyl isobutyl ketone (≥ 97.7%, MIBK), methyl-2-methylbutyrate (≥ 98%, Me2Bu), methyl levulate (98.0%, MeLev), octanoic acid (≥ 98%, HOct), 1-octanol (≥ 99%), oleic acid (≥ 99.5%, Fischer Scientific), phenol (≥ 99.5%, PhOH), 1,2-propanediol (≥ 99%), propylene glycol (99.0%, PG), tribenzylamine (≥ 99%, TBzA), tributylphosphate (99 +%, TRP), 2,2,4-trimethylpentane (≥ 9.5%, iso-octane), trioctylamine (98%, TOA), HVal (≥ 99%) and p-xylene (Honeywell, 99%).

2.2. Experimental methods

2.2.1. Ebulliometer
Fischer Labodest VLE602 ebulliometers were used for the VLE experiments. The equilibrium temperature of the mixtures
was measured with a Pt-100 thermocouple after setting the pressure. For each experiment the measurement cell was filled with 80 mL of sample, equilibration required between 30-90 min, depending on the mixture and the temperature of the previous measurement. After equilibration, 1 mL aliquots were taken from the liquid phase and the condensed vapor phase to determine the compositions. Solvent regeneration was investigated by measuring binary VLE data of the high-boiling component of the mixture and the solvent. For each case, the measurement and analysis errors were determined as they also depend on the temperature and pressure at which the measurement is carried out.

### 2.3. Analytical methods

#### 2.3.1. GC and GC–MS

For the DEMA-DIPE mixture samples were analyzed with a Varian CP-3800 GC with FID (accuracy > 98%) and Agilent DB-WAX column (60 m × 0.25 mm × 0.25 μm), using 100 μL sample and 100 μL internal standard (dodecane), diluted in acetone to a total of 1.7 mL. The temperature profile is as follows: injection and FID at 280 °C, initial measurement temperature of 40 °C with a linear ramp of 5 °C/min after 1 min to 50 °C, and after 1 min at 50 °C, again a ramp in 3 min to 250 °C at which the temperature was kept constant for 3 min. Analysis was also performed with 7890A Ms 5975C Agilent GC–MS with FID and helium as carrier gas (accuracy > 98%) and Agilent HP-5Ms, HP19191S-433 column. The sample concentration was approximately 5% in methylisobutylketone (MIBK). The injection and FID were kept at 280 °C, the initial column temperature was 45 °C with a linear increase after 4 min to 160 °C at a measurement time of 32 min, and after 2 min again a linear increase to 250 °C at 47 min, after which it was kept constant for 2 min. For the HVal – 2MBA mixture samples of binary VLE experiments were analyzed with an HPLC 1200 series with RID (accuracy > 99%), with either an Agilent Hi-plex H+ Column (300 × 7.7 mm) or GROM Resin H+EX (250 × 8 mm) and 0.6 mL/min 5 mM H2SO4 mobile phase. Samples of pseudo-binary VLE experiments were analyzed with a Varian CP-3800 GC with FID (accuracy > 98%) and VF1701ms (60 m × 0.25 mm × 0.25 μm) column. The temperature of injection and FID were 280 °C, initial column temperature 50 °C with a linear increase after 1 min to 130 °C at 14 min, and after 1 min again a linear increase to 180 °C in 1.3 min after which it was increased linearly to 190 °C in 3.3 min and then kept constant for 2 min. For the samples that also contain octanoic acid (HOCT) the procedure was extended with a linear temperature increase from 190 °C to 235 °C in 1.2 min followed by a last linear increase to 245 °C in 3.3 min where the temperature was kept constant for 2 min. For the 2 BuOH–2 BuO mixture samples were analyzed with the previously mentioned method with the Varian GC, using heptane as an internal standard in this case. The injection and FID temperature were at 280 °C, initial column temperature of 45 °C with a linear increase after 4 min to 150 °C at 15.5 min, after which there was a second linear increase to 250 in 4.5 min.

#### 2.3.2. Isothermal titration calorimetry (ITC)

ITC was performed using a TA Instruments TAM III Microcalorimeter with 1 or 4 mL stirred sample vials at 20 °C. The automatic syringe was filled with 300 μL of titrant and connected with the sample cell through a cannula. The titrant was injected periodically. For complex formation between HVal and TOA, the sequential reaction model described by Sprakel and Schuur (2018) was applied for fitting of the experimental data from which the stoichiometry, enthalpy and equilibrium constant of the reaction could be determined. The experimental data were corrected with the heat of injection of the last injection of a measurement series.

#### 2.3.3. Error analysis

For the study on HVal, the error in the equilibrium temperature measured was 0.4 °C. Based on results of experiments in triplo, standard deviations were calculated for the composition of the vapor and liquid phase. At 300 mbar the standard deviation in the liquid composition was 1.5 × 10⁻³ and 1.8 × 10⁻³ in the vapour composition. At 900 mbar this was 2.1 × 10⁻³ and 3.1 × 10⁻³, respectively. For the solvent screening VLE measurements the standard deviation of the GC analysis that was performed in triplo was 5.2% for. For the case with DEMA–DIPE, the standard deviation in the temperature equaled 0.4 °C at 1000 mbar and 0.7 °C at 300 mbar. For α the standard devia-
tion equaled 0.024 (GC) and 0.052 (GC–MS) at 1000 mbar and 0.013 (GC) and 0.060 (GC–MS) at 300 mbar. The resulting standard deviation based on GC–MS experiments was larger since in GC a triple injection was performed on each sample. For the 2-BuOH–2-BuO mixture, the absolute error in the equilibrium distillate temperature was 0.4 °C and 0.2 kPa in the pressure of the system. The absolute error in α was calculated to be 0.2, which is next to errors in the sample preparation (0.001 g error in mass) and in the GC analysis (0.5% in wt. fraction), mainly a result of a significant error in the solvent-to-feed ratio of ±10% that was calculated based on feed samples that were also analyzed with GC.

3. Results and discussion

3.1. The system N,N-diethylmethylamine (DEMA) – diisopropylether (DIPE)

3.1.1. Verification of ebulliometry measurements

The equilibration and temperature measurement of the ebulliometer was verified by measuring the pure component boiling temperatures of DEMA and DIPE at various pressures, see Fig. 1. From the figure it can be concluded that the experimental data correspond well with the theoretical values calculated with the Antoine equation (Gmeingh et al., 1991–2014).

3.1.2. Binary mixture VLE measurements

Binary mixture VLE data measured for DEMA and DIPE at 300 and 1000 mbar are displayed in Fig. 2, in which it is clear that α of this mixture is very low. At 1000 mbar the average α of DEMA over DIPE equals 1.05 ± 0.024. A decrease in pressure increased the average α to 1.09 ± 0.013 at 300 mbar. An ideal equilibrium curve with α = 1.09 is shown in Fig. 2a. Furthermore, although no clear azeotrope can be observed at this low relative volatility, there is a possibility of a minimum boiling azeotrope based on the Txy-diagrams (Fig. 2b and d). In this separation case ΔTy is very small, but the difference in acidity (basicity) and molecular structure between the components is large.

For this case solvents are selected with the aim to achieve a high selectivity, see Eq. (3). The solvent selectivity can be written as the ratios of the activity coefficients of both components with and without the presence of the solvent (Doherty and Knapp, 2004). In this equation $P_{\text{sat}}$ is the saturated vapor pressure of a component at a given temperature, $y_i$ is the vapor mole fraction and $x_i$ is the liquid mole fraction.

$$S_{ij} = \frac{\alpha_{ij} \gamma_i}{\gamma_{ij} \alpha_{ij}} = \frac{(\gamma_{ij} \alpha_{ij})^2}{\alpha_{ij}^2}$$

For DEMA–DIPE, the separation is complicated due to α being close to unity. In those cases, generally there are positive deviations from Raoult’s law (i.e. both activity coefficients greater than or equal to 1) and the ratio of activity coefficients is larger than the ratio of saturated vapor pressures. Thus, see Eq. (1), a solvent is desired that interacts ideally with the high-boiling component and repels the low-boiling component (or interact ideally with the low-boiling component and attracts the high-boiling component) (Doherty and Knapp, 2004). Next to improving α of the binary mixture, the solvent should be chemically and thermally stable, non-toxic and non-corrosive, inexpensive, readily available and not reacting with one of the mixture components (Kockman, 2014; Doherty and Knapp, 2004). Furthermore, it should be possible to regenerate the solvent so it can be recycled to the process (Jongmans et al., 2012b). For the regenerability of the solvent moderate interactions are favored over very strong interactions (Jongmans et al., 2012b). Also, the solvent should not form an azo trope with one of the components (Doherty and Knapp, 2004), which can in general be achieved by keeping a boiling point difference of at least 30 °C and for the economic viability a relatively low heat of evaporation is favored. For binary mixtures with a low α it is in general easier to respect the natural difference in vapor pressure of the components and not select a solvent that will invert the relative volatility of low-boiling and high-boiling component (Doherty and Knapp, 2004; Seader et al., 2011).

Different types of solvents were applied, several solvents were selected based on similarity and homologues (dibutylether (DBE), diglyme, dibutylamine (DBA), dipropylamine (DPA)), others on acidity (acetic acid (HAc), HVal, oleic acid), polarity and the potential of hydrogen bond formation. Hydrogen bonding is expected to play an important role as both DEMA and DIPE contain significantly different hydrogen bond accepting groups which most likely show different affinity with a solvent. This potential of differences in hydrogen bond formation was also studied based on qualitative predictions of deviations from Raoult’s law for interaction of different compounds classes, see Table 2 (Robbins, 1980). Ideally, the solvent shows a different effect on the deviations of Raoult’s law to induce and increase in α, as is the case for acids, alcohols, secondary amines, and paraffins. Solvents in each of these categories were selected. Especially for the alcohols, positive deviations from Raoult’s law are expected for interaction with the ether and ideal behavior with the amine making this an interesting group of solvents, a result of the difference in electronegativity between the nitrogen and oxygen atom. Also for glycols interesting solvent properties in terms of hydrogen bonding possibilities are expected, and in addition they are cheap and commercially available on large scales.

Pseudo-binary VLE data were measured for all selected solvents at a S/F ratio of 1, the results for the effect on the relative volatility in the system are displayed in Fig. 3, based on only the fractions of the mixture components and not the solvent.
For the carboxylic acids the interactions with the mixture of DEMA and DIPE were too strong and no equilibrium could be obtained in the experiments. When m-cresol was applied as solvent, a miscibility gap was observed, so for this solvent no \( \alpha \) could be measured at S/F = 1. For all other solvents except when diglyme was applied, the measured volatility of DIPE was larger than that of DEMA.

The secondary amines, alkanes and ethers had no to little effect on \( \alpha \), indicating that for these solvents the difference in affinity for the two components is too small to have a significant effect on \( \alpha \). Secondary amines are able to form hydrogen bonds, nevertheless it can be concluded that the hydrogen bond basicity of the secondary amines is too weak to affect \( \alpha \). The alcohols cyclohexanol, PhOH and propylene glycol (PG) each have a positive effect on \( \alpha \). Interaction with each of these solvents is based on hydrogen bonding and the increased \( \alpha \) confirms the positive deviations from Raoult’s law that were expected for interaction with the ether and ideal behavior with
the amine (see Table 2). These differences are a result of the difference in electronegativity between the nitrogen and oxygen atom. The effect of PhOH is significantly larger than the other two solvents, which is a result of the more acidic proton of PhOH.

The increased relative volatility of DIPE over DEMA indicates that there is a larger hydrogen bonding basicity of the tertiary amine as compared to the ether, which can be expected based on the nitrogen atom in DEMA. Increasing the solvent to feed ratio (Fig. 3b) also increases the relative volatility, although based on that also for PhOH at 1000 mbar a higher α would be expected. The α at increased S/F-ratio for PhOH may be influenced by more pronounced self-aggregation of the PhOH at higher S/F-ratios instead of hydrogen bonding with the amine. Moreover, at 1000 mbar the equilibrium temperature is increased, resulting in less strong hydrogen bonding in general. Because of the possibility of a minimum boiling azeotrope in the binary VLE data (Fig. 2), for the three solvents that successfully increased the relative volatility (cyclohexanol, PhOH and PG), VLE data were also measured at x\textsubscript{DEMA} of 0.05 and 0.95 and all showed a relative volatility above 1 (see Table 3, data was previously reported (Sprakel et al., 2018)). Based on this the presence of an azeotrope in the pseudo-binary system could be excluded. Also in these results, the solvent effect of PhOH is more pronounced. At higher S/F-ratio miscibility gaps appeared, because of which no equilibrium data could be measured. The most straightforward method to test the regeneration is by measuring the binary VLE data of the high boiling component (DEMA) and the solvent. For all three solvents a very high or infinite relative volatility was obtained as either no or a very small signal was obtained for DEMA in the GC chromatogram. Based on this the recovery of the solvents is not expected to be problematic.

From the results on DIPE-DEMA, it can be concluded that even for mixtures of components with (almost) equal volatility, a large difference in hydrogen bonding affinity offers opportunities for hydrogen bond donating solvents to increase α. An advantage of a mixture of components with (almost) equal volatility is that the natural difference in volatility is not important and solvents may be selected to target either of the mixture components, based on the most appropriate attractive or repulsive interactions.

<table>
<thead>
<tr>
<th>Solvent Bonding</th>
<th>Tertiary amine</th>
<th>Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen bonding</td>
<td>Phenol</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Acid</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Alcohol</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ketones</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Tertiary amines</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Secondary amines</td>
<td>+</td>
</tr>
<tr>
<td>Acceptors</td>
<td>Primary amines</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Ether, oxides</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ester</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Aromatics and olefins</td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>Paraffins</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2 – Predicted qualitative deviations (positive +, negative – or none (0)) from Raoult’s law based on functional groups and hydrogen bonding interactions for the selected case of tertiary amine and ether, data are adapted from (Robbins, 1980).

Fig. 4 – Integrated ITC data for interaction of HVal with DEMA (0.13 M) at 20 °C in diluent ● DIPE and ● dodecane, with the isotherms fitted by the sequential reaction model (dotted lines, ...) (Sprakel and Schuur, 2018). Fitted parameters for the sequential reaction model are: in dodecane K\textsubscript{1,1} = 21, ΔH\textsubscript{1,1} = −19.5 kJ/mol, K\textsubscript{n+1,1} = 112, ΔH\textsubscript{n+1,1} = −12.5 kJ/mol and n = 1.58; and in DEMA K\textsubscript{1,1} = 9.5, ΔH\textsubscript{1,1} = −21.1 kJ/mol, K\textsubscript{n+1,1} = 11, ΔH\textsubscript{n+1,1} = −16.4 kJ/mol and n = 1.59.

3.1.3. Interaction between DEMA and DIPE

With isothermal titration calorimetry (ITC) two different experiments were performed with the aim to obtain more insight in the interactions between DEMA and DIPE, as well as with the solvent HVal, because no equilibrium could be reached in experiments with HVal. In the first ITC experiment HVal was titrated to a mixture of DEMA in the apolar and inactive diluent dodecane, whereas in the second experiment HVal was titrated to a mixture of DEMA in DIPE as a diluent. The integrated ITC results are shown in Fig. 4.

Based on the integrated data and the sequential reaction model described by Sprakel and Schuur (2018) the parameters that describe the interactions and complex formation between the mixture components were fitted. For interaction of HVal with DEMA diluted in dodecane the calculated fit parameters are K\textsubscript{1,1} = 21, ΔH\textsubscript{1,1} = −19.5 kJ/mol, K\textsubscript{n+1,1} = 112, ΔH\textsubscript{n+1,1} = −12.5 kJ/mol and n = 1.58; and in DIPE K\textsubscript{1,1} = 9.5, ΔH\textsubscript{1,1} = −21.1 kJ/mol, K\textsubscript{n+1,1} = 11, ΔH\textsubscript{n+1,1} = −16.4 kJ/mol and n = 1.59. These parameters indicate that the stoichiometry of the complexes is not affected by the choice of diluent. Furthermore, the moderate reaction enthalpies (<25 kJ/mol) indicate hydrogen bonding, there is no indication of the stronger proton-transfer in the carboxylic acid-amine complex (Tamada and King, 1990a, b). The enthalpy of reaction is higher in case the complexes are diluted in DIPE, indicating a more favorable environment for complexation in the polar and hydrogen bond accepting DIPE and therefore suggesting interactions between DEMA and DIPE. The experimental stability problems and not obtaining a vapor-liquid equilibrium can therefore not be explained by too strong interactions and may be a result of the formation of a second liquid phase.

3.2. The system valeric acid (HVal) and 2-methylbutyric acid (2MBA)

Fig. 5 shows the binary VLE data for the system of HVal and 2MBA at both 300 and 900 mbar. The average α is low and equals 1.35 ± 0.02 at 300 mbar and 1.30 ± 0.03 at 900 mbar. At all pressures the xy-diagrams (Fig. 5a and c) show the typi-
Table 3 – VLE data (relative volatility $\alpha$) for the three most promising solvents for separation of DEMA and DIPE. (n.e. = no equilibrium achievable). Data previously reported in Sprakel et al. (2018).

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>$\alpha$</th>
<th>1000</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/F</td>
<td></td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Solvent</td>
<td>$x_{DEMA}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>3.7</td>
<td>n.e.</td>
<td>n.e.</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>1.5</td>
<td>1.6</td>
<td>1.1</td>
</tr>
<tr>
<td>Phenol</td>
<td>7.6</td>
<td>3.6</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Fig. 5 – Binary VLE data of mixture of HVal and 2MBA at 300 mbar (standard deviation in $x_{DEMA} = 0.0015$ and $y_{2MBA} = 0.0018$) (a) xy diagram from Sprakel et al. (2018) and (b) Txy diagram, and 900 mbar (standard deviation in $x_{DEMA} = 0.0021$ and $y_{2MBA} = 0.0031$, see Section 2.3.3. for more information) (c) xy diagram and (d) Txy diagram. In (b) and (d): ■ equilibrium composition and temperature of the vapor phase and □ of the liquid phase.

cal shape of ideal binary data. The Txy-diagrams (Fig. 5b and d) show a narrow plateau in the region around an equimolar composition, this effect is stronger at the lowest pressure of 300 mbar.

The narrow plateau in (Fig. 5b) may be caused by the dimerization of acids in the vapor phase (Miyamoto et al., 1999). In literature, similar xy and Txy-diagrams are reported for binary mixtures of HBu and isobutyric acid, and as well for HBu and isoHVal (Sewnarain et al., 2002). Also in those cases, the relative volatility is low and the slopes in the temperature profile are flattening close to equimolar compositions.

Also for this case, potential solvents for improving $\alpha$ were selected based on different aspects, i.e. a group of basic solvents, acidic solvents, solvents based on similarity with one of the components of the mixture and apolar solvents. With both the acidic and basic solvents the aim is to induce negative deviations from Raoul’s law by double hydrogen bonding or acid-base interactions, respectively. On the other hand, for the apolar solvents and the solvents based on similarity that may induce steric hindrance, the aim is to induce positive deviations from Raoul’s law. Because of the structural difference between HVal and 2MBA also other solvents were selected based on steric hindrance, e.g. for tribenzylamine (TBzA) that contains three aromatic rings a difference in affinity is expected with the linear HVal and the branched structure of 2MBA. A similar effect may be expected for the Proton Sponge® where the cavity for interaction with the solvent is also relatively narrow based on the molecular structure. Pseudo-binary VLE experiments to determine the solvent effect on the relative volatility of the system were performed with all selected solvents at 300 and 900 mbar, see Fig. 6.
With both the acidic and basic solvents the aim is to induce negative deviations from Raoult’s law by double hydrogen bonding or acid-base interactions, respectively. On the other hand, for the apolar solvents and the solvents based on similarity that may induce steric hindrance, the aim is to induce positive deviations from Raoult’s law. However, most solvents (Fig. 6) have no or only limited effect on $\alpha$. For the apolar solvents, apparently the difference affinity with HVal that has a longer carbon chain is too small to increase $\alpha$. Moreover, at 900 mbar the temperature is increased which results in more ideal behavior, as the activity coefficients with dodecane are expected to be $>1$, a decreased $\alpha$ is expected at 900 mbar. The expected difference in hydrogen bonding ability between the mixture components is also not strong enough for increased $\alpha$ with the ether-based solvents. For tribenzylamine (TBzA) that contains three aromatic rings a difference in affinity could be expected based on differences in steric hindrance with the linear HVal and the branched structure of 2MBA, however $\alpha$ is not increased. For tributylphosphate (TBP) no color change was visible, however additional peaks appeared in the GC chromatogram, indicating decomposition or instability.

The two solvents increasing $\alpha$ are Proton Sponge® and MeMeBu. MeMeBu was selected based on steric hindrance because of the structural difference between HVal and 2MBA and also because of structural resemblance with 2MBA, which results in either increased interaction between the solvent and 2MBA or positive deviations from Raoult’s law for HVal. An effect based on steric hindrance may also be expected for the Proton Sponge®, a solvent that is also strongly basic, where the cavity for interaction with the solvent is also relatively narrow based on the molecular structure. For the experiments with Proton Sponge® (as well as with trioctylamine (TOA)) the color of the mixture significantly changed and after the experiments the sample was completely dark, indicating a low thermal stability which is most likely a result of too strong interactions with the acids, as was previously also reported for monochloroacetic acid and dichloroacetic acid (Jongmans et al., 2012b). Thermal instability may also be the reason that no increased $\alpha$ was measured at 900 mbar for Proton Sponge®.

as the equilibrium temperature is approximately 30 °C higher at 900 mbar.

Applying the solvent MeMeBu increased $\alpha$ to 1.84 ± 0.18 at 300 mbar. Especially in the range of low relative volatility this is an increase that can strongly reduce the heat duty in extractive distillation processes (Blahusiak et al., 2018). The solvent is an ester with a lower boiling point than the mixture components and will therefore release an exiting distillation process with the distillate stream. Because 2-methylbutyrate is also a product of the hydrolysis of MeMeBu additional validation was performed to exclude that the increased $\alpha$ measured is not a result of that. The maximum water content in the initial sample was 0.5 wt% and therefore the increased relative volatility cannot be a result of the hydrolysis, since even if based on this all the formed 2MBA would hypothetically end up in the vapor phase without being part of the equilibrium, the relative volatility would only increase to 1.6. However, at 900 mbar at which the temperature is higher, which results in more ideal behavior based on which no significant decrease in $\alpha$ is expected, the measured value for $\alpha$ is lower for MeMeBu. The decreased $\alpha$ is most likely a result of transesterification of the solvent with HVal, which means that MeMeBu is not a good solvent because of reactivity. Nevertheless, there is still an effect of MeMeBu on $\alpha$, as the additional 2MBA that is formed is simply part of the equilibrium and only slightly decreases the S/F-ratio.

From the observations with the various solvents investigated for HVal and 2MBA, it can be concluded that the difference of 0.1 in $p\alpha$ is too small to induce a significant increase in the relative volatility through attractive interactions by acid-base pairing or hydrogen bonding. Although applying an even stronger basic solvent may possibly increase $\alpha$, as observed with the Proton Sponge®, the interactions with the mixture components are so strong that in those cases thermal and chemical stability is compromised. Jongmans et al. (2012b) also report that solvents with the strongest interactions with the mixture components could not be regenerated, but in their case the difference in $p\alpha$ (1.6) was large enough to apply moderately strong solvents to increase the relative volatility by inducing negative deviation from Raoult’s law. Further study of mixtures with differences in acidity is required to determine the minimum difference in $p\alpha$ that allows for applying moderately strong solvents that can be regenerated.

3.2.1. Interaction between valeric acid and TOA

The heat of interaction in the system of HVal, 2MBA and TOA was measured with ITC by performing titrations of the acids on samples with compositions that resemble the sample composition in the extractive distillation process, see Fig. 7. Based on these results the interactions between TOA and the acids can be explored. Fig. 7a shows the interaction of HVal with a mixture of 2MBA and TOA in a polar environment (1-octanol), where the molar ratio is the ratio of total acid concentration over the amine concentration (and since there was already acid in the sample, the curves do not start at zero). The energy released upon interaction is between 10 and 20 kJ/mol, which is a moderate interaction energy in the range of values reported for hydrogen bonding interactions (Sprakel and Schuur, 2018; Tamada and King, 1990a). In a second experiment, see Fig. 7b where the molar ratio is the ratio of total acid concentration over amine concentration, the stronger acid lactic acid (50 vol% in 1-octanol) was titrated to a sample consisting of HVal, TOA and 1-octanol. This type of experiment
is called a displacement experiment, because the acid-base interaction for the stronger acid is preferred over the interaction of the base with the weaker acid, and complexes with the weaker acid are displaced by complexes with the stronger acid. These experiments may be used to distinguish plateaus in the isotherm, a method that can be applied in ITC of higher affinity interactions (Kraimer and Keller, 2015). For this experiment however there is only one step (two plateaus) in the measured energy instead of the three expected plateaus that are expected as a result of (1) additional loading of the complexes with acid titrant, (2) the replacement of acid that was already present with acid titrant, and (3) the solvation of acid titrant in the sample with fully loaded complexes. The single step indicates that there is similar interaction energy of the stronger lactic acid and HVal upon interaction with TOA. Moreover Fig. 7b shows a steep decrease in the energy around a stoichiometry of 2, indicating the formation of complexes with overloading of acid, which also confirms the hydrogen bonding that was concluded based on the results in Fig. 7a. The spread in the first few data points is most likely a result from errors in the injection volume as a consequence of the high viscosity of the lactic acid–1-octanol mixture. Thus, the interactions in the mixtures are (mainly) based on hydrogen bonding and the formed complexes are overloaded with acid compared to amine.

3.3. The system 2-butanol (2-BuOH) and 2-butanone (2-BuO)

Fig. 8 shows the binary VLE data for the system of 2-BuO and 2-BuOH at 1000 mbar, with an average α of 1.9 at 1000 mbar. The xy-diagram as well as the Txy-diagram have the typical shape of those of an ideal mixture and the average α is not very low in this case. Because of this relative volatility, distillation is an intrinsically feasible process for this separation case, however the required energy input can still be significantly reduced when α could be increased to above 3 (Blahusjak et al., 2016). Therefore the application of extractive distillation is also potentially interesting in this case. The xy-diagram of the VLE data (Fig. 8a) measured in this study was compared with the data of Miller and Huang (1972) and Tanaka et al. (1992) that were not consistent with each other, although measured at almost equal pressure of 1 atm and 1000 mbar, respectively. The data in this study is in good agreement with the data of Tanaka et al. (1992). The differences with the work of Miller and Huang (1972) may be a result of the presence of impurities in their system that affect the relative volatility.

For this case there is a significant difference in functional groups as one of the components is an alcohol and one a ketone. Although the average α is already 1.9 for the case of 2-BuO–2-BuOH, partly induced by the relatively large ΔT, of approximately 20 °C, solvents were selected with the aim to further increase α, in which the effect of different types of solvents could be compared. In the mixture of 2-BuO and 2-BuOH, the activity coefficient of 2-BuOH is around 1 and that 2-BuO is larger than one 1 (Miller and Huang, 1972). Thus, a good solvent should increase the ratio of the activity coefficients of 2-BuO and 2-BuOH to improve α. This is achieved by making the interaction with the –OH group stronger or more probable and/or the interaction with the >C=O group weaker or less probable.

Because of the –OH group in the higher-boiling 2-BuOH, the solvent should have an attracting interaction with this OH group (hydrogen bond acceptor), therefore oxides (DMSO), alcohols (EG, PG, 1-octanol, glycerol), esters (methyl levulinate (MeLev)), ethers (diglyme, DME), acids (HBU) and ketones (5-methyl-2-hexanone, cyrene) were selected. Especially for the components with a larger functional group density a strong effect is expected, as for example in the case of the di-alcohol EG the probability of hydrogen bonding is increased compared to 2-BuOH itself, whereas for 1-octanol with a lower functional group density the probability is decreased. DMSO and HBU are expected to have strong effects as they are able to form stronger hydrogen bonds with their C=O group in comparison to the oxygen atoms in 2-BuO and 2-BuOH. The α-bond in aromatic rings creates a quadrupole that interacts with the dipoles of the alcohol and ketone groups. Since the dipole moment of 2-BuO larger than that of 2-BuO, a stronger interaction between the aromatic ring and 2-BuO is expected. Therefore p-xylene and ethylbenzene are predicted to show attractive interaction with 2-BuO and to be suitable as solvents a very strong difference in affinity is required in order to invert the relative volatility of the binary mixture and have 2-BuOH as the top stream (considering the relative volatility of the binary mixture) (Kossack et al., 2008).

The effect on the relative volatility of the systems was tested for all solvents in pseudo-binary VLE experiments of which the results are shown in Fig. 8c, except for the solvent
glycerol that appeared to be not fully miscible with the binary mixture. As expected based on the interaction with the aromatic ring, p-xylene and ethylbenzene decrease $\alpha$. However, the difference in solvent affinity with the mixture components is not large enough to allow for a top stream of 2-BuOH, a result of the interaction between the aromatic ring of the solvent and the alcohol group. A decreased $\alpha$ is also observed for MeLev, diglyme, DBE and 5-methyl-2-hexanone, which means their affinity towards 2-BuOH is not sufficiently larger than the affinity towards 2-BuO. For 1-octanol and HBu there is no or only a very small effect, indicating similar affinity with the mixture components. For 1-octanol this may be a result of the low functional group density. The interaction of HBu may be not specific enough because of the strongly interacting acid group. EG, PG and DMSO all increase $\alpha$, indicating their larger affinity for (hydrogen bond) interaction with 2-BuOH than with 2-BuO. VLE data over the whole range of compositions are required for a more detailed process design of extractive distillation. To further explore the solvent effect on the relative volatility of the mixture, the pseudo-binary xy-diagram was measured over the whole range of compositions for EG and DMSO, see Fig. 8d. Both solvents appear to be successful and EG is suggested as the best solvent because of price, availability and the larger effect on $\alpha$ compared to PG. Solvents were selected with their boiling points between 130–200 °C with the aim to ensure recoverability by having a boiling point difference of more than 30 °C with the mixture components. The recoverability of the solvent EG was investigated in the same way as for Case B and full recovery of EG is possible, as no solvent could be detected in the condensed vapor phase of the VLE measurements covering the range of (initial) EG volume fractions of 0.19–0.93. By optimizing the solvent-to-feed ratio an even further improvement of $\alpha$ can be expected compared to the $\alpha$ of approximately 3 that was obtained with EG at a volume based ratio of 1, although there is a limitation as a two phase system occurred in experiments with a 5:1 solvent-to-feed ratio. For the industrial process the stream of 2-BuO and 2-BuOH that requires purification will most likely not have an equimolar composition. For a more realistic feed stream with larger concentration of 2-BuO the effect of the extractive distillation process on the energy input of the process is expected to be smaller.

The results for this system indicate that improving $\alpha$ is possible based on difference in hydrogen bonding affinity of the solvent and mixture components. As the differences between the mixture components are larger for this system and also the binary VLE data show a moderate relative volatility, interactions with the solvent are required to be less strong. However,
another consequence is that the natural difference in volatility, i.e. 2-BuO being the most volatile component, should be taken into account in the solvent selection. Therefore attractive interactions with the least volatile component and/or repulsive interactions with the most volatile component are required.

3.3.1. Interaction between 2-BuOH and 2-BuO
As the interaction energy between the solvents that are selected for this separation case and the mixture components is relatively low compared to the acid-base interactions of the other cases, the mixing interaction of the two mixture components was measured with ITC instead of their interaction with a solvent. The heat of mixing of 2-BuOH and 2-BuO (Fig. 9), is relatively low and positive in sign, i.e. endothermic, which means that the energy of intermolecular interactions is similar for both compounds and the combination of compounds. This also implies that the components do not (strongly) attract each other and a successful solvent may be found based on moderate or even weak repulsion of 2-BuO or attraction of 2-BuOH. For very large mole fractions of either of the two components, the heat effects are more strongly endothermic.

4. Conclusion
Solvent effects on the relative volatility were measured for three different industrially relevant cases, that are separation of (a) diethylmethylamine and diisopropyylether ($\Delta T_{\text{boil}} = 3-5, \alpha_{\text{DEMA over Dipe}} = 1.05 \pm 0.028$ at 1000 mbar, $\alpha = 1.20 \pm 0.036$ at 300 mbar), (b) valeric acid and 2-methylbutyric acid ($\Delta T_{\text{boil}} = 10, \Delta P_{K_a} = 0.1, \alpha = 1.35 \pm 0.02$ at 300 mbar and $1.30 \pm 0.03$ at 900 mbar) and (c) 2-butanol and 2-butanone ($\Delta T_{\text{boil}} = 20, \alpha = 1.9$ at 1000 mbar). For each of the cases potential solvents were selected based on different aspects, including acidity/basicity, structural similarity, steric hindrance, polarity and predicted differences in hydrogen bonding affinity.

For DEMA-DPE, although $\Delta T_{\text{boil}}$ is very small, the difference in acidity and molecular structure of the components could be used to find suitable solvents. PhOH ($\sim 5$ at $S/F = 3$ and 300 mbar), cyclohexanol ($\alpha = 2$) and PG ($\alpha = 3.1$) each increase $\alpha$ of the binary mixture. For HVal–2MBA the solvent MeMeBu increased $\alpha$ ($\alpha = 1.84 \pm 0.18$ at 300 mbar), a solvent based on structural similarity with the mixture components. However, experiments at 900 mbar and thus higher temperature showed reactivity of the solvent in the form of transesterification. The difference of 0.1 in $p K_a$ in combination with the small $\Delta T_{\text{boil}}$ is too small to allow for separation using a moderately basic solvent, and applying a stronger basic solvent resulted in chemical instability. For this specific case crystallization would be a promising alternative process. For the case with 2-BuOH–2-BuO, $\Delta T_{\text{boil}}$ is relatively large and a difference in functional group allowed for separation through hydrogen bonding with the solvent. All successful solvents are hydrogen bond acceptors that show a larger affinity for 2-BuOH than for 2-BuO.

Generalizing, for mixtures of very similar components in terms of acidity, boiling point and structure, stronger interaction with the solvent is required (e.g. complex formation, proton transfer), which may be problematic in terms of chemical stability. Therefore, before applying a solvent in the actual pseudo-binary VLE measurements, the thermal and chemical stability with the mixture should be checked. For less similar components, weaker interactions with the solvent such as hydrogen bonding are sufficient to affect $\alpha$. Solvents should be selected for which specific attractive or repulsive interactions with the mixture components are expected, taking into account the extent of the natural difference in volatility of the mixture components. Knowing this, isothermal titration calorimetry (ITC) may be applied for initial solvent effect prediction based on measurement of excess enthalpy of mixing.

Acknowledgement
This is an ISPT (Institute for Sustainable Process Technology) project.

References