Influence of Solvent and Acid Properties on the Relative Volatility and Separation Selectivity for Extractive Distillation of Close-Boiling Acids

T. Brouwer, R. van Lin, A. J. B. ten Kate, B. Schuur,* and G. Bargeman*

ABSTRACT: The increasing need for sustainable processes stimulates the production and recovery of renewable organic acids. The purification of these acids is often difficult because of similar acid volatilities but can be improved through extractive distillation. Generic insights into solvent effects on the separation efficiency for close-boiling acids are however lacking. This study provides insights into the effect of acidity, the acidity difference between the acids, the hydrogen-bonding strength of the solvent, and the solvent-to-feed ratio on organic acid separation efficiency. For an acetic acid–formic acid (AA–FA) mixture, the addition of high-boiling organic acids increases the relative volatility of FA over AA significantly. The addition of a Lewis base reverses the relative volatility, which depends on the applied solvent-to-feed ratio and the Lewis base BF3 affinity. For several binary acid mixtures (such as AA–FA and monochloroacetic acid–dichloroacetic acid), where the acids have a relatively big difference in acidity (ΔpK_a ≥ 1), the separation selectivity appears practically independent of the acid strength of the individual acids and increases with increasing BF3 affinity of the Lewis base. For acid mixtures with a lower ΔpK_a, a lower separation selectivity is obtained, as observed for separation of the pivalic acid–butyric acid and valeric acid–2-methyl butyric acid mixtures. When one of the acids in the mixture contains a secondary ketone group (i.e., levulinic acid in a levulinic acid–octanoic acid mixture), the strongest acid based on pK_a is not necessarily attracting the added Lewis base. This, at first sight, unexpected behavior is most likely the result of complex intra- and intermolecular interactions and is quantitatively in line with COSMO-RS-based selectivity predictions.

1. INTRODUCTION

Sustainability and circular economy initiatives have an increasing impact on the chemical industry, especially on how this industry needs to develop and execute its production processes. In recent years, a clear shift from oil-based raw materials to chemical building blocks from renewable sources (sustainability)1 or from waste streams (circular economy)2 has occurred. This shift has among others resulted in a stronger focus on the production and separation of chemical building blocks with acid functionality, such as the volatile fatty acids acetic acid and butyric acid,1,4 and the lignocellulosic-based levulinic acid (LA).5,6 Sustainability strategies often imply that the required raw materials need to be separated from dilute solutions and/or from mixtures containing a variety of similar molecules. Separation of the target molecule from the solution at the required purity is therefore often difficult and expensive. An example of such a difficult purification is the separation of acetic acid (AA) from aqueous streams containing formic acid (FA). This separation seems to be feasible via the Lenzing process7 and the Wacker process,8 which consist of an extraction step using trioctylphosphine oxide (TOPO) and methyl tert-butyl ether (MTBE), respectively, followed by several distillation steps. Damesa et al.9 have evaluated several other solvents for the extraction step and found 2-methyltetrahydrofuran (2-MTHF) and tri-n-octylamine (TOA) in toluene to be very suitable extractants. Although some information about these Lenzing and Wacker processes can be found in patents, limited information about the separation steps, and especially about the distillation step to separate formic acid from acetic acid, is available in the open literature.

The separation of formic acid and acetic acid via distillation appears to be difficult since these molecules have similar boiling points, and the relative volatility is reported to be low (1.15–1.2).10–13 Separation of other organic acids shows
similar low relative volatilities, and it is therefore difficult to obtain pure individual acids via distillation for these cases as well. Examples are the separation of monochloroacetic acid (MCA) and dichloroacetic acid (DCA) with a relative volatility of 1.25,14 the separation of octanoic acid (OA) and levulinic acid (LA, also called 4-oxo pentanoic acid) with a relative volatility of 1.2,15 and the separation of 2-methyl butyric acid (2MBA) and valeric acid (VA) with a relative volatility of 1.30–1.35.16,17

Blahušiak et al.18 have shown that for mixtures with a relative volatility below 1.3, affinity separations appear to be proper alternatives for distillation, and even for relative volatilities between 1.3 and 3, the use of a solvent to increase the relative volatility is worth considering. Thus, one of the options to improve the separation efficiency for the organic acid separations mentioned earlier is extractive distillation, where a solvent or extractive agent is added to the acid mixture.10–17 This added solvent either needs to show preferential affinity for one of the molecules to be separated through, e.g., hydrogen-bonding or acid–base interaction, thus showing a negative deviation from Raoult’s law, or needs to preferentially repel one of the components more than the other, thus showing a positive deviation from Raoult’s law.16

For the improved separation of organic acids using extractive distillation, different approaches were reported in the open literature. For the separation of DCA from MCA,14 LA from OA,15 and VA from 2MBA,16,17 Lewis bases were considered as the solvent. The interaction between Lewis base solvents and the organic acids to be separated is based on a difference in hydrogen bonding between the Lewis base and the organic acids to be separated. For the MCA–DCA separation, the hydrogen-bonding capability of the solvents was characterized by their BF₃ affinity14 (which is a scale based on the complexation enthalpy of the solvent with the BF₃ Lewis acid, as outlined in more detail in ref 19), and it was shown that only solvents within a specific BF₃ affinity range were able to sufficiently improve the relative volatility during the extractive distillation step, while still allowing for proper recovery of the solvent in a subsequent distillation step. The feasibility of the use of Lewis base solvents to create higher relative volatilities for the MCA–DCA separation case is based on the difference in acidity between MCA and DCA, which is reflected by a difference in pK⁺ between the two acids of ΔpK⁺ ≥ 1.5.15,19 However, the use of Lewis base solvents for the separation of the other acid mixtures with ΔpK⁺ = 0.25–0.4 for OA and LA15,20,21 and ΔpK⁺ = 0–0.1 for 2MBA and VA15,16 appeared to be less successful. Based on the available information, we hypothesize that for mixtures with a relatively low ΔpK⁺, a relatively strong Lewis base and a relatively high solvent-to-feed ratio would be required to obtain a sufficiently high separation efficiency. For the improved separation of AA and FA with ΔpK⁺ = 1.0, other acids and nitro-containing aromatic and alkane molecules were used with some success, claiming a relative volatility of 1.7 at maximum.10–13 However, available information on this separation from these published patents10–13 is very limited, and results can hardly be validated from the information provided.

Despite the efforts to generate a more general knowledge base regarding the separation of close-boiling acid mixtures, efforts are still scattered. A better understanding of the effect of solvent characteristics, the acidity of the acids, and the difference in acidity between the acids to be separated on the change in relative volatility for close-boiling acid mixtures is needed. This study aims at making a start with creating better insight into the effect of Lewis base solvents on the separation efficiency for close-boiling organic acids as a function of the difference in pK⁺ between the acids to be separated, and at providing information on the effect of the solvent-to-feed ratio on the change in relative volatility for different organic acid mixtures. Furthermore, the effect of the addition of acid solvents on the separation of acetic acid from formic acid will be shown.

### 2. Materials and Methods

Various methods will be used to make the influence of solvent and acid properties on the relative volatility and separation selectivity for extractive distillation of close-boiling acids insightful. In the first sections, the solvent selection method (Sections 2.1 and 2.2) will be explained. Subsequently, the equipment and experimental procedures (Sections 2.3 and 2.4), which describe how each experiment was performed and analyzed, will be outlined. The mathematical formulation of the relative volatility and separation selectivity is defined in Section 2.5, and in Section 2.6, three simulation methods are introduced. These simulation methods allow detailed understanding of the obtained experimental results.

#### 2.1. Solvent Selection Method.

The scope of this study was limited to the solvents listed in Table 1. The basis for the selection of these solvents is explained below. For the separation of FA and AA, other acids were selected as potential solvents based on the work reported in patent literature10–13 and Lewis base solvents were selected to allow a comparison of the separation of these relatively weak acids with results reported by Jongmans et al.14 for the separation of the strong acids MCA and DCA. The boiling point of the selected solvents is at least 40–50 °C higher22 than that of the highest boiling acid in the mixture to be separated and should allow for thermal and chemical stabilities of the components during extractive distillation and the solvent recovery step. Similar to the study of Jongmans et al.14 solvents with a broad

<table>
<thead>
<tr>
<th>solvent</th>
<th>chemical formula</th>
<th>abbreviation</th>
<th>Tᵣ (°C)</th>
<th>BF₃ affinity (kJ/mol)b</th>
<th>pK⁺ (−)</th>
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<tr>
<td>sulfolane</td>
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<td>tetraethylene glycol di-methyl ether</td>
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<td>TGDE</td>
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<tr>
<td>n,n-diethyl-m-toluamide</td>
<td>C₈H₁₈NO</td>
<td>DEET</td>
<td>160</td>
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<td></td>
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<tr>
<td>trioctlyphosphine oxide</td>
<td>OP(C₅H₇)₃</td>
<td>TOPO</td>
<td>411</td>
<td>119.288</td>
<td></td>
</tr>
<tr>
<td>quinoline</td>
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<td>QN</td>
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</tr>
<tr>
<td>butyric acid</td>
<td>C₄H₈O₂</td>
<td>BA</td>
<td>163</td>
<td></td>
<td>4.83 at T = 25 °C²⁰</td>
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<tr>
<td>2-ethyl hexanoic acid</td>
<td>C₈H₁₆O₂</td>
<td>2EHA</td>
<td>209</td>
<td></td>
<td>4.82</td>
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</tbody>
</table>

“Assumed to be similar to triethylphosphine oxide. “Taken from refs 14, 19.
range of BF₃ affinities (between 50 and 130 kJ/mol) were used for the separation of FA and AA (see Table 1). The use of these solvents also allows the comparison of the obtained results with some results of earlier studies targeting the separation of OA and LA, and the separation of 2MBA and LA. Since the publicly available information for the separation of LA (a ketoacid) and OA is limited, experiments with the Lewis base trioctylphosphine oxide (TOPO) at different solvent-to-feed ratios have been conducted. This solvent with relatively high BF₃ affinity has been selected since the pKₐ difference between LA and OA is relatively small and we hypothesized that a relatively strong Lewis base would be needed to obtain sufficient separation efficiency for a mixture of acids with a relatively small ΔpKₐ. TOPO has also been used at different solvent-to-feed ratios for the separation of pivalic acid (PA) and butyric acid (BA), two other close-boiling acids with a ΔpKₐ similar to that for the LA–OA mixture and pKₐ values close to those for LA and OA. The main difference between these mixtures, next to their boiling point, is that the LA–OA mixture consists of two linear acids of which one acid (LA) contains a secondary ketone group, whereas the PA–BA mixture consists of a linear acid (BA) and a branched acid (PA) without any additional functional groups.

### 2.2. Chemicals

Formic acid (≥99%) was obtained from Fluka. Acetic acid (≥99%), tetraethylen glycol di-methyl ether (≥99%), methyl acetate (≥99%), sulfolane (≥99%), 2-ethyl hexanoic acid (≥99%), octanoic acid (≥98%), butyric acid (≥99%), pivalic acid (99%), and hydralan composite 5 were obtained from Sigma-Aldrich. Ethyl acetate (≥99%), sulfuric acid (98%), and n,n-diethyl-m-toluamide (≥99%) were obtained from Baker, and quinoline (≥96%), levulinic acid (≥98%), and TOPO (99%) were obtained from Acros Organics. The purities of the chemicals in weight percentages were provided by the suppliers. Demineralized water was obtained from a Millipore Milli-Q A10 water purification system. All chemicals were used without further purification.

Boiling temperatures and pKₐ values for the acids used and discussed (other than those used as solvents) are listed in Table 2.

### 2.3. Equipment and Experimental Procedure

Solutions of approximately 100 mL were prepared for the experiments. For the AA–FA mixture, acid molar ratios in the feed of 0.11 and 3.0 were used, leading to a molar fraction of FA in the feed solution of xₐFₐ = 0.90 and xₐFₐ = 0.25, respectively. For the OA–LA and PA–BA mixture experiments, molar ratios of 3.0 were used, leading to xₐLₐ = 0.25 and xₐBₐ = 0.25, respectively. For the OA–LA mixture, experiments at higher pressures were done using xₐLₐ = 0.12 and 0.05 to facilitate comparison with results from Sprakel et al. Vapor and liquid compositions under isobaric equilibrium conditions were obtained using a Fisher Scientific model Labodest VLE 602. The equilibrium vessel is a dynamic recirculating still, equipped with a Cottrel circulation pump. This pump stimulates the contact between the vapor and the liquid. The boiling liquid- and vapor-phase temperatures were measured using separate PT100 sensors. The evaporator duty and system pressure were kept constant using the i-Fischer [VLE]3 control unit. The pressure variation stayed within 0.05 kPa, while the equilibrium temperature was determined with an uncertainty of 0.1 K. Equilibrium was typically achieved within 45–60 min, when the equilibrium temperature and vapor condensation rate were both constant. Sampling was performed using the control unit operated actuator valves, collecting approximately 0.5–1.0 or 5 mL (depending on the analytical requirements) of both the liquid and condensed vapor phases.

Solvent-to-FA ratios of 0.5 or 2.0 (mole-based) were used for the AA–FA mixture for all solvents apart from TGDB, for which the solvent-to-FA ratio (mole-based) was varied between ratios of 0.5, 1.0, 2.0, and 4.0. For the acid solvents, the solvent-to-AA ratio (mole-based) was varied from 0 to 2.0 in 4 individual steps. To study the effect of pressure/temperature on the equilibrium vapor and liquid composition and consequently on the relative volatility, the AA–FA separation experiments were performed at pressures of 50, 25 kPa, and in individual cases, 10 kPa. Vacuum conditions were applied as FA is prone to decomposition at elevated temperatures. Several solvent-free experiments were performed to determine the binary relative volatility for AA/FA. For the OA–LA mixture, experiments were performed at 50, 20, and 2 kPa. The solvent (TOPO)-to-LA molar ratio for liquid feed samples provided to the VLE equipment was varied between 0 and 2.0. The pressure used for the PA–BA mixture experiments was 30 kPa. The solvent (TOPO)-to-BA molar ratios for liquid feed samples provided to the VLE equipment was varied between 0 and 2.5. In all cases, the Lewis base solvent-to-acid ratio was based on the strongest acid in the mixture (FA, LA, and BA, respectively), hypothesizing that the Lewis base would interact most strongly with the strongest acid in the solution as reported for the separation of the MCA–DCA mixture, and for the OA–LA mixture at 20 kPa. For the addition of high-boiling acids to the AA–FA mixture, the solvent-to-feed ratio was related to the AA mole fraction xₐFₐ, hypothesizing that the acids would interact most strongly with acetic acid based on patent information.

### 2.4. Sample Analyses

The samples from the FA–AA VLE experiments were added to a 15 mL vial (100 mg sample was weighed in) and diluted with 12 mL of water before being analyzed using high-pressure liquid chromatography (HPLC, Varian Prostar). A silica-based Grace Alltech organic acid column (300 mm × 7.8 mm) with a 5 μm particle size was used. The temperature was kept constant in an oven (Varian Prostar model 510) at 60 °C. The concentrations of FA and
AA were determined using a refractive index detector. The concentrations of the extractants were determined by means of a mass balance over the sample. The mobile phase was 0.01 N sulfuric acid in Milli-Q water at a volume flow rate of 0.5 mL/min. To validate whether FA decomposition occurred, all samples were analyzed for water content using Karl Fischer titration Metrohm 870KF Titrino Plus, equipped with the Metrohm 803TI Standard. Honeywell Hydralan Composite 5 was used as a titrant, and methanol was used as a solvent. Approximately 1 mL of sample was injected, and the added amount was determined using a Mettler AT460 Delta range. For the reported results, water formation during VLE was not encountered, meaning that decomposition of formic acid was not observed.

The samples from the OA–LA mixture experiments were analyzed using proton nuclear magnetic resonance (1H NMR) spectroscopy with a Bruker 400 MHz spectrometer. Samples were diluted in deuterated chloroform. The intensities of the characteristic signals of LA, OA, and TOPO at, respectively, 2.72, 2.21, and 0.88 ppm were used to determine the composition.

A Thermo Scientific Trace 1300 gas chromatograph with two parallel ovens and autosampler TriPlus 100 liquid sample was used for the analyses of the PA–BA mixture experiments. The samples were analyzed using an Agilent DB-WAX column (60 m × 0.25 mm × 0.25 μm) with an injection volume of 1 μL diluted in analytical ethanol. A ramped temperature profile was used, in which the initial temperature was 30 °C, followed by a ramp of 10 °C/min to 160 °C and kept at this temperature for 2 min. The second ramp was 1 °C/min to 180 °C, and the third ramp of 50 °C/min to 250 °C, which lasted 39 min, finished the program. A TCD detector was used at 270 °C. A column flow of 2 mL/min with a split ratio of 50, an airflow of 350 mL/min, a helium make-up flow of 40 mL/min, and a hydrogen flow of 35 mL/min was used.

2.5. Calculation Methods. The relative volatility of acid component i over acid component j (αi/j) can be described as a function of the activity coefficients, fugacity coefficients, and saturated vapor pressures for components i and j according to

\[
\alpha_{i/j} = \frac{y_i x_j}{x_i y_j} \frac{P_{i, \text{sat}}}{P_{j, \text{sat}}} \frac{q_{i, \text{vap}}}{q_{j, \text{vap}}} \approx 1
\]

with

\[
\frac{q_{i, \text{vap}}}{q_{j, \text{vap}}} \approx 1
\]

In the absence of a solvent, the relative volatility (αi/j, pseudo binary (with solvent)) can be determined directly from measured vapor and liquid fractions for the two components i and j. In the presence of the solvent, the relative volatility as defined in eq 1 is called a pseudo-binary relative volatility (αi/j, pseudo binary (with solvent)) due to the presence of the solvent in the ternary mixture. The pseudo-binary relative volatility can be determined directly from the measured vapor and liquid fractions for the two components i and j, neglecting the solvent fraction in the vapor and liquid fractions, which provides the same result for the pseudo-binary relative volatility. When the affinity of the added solvent to the most volatile acid of the mixture is stronger than the affinity to the least volatile acid in the mixture, the relative volatility may change from a value higher than 1 to a value lower than 1 (or the other way around). The effect of the solvent on the (relative change in) relative volatility can then be determined from the solvent selectivity Sji. This value represents the ratio of the (pseudo-binary) relative volatility in the presence of the solvent over the relative volatility in the absence of the solvent as defined by eq 3

\[
S_{i/j} = \frac{\alpha_{i/j, \text{pseudo binary (with solvent)}}}{\alpha_{i/j, \text{binary (without solvent)}}}
\]

where j is the most acidic component and i is the least acidic component in the binary mixture without the presence of solvent.

2.6. Simulation Methods. 2.6.1. Validation of Experimental Results Using Aspen Modeling. AspenPlus version 9.0 modeling using NISTV90 NIST-HOC was used to check experimental vapor–liquid equilibria results for FA–AA separation in the absence of solvent at pressures of 25, 50, and 100 kPa. This parameterization includes the NIST database and used the Hayden-O’Connell equation of state to include associative behavior. AspenPlus version 10.0 using the modified UNIFAC (Dortmund) was used to validate experimental binary vapor–liquid equilibria results for OA–LA separation in the absence of a solvent at a pressure of 2 kPa. It should be noted that the use of the different AspenPlus versions does not change the mathematical framework of the calculations performed. Furthermore, binary interaction parameters standardly available in AspenPlus have been used to generate the modeling results and consequently, binary interaction parameters have not been fitted based upon experimental results.

2.6.2. SPARTAN Modeling. The interaction energy between the acids and TOPO, and the dimerization interaction energy were estimated quantum mechanically with SPARTAN ‘18 by Wavefunction, Inc. The ground state of two, later specified, molecules in a polar solvent was calculated with density functional theory (DFT) with the ωB97X-D 6-311+G** method, while a dielectric continuum with a relative permittivity of 37.22 was applied to simulate intermediate polar conditions. An energy profile was created as a function of the intermolecular distance between the basic oxygen of TOPO, LA, or OA and the acidic proton on either OA or LA, or the carbonyl group of LA. The intermolecular distance was varied between 15 and 0.5 Å with a step count of 100. The results were normalized to the case of 15 Å intermolecular distance, and each simulation was performed five times, each with different starting geometries, to avoid ending up in a local minimum instead of a general minimum interaction energy.

2.6.3. COSMO-RS Modeling. COSMO-RS, which stands for CoUnctor like Screening MOdel for Real Solvents, is a software package developed by Klamt. The model uses a combination of statistical thermodynamics and quantum chemistry to predict the chemical potential of compounds and solution thereof. This allows for fast screening of among others phase equilibria. The (pseudo-)binary relative volatility based on vapor–liquid equilibria (VLE) for the LA–OA–TOPO system was estimated in COSMOTHERM X v17.0 C30_1705 with the triple-ζ valence polarized (TZVP) basis set. OA was already present in the COSMO-RS database, whereas LA and TOPO were calculated via the density functional theory (DFT) with a Becke–Perdew (BP86) functional set and the TZVP basis set in TurboMoleX 16.0.
and later optimized in COSMOconf 4.0 using the same functional and basis set. All conformers obtained from the modeling were used in the prediction of the relative volatilities, unless specifically mentioned in the results. The relative volatilities for LA–OA have been determined based on the activity coefficients obtained from COSMO-RS modeling and saturated vapor pressures obtained from the well-known Antoine equation

\[
 \log_{10}\left(\frac{P}{10^5}\right) = A - \frac{B}{(C + T)}
\]

The Antoine coefficients A, B, and C for LA\(^{28}\) and OA\(^{29}\) as listed in Table 3 have been obtained from the NIST database.\(^{30}\)

**Table 3. Antoine Coefficients for Levulinic Acid\(^{28}\) and Octanoic Acid\(^{29}\) Obtained from the NIST Database\(^{30}\)**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>levulinic acid (LA)</td>
<td>6.63219</td>
<td>3152.908</td>
<td>-43.564</td>
</tr>
<tr>
<td>octanoic acid (OA)</td>
<td>4.25235</td>
<td>1530.446</td>
<td>-150.12</td>
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</table>

3. RESULTS AND DISCUSSION

3.1. Separation of Formic Acid (FA) and Acetic Acid (AA). Relative volatilities (\(\alpha_{FA/AA}\)) for the separation of a binary FA–AA mixture have been measured at compositions with a formic acid mole fraction in the liquid phase of \(x_{FA} = 0.25\) and 0.9, and are compared with AspenPlus simulations as well as with the data reported by Berg\(^{13}\) in Figure 1. This figure shows that the measured relative volatilities at \(x_{FA} = 0.25\) are larger than 1.5 for applied pressures of 50 and 25 kPa, whereas the relative volatility drops to around 1.3 for \(x_{FA} = 0.9\). As expected, the use of a lower pressure leads to a slightly higher relative volatility \(\alpha_{FA/AA}\). The measured relative volatilities are in line with the \(\alpha_{FA/AA}\) values predicted by the AspenPlus simulations (see Figure 1), albeit that experimental relative volatilities appear to be marginally lower than the results obtained from AspenPlus modeling. Comparison of our results with the relative volatility reported by Berg\(^{13}\) at atmospheric pressure is difficult since the exact composition of the liquid for which this relative volatility was reported is not disclosed. Based on the triplicate measurements, for which the error bars are displayed in Figure 1, we have determined the accuracy in composition to be \(+/- 2\%\) relative to the measured composition, which is well in line with earlier studies in our laboratories.\(^{14-17}\)

Since ebulliometry is very time-consuming and labor-intensive, it was decided to do all other measurements just once, and it is assumed that there also the error is \(+/- 2\%\) relative to the measured composition.

The addition of an acid solvent increases the (pseudo-binary) relative volatility for FA over AA (see Figure 2 left), in line with reported claims of Berg.\(^{13}\) The slight increase leads to a (pseudo-binary) relative volatility for formic acid over acetic acid of 1.9 for the addition of butyric acid and of 2.1 for the addition of 2-ethyl hexanoic acid at maximum and depends on the solvent-to-acetic acid ratio applied. Berg\(^{13}\) reported a lower (pseudo-binary) relative volatility of 1.54 for the addition of 2EHA but showed results at a higher pressure (100 kPa), a lower mole fraction of FA in the liquid phase, and a solvent-to-FA ratio of only 0.32.\(^{13}\) Although 2EHA and BA have a similar \(pK_a\), the more hydrophobic 2EHA seems to have a slightly stronger effect on the change in relative volatility than the smaller and less hydrophobic BA. An increase in pressure from 25 to 50 kPa only has a minor effect on the obtained relative volatility (see Figure 2), which slightly decreases at a higher pressure, as expected. Furthermore, a higher solvent-to-acetic acid molar ratio in the feed (\(x_{FA}/x_{AA}\)) supplied to the VLE unit leads to an increase in \(\alpha_{FA/AA}\). This increase levels off at a higher \(x_{FA}/x_{AA}\) value.

The addition of a Lewis base solvent reduces the (pseudo-binary) relative volatility \(\alpha_{FA/AA}\) and consequently increases \(\alpha_{AA/FA}\) (see Figure 2 right). An increase in pressure from 25 to 50 kPa has a negligible effect on the obtained \(\alpha_{FA/FA}\) as illustrated for quinoline (QN) and tetraethylglycol dimethyl ether (TGDE; see Figure 2, right). The increase in \(\alpha_{FA/FA}\) is more pronounced when the molar-based solvent-to-formic acid ratio \(x_{SF}/x_{FA}\) increases from 0 to 2 and seems to level off beyond \(x_{SF}/x_{FA} = 2\), at least for the use of TGDE (see Figure 2, right). Values of \(x_{SF}/x_{FA}\) > 1 are obtained for all Lewis base solvents (starting from \(x_{AA}/x_{FA} = 0.62\) for a situation without solvent) apart from sulfolane, provided that \(x_{SF}/x_{FA} = 2\) is used. This indicates that the use of specific Lewis base solvents can revert the relative volatility and can produce a pure acetic acid top product in an extractive distillation process using a sufficiently strong high-boiling Lewis base. For the use of QN, a (reversed) pseudo-binary relative volatility for acetic acid over formic acid as high as \(\alpha_{AA/FA} = 1.63\) has been obtained. The addition of another (less strong) Lewis base led to a lower \(\alpha_{AA/FA}\). Consequently, the addition of a solvent to a formic acid–acetic acid mixture at \(x_{FA} = 0.25\) can reverse the volatility order, but it hardly improves the separation efficiency between formic acid and acetic acid compared to a situation where no solvent at all is used.

In general, the use of a stronger Lewis base (having a higher \(BF_3\) affinity) seems to lead to a stronger reduction in \(\alpha_{FA/AA}\) or a stronger increase in \(\alpha_{AA/FA}\) as concluded from Figure 3, where the selectivity \(S_{AA/FA}\) is shown as a function of the \(BF_3\) affinity for different solvent-to-FA ratios \(x_{SF}/x_{FA}\).

This observed behavior can be explained by the fact that formic acid is the most volatile of the two acids, but at the same time the strongest acid, therefore showing a stronger affinity for the Lewis base than acetic acid. It also means that a stronger Lewis base has a higher complexation constant for formic acid relative to acetic acid than a less strong Lewis base.
and therefore induces a larger change in relative volatility at a specific solvent-to-acidic acid ratio.

### 3.2. Separation of Levulinic Acid and Octanoic Acid and of Pivalic Acid and Butyric Acid

Although Sprakel et al.\textsuperscript{16} reported results at 50 and 20 kPa, in this study, only for experiments at 2 kPa, boiling temperatures were sufficiently low to avoid chemical/decomposition reactions. Vapor–liquid equilibria at higher pressures (20 and 50 kPa) with boiling temperatures in excess of 183 °C could not be determined as a result of the chemical instability of the system. The vapor–liquid equilibrium for OA and LA with $x_{LA} = 0.25$ obtained at $P = 2$ kPa is in line with model predictions based on modified UNIFAC (Do) as shown in Figure 4.

The relative volatility ($\alpha_{OA/LA}$) for the separation of the OA–LA mixture at $x_{OA}/x_{LA} = 3.0$ is 1.3 at a pressure of $P = 2$ kPa (see Figure 5, left). The addition of TOPO as a solvent to improve the separation between OA and LA at $P = 2$ kPa and increasing the mole-based TOPO/LA ratio $x_{TOPO}/x_{LA}$ from 0 to 1.9 resulted in a decrease in the relative volatility $\alpha_{OA/LA}$ from 1.3 to 0.9 (see Figure 5, left) and thus a decrease in selectivity $S_{OA/LA}$ from 1 to 0.73 in this $x_{TOPO}/x_{LA}$ range (see Figure 5, right). The vapor–liquid equilibrium at a higher mole-based $x_{TOPO}/x_{LA}$ ratio of 2.8 could not be obtained due to the occurrence of a chemical reaction.

The observed reduction in $\alpha_{OA/LA}$ due to the addition of TOPO to the LA–OA mixture implies that the volatility of OA was reduced to a larger extent than the volatility of LA, even though LA has a lower pKₐ than OA. Since LA is therefore the stronger acid of the two (at least in water), the effect of the addition of TOPO seems unexpected. Since LA is a molecule with dual functionality (next to the acid functionality this ketoacid also contains a ketone group), the reduction of the relative volatility may be the result of multiple, competing interactions. To obtain insight into the possible interactions, various computer simulations were performed using SPAR-TAN and COSMO-RS.

The results of SPAR-TAN modeling using intermediate polar conditions ($\varepsilon = 37.22$) confirm that the OA–LA mixture is a complex mixture in which several molecular interactions are possible (see Figure 6). Dimerization interactions (hetero and homo) between the acids groups of OA–OA ($–20 \pm 0.5$ kJ/mol), OA–LA ($–19 \pm 2.0$ kJ/mol), and LA–LA ($–30 \pm 3.9$ kJ/mol), between the ketone group of LA and the acid group of OA ($–30 \pm 2.6$ kJ/mol) or LA ($–26 \pm 1.4$ kJ/mol), and between the ketone groups of LA–LA ($–23 \pm 2.5$ kJ/mol) are observed. The observed energy order for the LA–LA acid–acid interaction, LA–LA acid–ketone interaction, and the LA–LA ketone–ketone interaction is in line with Monte Carlo simulation results of Chakraborti et al.\textsuperscript{31} Furthermore, LA can stabilize its molecular conformation via an intramolecular hydrogen bond ($–18 \pm 0.0$ kJ/mol). In the presence of TOPO, the molecular interaction of TOPO with LA appears to be the strongest molecular interaction in the system ($–51 \pm 4.6$ kJ/mol) followed by the TOPO–OA interaction ($–44 \pm 0.2$ kJ/mol). Although insights into these interaction energies can assist in the interpretation of the observed VLE behavior, it should be realized that the reported energies are based on
relatively simple bimolecular energy levels in a dielectric continuum, and real mixtures include complex multimolecular enthalpic contributions, e.g., through hydrogen bonding of multiple molecules. In addition, VLE behavior is also affected by entropic contributions. Therefore, the main value of these SPARTAN modeling results is the confirmation of the complexity of this mixture and the improved insights into the possible interactions occurring in the mixture.

COSMO-RS modeling revealed that due to conformational flexibility, OA exists in 6 clusters conformations with similar energies and sigma profiles (conformers in short) and TOPO exists in 11 conformers, while LA exists in 7 conformers, of which 1 displays the intramolecular hydrogen-bond interaction between the ketone and the acid group as also concluded from the SPARTAN modeling. The pseudo-binary relative volatility based on the experimental VLE results using TOPO as a solvent and COSMO-RS modeling results obtained for three cases (LA with intramolecular hydrogen bonding, a statistical Boltzmann distribution over all the LA conformers apart from LA with intramolecular hydrogen bonding and a statistical Boltzmann distribution over all LA conformers) can be seen in Figure 7. The obtained quantitative relations between the relative volatility and the $x_{\text{TOPO}}/x_{\text{LA}}$ ratio depend on the conformers included in the modeling, but show a similar quantitative trend (see Figure 7). The modeling results all indicate a reduction in relative volatility $\alpha_{\text{OA/LA}}$ with increasing $x_{\text{TOPO}}/x_{\text{LA}}$ ratio and are thus quantitatively in line with the results obtained from the VLE experiments and therefore confirm the experimentally observed effect of TOPO on the relative volatility for this mixture.

The relative volatility ($\alpha_{\text{PA/BA}}$) for the separation of the PA–BA mixture at $x_{\text{PA}}/x_{\text{BA}} = 3.0$ is 0.99 for a pressure of $P = 30$ kPa (see Figure 5, left), in line with expectations based on their practically equal boiling temperature (which is 0.5 °C higher

![Figure 5](image_url)

**Figure 5.** (Pseudo-binary) relative volatility $\alpha_{\text{OA/LA}}$ and $\alpha_{\text{PA/BA}}$ as a function of $x_{\text{TOPO}}/x_{\text{LA}}$ (at $P = 2$ kPa and $x_{\text{LA}} = 0.25$), respectively (left) and the selectivity $S_{\text{OA/LA}}$ and $S_{\text{PA/BA}}$ as a function of $x_{\text{TOPO}}/x_{\text{LA}}$ (at $P = 2$ kPa and $x_{\text{OA}}/x_{\text{LA}} = 3.0$) or $x_{\text{TOPO}}/x_{\text{BA}}$ (at $P = 30$ kPa and $x_{\text{PA}}/x_{\text{BA}} = 3.0$), respectively (right). The represented lines are trend lines.

![Figure 6](image_url)

**Figure 6.** Molecular interactions in the LA (black)—OA (red)—TOPO (blue) system.
for PA; see Table 2). The addition of TOPO to the mixture leads to an increase (gradual at first) of the relative volatility to \( \alpha_{\text{PA/BA}} = 1.2 \) at \( \alpha_{\text{TOPO/LA}} = 2.0 \). Since the relative volatility without the presence of TOPO is close to 1, the selectivity at this TOPO-to-BA ratio in the feed has practically the same value (\( S_{\text{PA/BA}} = 1.2 \); see Figure 5, right). The effect of the addition of TOPO on \( \alpha_{\text{PA/BA}} \) (and thus \( S_{\text{PA/BA}} \)) is in line with expectation based on the \( \alpha \) values of the acids (4.83 for BA and 5.03 for PA; see Table 2), BA thus being the slightly stronger acid.

### 3.3. Comparison of the Effect of the Addition of Lewis Bases for Different Close-Bubbling Acids

For the separation of acetic acid and formic acid, having a difference in \( \alpha \) of \( \Delta \alpha_{\text{K}} = 1.0 \) (3.75 for FA and 4.76 for AA, see Table 2), the effect of the addition of a Lewis base solvent with a specific BF3 affinity on the selectivity (\( S_{\text{FA/FA}} \)) is practically the same as the effect of the same solvent on the selectivity (\( S_{\text{FA/FA}} \)) for the separation of monochloroacetic acid and dichloroacetic acid, with a difference in \( \alpha \) of 1.5, as shown in Figure 8 (left) for a solvent-to-strongest acid molar ratio of \( x_{\text{LA}}/x_{\text{FA}} = x_{\text{AA}}/x_{\text{FA}} = 0.5 \) and in Figure 8 (middle) for a solvent-to-strongest acid molar ratio in the feed of \( x_{\text{LA}}/x_{\text{FA}} = x_{\text{AA}}/x_{\text{DCA}} = 1.0 \). For the separation of the pivalic acid–butyric acid mixture and the valeric–2-methyl butyric acid mixture, all relatively weak acids with a smaller difference in acidity than acetic acid and formic acid (\( \Delta \alpha \approx 0.25 \) for OA–LA and \( \Delta \alpha \approx 0.03 \) for LA–2MBA versus \( \Delta \alpha = 1.0 \) for AA–FA), addition of Lewis bases could hardly improve the separation, as illustrated by a selectivity of \( S_{ij} \approx 1 \) for these systems (see Figure 8). Especially for the latter case, this is in line with expectations, since acid–base interactions or hydrogen-bonding interactions for the added solvent are expected to be similar for these acids with similar acidity. For the pivalic acid–butyric acid mixture, the increase in the solvent-to-butyric acid ratio to 2 leads to a slightly higher selectivity as mentioned earlier; however, the selectivity is still substantially lower than that obtained for the separation of acetic acid from formic acid for a Lewis base with the same BF3 affinity (see Figure 8, right). Consequently, based on the results obtained, it seems that, like for the separation of MCA and DCA, the use of Lewis bases affects the separation efficiency for the separation of two weaker acids as well, provided that these weaker acids show sufficient difference in \( \alpha \). Based on the current results, quantification of the required difference in \( \alpha \) is not possible, but the required difference appears to be between 0.2 and 1.0. Furthermore, the difference in \( \alpha \) seems to be more important for the separation efficiency than the acidity of the individual organic acids. The results presented in Figure 8 are summarized in Table 4, based on which individual solvents shown in Figure 8 can be identified.

### 3.4. Solvent Recovery

The focus of our work has been to study the effect of different solvents on the separation selectivity of two close-boiling acids, and the generated results provide first insights into the selection of a suitable solvent for an extractive distillation process. The recovery of the solvent in such a process, although very important for the feasibility of the process, has not been studied in detail. The solvents applied were selected based on the criterion that the boiling temperature of the solvent was more than 40–50 \(^\circ\)C higher than the boiling temperatures of the acids to be separated, as mentioned in the Materials and Methods section. Therefore, the recovery of the solvents applied should not be an issue, provided that the components in the regeneration step remain chemically stable and the interaction between the acid and the solvent is not too strong. Before any of the described solvents would be advised for application in an extractive distillation process, a more in-depth study on the recovery of the solvent would be advised.

### 4. CONCLUSIONS

The effect of the addition of a solvent to a binary mixture of close-boiling organic acids on their relative volatility and separation selectivity has been investigated to evaluate the potential of extractive distillation as a separation step for close-boiling organic acids. For the separation of formic acid and
Table 4. Overview of the Obtained Selectivities for Organic Acid Mixtures and Solvents Used

<table>
<thead>
<tr>
<th>organic acid mixture ( i/j )</th>
<th>( \Delta \text{pK}_a ) (( i/j ))</th>
<th>solvent used</th>
<th>BF₃ affinity (kJ/mol)</th>
<th>selectivity ( S_{ij} ) (( \cdot ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>for solvent-to-strongest acid molar ratio of ( x_i/x_j = 0.5 )</td>
<td></td>
<td>for solvent-to-strongest acid molar ratio of ( x_i/x_j = 1.0 )</td>
</tr>
</tbody>
</table>

**MCA/DCA**¹⁴

| | | Sulfolane (SF) | 51.32 | 1.13 | 1.25 |
| | | Succinonitrile (SN) | 60.39 | 1.02 | 1.08 |
| | | Dihexylketone (DHK) | 70.7 | 1.24 | 1.46 |
| | | Tetraethylene glycol dimethyl ether (TGDE) | 78.57 | 1.46 | 1.84 |
| | | Diethyleneglycol dipentylether (DGDP) | 78.57 | 1.38 | 1.71 |
| | | Diethyleneglycol dibutylyether (DGDB) | 78.57 | 1.37 | 1.74 |
| | | Dihexylether (DHE) | 78.57 | 1.28 | 1.57 |
| | | Tri-n-butylphosphate (TBP) | 84.75 | 1.37 | 1.74 |
| | | n-n-Diethyl-m-toluamide (DEET) | 101.75 | 1.37 | 1.78 |
| | | Tri-n-octylphosphate oxide (TOPO) | 119.28 | 1.54 | 2.10 |
| | | Tri-n-hexylamine (THA) | 135.87 | 2.25 | 3.93 |

**AA/FA**¹⁰

| | | Sulfolane (SF) | 51.32 | 1.20 | 1.49 |
| | | Tetraethylene glycol dimethyl ether (TGDE) | 78.57 | 1.46 | 1.64 |
| | | n-n-Diethyl-m-toluamide (DEET) | 101.75 | 1.31 | 1.95 |
| | | Quinoline (QN) | 128.08 | 2.30 | 2.55 |

**PA/BA** ⁰²

| | | Tri-n-octylphosphate oxide (TOPO) | 119.28 | 1.02 | 1.03 |

**VA/2MBA**²⁰⁶,²¹⁷

| | | Diethyleneglycol dibutylyether (DGDB) | 78.57 | 0.98 | 0.98 |
| | | Tri-n-butylphosphate (TBP) | 84.75 | 0.98 | 0.98 |

¹⁴Taken from refs 14, 19.
acetic acid, the addition of a high-boiling organic acid improves the relative volatility and separation selectivity of formic acid over acetic acid, in line with available patent information. An increase in the solvent-to-acetic acid mole fraction ratio leads to an increase in relative volatility and separation selectivity. This increase seems to level off from a solvent-to-acetic acid mole fraction ratio of 1 onward. The addition of a Lewis base leads to reversal of the relative volatility in this case, as expected based on the acidity of both acids. However, unlike the addition of high-boiling acids, the addition of Lewis bases does not result in a significantly improved separation between acetic acid and formic acid, since the relative volatility of acetic acid over formic acid due to the presence of the Lewis base is similar to the relative volatility of formic acid over acetic acid without the presence of a solvent.

The addition of a Lewis base to close-boiling organic acid mixtures affects the relative volatility and the separation selectivity significantly, provided that the difference in $pK_a$ is sufficiently high (approximately 1 or higher), practically independent of the acid strength of the acids to be separated. This is indicated by similar separation selectivities for the separation of the relatively weak acids formic acid and acetic acid compared to the much stronger acids monochloroacetic acid and dichloroacetic acid. The effect on the relative volatility and separation selectivity is caused by a difference in hydrogen-bonding interaction between the Lewis base and the two acids to be separated. The effect of the Lewis base is stronger when the Lewis base has a higher $B_F$ affinity, an indication of its hydrogen-bonding strength, and with an increased solvent-to-acid molar ratio. When the difference in $pK_a$ between the organic acids to be separated is relatively low, the effect of the Lewis base on the relative volatility and separation selectivity is less, as found for the separation of pivalic acid–butyric acid and valeric acid–2-methyl butyric acid binary mixtures. For the octanoic acid–levulinic acid binary mixture, the presence of the ketoacid (levulinic acid), an organic acid having a ketone functional group, has a clear impact on the effect of a Lewis base trioctylphosphine oxide (TOPO) on the separation. Although levulinic acid appears to be a stronger acid than octanoic acid based on their $pK_a$, the addition of TOPO leads to a reduction of the relative volatility of octanoic acid over levulinic acid. This obtained experimental result is qualitatively in line with COSMO-RS predictions, probably due to many hydrogen-bonding and association interactions between the acids and ketone functional groups present in the complex matrix. A more generalized conclusion regarding the effect of the presence of a ketone functional group in one of the acids would require more experimental results for different organic acid–ketocacid mixtures.

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**NOMENCLATURE**

**Symbols**

$P^{sat}$ saturated vapor pressure (Pa)

$S_{i,j}$ selectivity (defined as the ratio of pseudo-binary relative volatility over binary relative volatility in eq\(^1\))

$T$ temperature (K/oC)

$x_i$ mole fraction in the liquid phase for component $i$ in feed solution

$x_{i,j}$ mole fraction in the liquid phase for component $j$ in feed solution

$y_j$ mole fraction in the vapor phase for component $j$

$a_{i,j}$ relative volatility for component $i$ over component $j$

$q_{i,j}$ activity coefficient for component $j$

$\varepsilon$ dielectric constant

$\phi_{j,vap}$ fugacity coefficient for component $j$ in vapor phase

**Abbreviations Used**

AA acetic acid

BA butyric acid

DCA dichloroacetic acid

DEET $n,n$diethyl-m-toluamide

2EHA 2-ethyl hexanoic acid

FA formic acid

LA levulinic acid

MCA monochloroacetic acid

2MBA 2-methyl butyric acid

OA octanoic acid

PA pivalic acid

QN quinoline

S solvent

SF sulfolane

TGDE tetraethylene glycol di-methyl ether

TOPO trioctylphosphine oxide

VA valeric acid

**REFERENCES**


