

# Development of Extractive Distillation Processes for Close-Boiling Polar Systems

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Extractive distillation is a distillation technique that can be applied for separation of azeotropic mixtures and mixtures of close-boiling compounds. In extractive distillation a solvent is applied to increase the relative volatility by interacting with the components in the system, typically with a difference in affinity for the components. To study the relation between the affinity strength and the effect of the solvent on the relative volatility, the research here presented focused on a solvent selection for the separation of two close-boiling, highly polar binary systems. 1) The acids valeric acid and its isomer 2-methylbutyric acid ( $\Delta T_{boil} = 10^\circ\text{C}$ ,  $\Delta pK_a = 0.1$ ), and 2) the bases diethyl methylamine and diisopropylether ( $\Delta T_{boil} = 3 - 6^\circ\text{C}$ ,  $\Delta pK_b \approx 14$ ). For both the acids and the bases the binary VLE-data and ternary data with solvents were measured using an ebulliometer. The solvents resulted in negative deviations of Raoult's law. The solvent selection was performed based on literature, followed by an experimental evaluation of the possible solvent types. For the valeric acid mixture the solvent 2-methylbutyrate, which is similar in structure to the components in the mixture, appeared to be most promising. In the ether-amine mixture a series of hydrogen bonding solvents with a hydroxyl group were found most promising, and also the regeneration of the solvent was an important factor in the study.

## 1. Introduction

Distillation is the most important and most often applied method of separation of liquid mixtures. (Kockmann, 2014) The method of distillation is based on a sufficient difference of boiling point of the two components that need to be separated. Despite the wide variety of applications, distillation may be difficult or even impossible to apply in traditional approach due to azeotrope formation or a relative volatility of the components that is close to unity. This is often the case in the separation of close-boiling mixtures. (Doherty, Knapp, 2000) In the case of azeotropic mixtures, extractive distillation is widely applied. (Gracsová, 2015) Already in 1945, research was performed on the topic of extractive distillation. (Kockmann, 2014) Extractive distillation uses a solvent that is fed to the column and interacts with the mixture to be separated. In a second column the solvent is regenerated. The solvent typically has a preferred affinity for one of the components, thereby changing the relative volatility of the mixture, and possibly 'break' an azeotrope. Extractive distillation may be more economical than normal distillation processes for difficult mixtures, because the energy demand may be reduced. (Doherty, Knapp, 2000) Extractive distillation is for example applied to separate ethanol-water using ethylene glycol as an entrainer, (Kiss et al., 2013) or using ionic liquids as entrainers. (Kulujanpeng et al., 2014)

The choice of solvent is crucial for a successful extractive distillation process. Not only should the solvent enable successful separation of the mixture, the solvent should also be chemically and thermally stable. (Kockmann, 2014) Furthermore, it should be possible to regenerate the solvent so it can be recycled to the process. (Jongmans et al., 2012) Jongmans et al. (2012) studied the extractive distillation of the binary mixture of monochloroacetic acid and the more acidic dichloroacetic acid (boiling point difference,  $\Delta T_{boil}$ , of  $5^\circ\text{C}$ , and a difference in  $pK_a$  of 1.6). Solvents resulting in the strongest increase in relative volatility due to initiating a strong negative deviation from Raoult's law appeared to be too difficult to regenerate, more moderately strong solvents were better regenerable.

The focus of this work was to find appropriate solvents that have enough affinity to increase the relative volatility, and are still regenerable for the separation of two close-boiling mixtures, i.e. valeric acid (HVal) and its isomer 2-methylbutyric acid (2-meHBu) ( $\Delta T_{boil} = 10^\circ\text{C}$ ,  $\Delta pK_a = 0.1$ ) and b) diisopropylether (DIPE) and N,N-diethylmethyl amine (DEMA) ( $\Delta T_{boil} = 3 - 6^\circ\text{C}$ ,  $\Delta pK_b \approx 14$ ). A solvent screening was performed after which the effect on the vapour-liquid-equilibria was investigated for the most promising solvents.

## 2. Materials & Methods

### 2.1 Chemicals

Chemicals were obtained from Sigma-Aldrich, unless mentioned otherwise, i.e. diisopropylether ( $\geq 99\%$ , DIPE), N,N-diethylmethylamine ( $\geq 98\%$ , Acros Organics and TCI-GR, DEMA), valeric acid ( $\geq 99\%$ , HVal), isovaleric acid (99%, isoHVal) 2-methylbutyric acid ( $\geq 98\%$ , 2MBA), acetic acid ( $\geq 99.5\%$ ), oleic acid ( $\geq 99.5\%$ , Fischer Scientific), ethylene glycol ( $\geq 99.8\%$ ), 1,2-propane diol ( $\geq 99\%$ ), diethylene glycol ( $\leq 100\%$ , Merck KGaA), diethylene glycol dimethyl ether ( $\geq 99.5\%$ ), phenol ( $\geq 99.5\%$ ), m-cresol ( $\geq 98\%$ ), cyclohexanol ( $\geq 99\%$ ), dibutylamine ( $\geq 99.5\%$ ), 2,2,4-trimethylpentane ( $\geq 99.5\%$ ), dibutylether ( $\geq 99.3\%$ ), 18-crown-6 (TCI-GR), beta-cyclodextrin ( $\geq 98\%$ , Acros Organics), diethylene glycol dibutyl ether ( $\geq 99\%$ , Sigma-Aldrich), dodecane ( $\geq 99\%$ ), itaconic acid ( $\geq 99\%$ ), methyl-2-methylbutyrate ( $\geq 98\%$ ), octanoic acid ( $\geq 98\%$ ), 1-octanol ( $\geq 99\%$ ), 1,8-bis(dimethylamino)naphthalene (Proton Sponge®, 99%), tribenzylamine ( $\geq 99\%$ ), tributylphosphate (99+%), trioctylamine (98%) Acetone Lichrosolv® ( $\geq 99.8$ , Merck KGaA), methyl isobutyl ketone ( $\geq 99.7\%$ , Sigma-Aldrich), and n-heptane anhydrous (99+%, Alfa Aesar) were used for analysis.

### 2.2 Procedure VLE experiments

Experiments were performed in two Fischer Labodest VLE602 ebulliometers, having both the same principle of operation. In the ebulliometer an equilibrium cell in which a magnetic stirrer is present is connected to a Cottrell circulation pump and coupled to an immersion heater. The experimental setup can be used under vacuum conditions, for which it is connected to an Edwards E2M1.5 vacuum pump or Pfeiffer DUO 3 vacuum pump. The operating pressure, the power supplied to the reboiler and the temperature of the heating mantle can be controlled. The temperature of the liquid in the reboiler and the equilibrium temperature were measured using Pt-100 thermocouples. One of the ebulliometers is also equipped with an ILUDEST® control unit by which measurement data can be recorded.

VLE data were measured for a set of mixtures of the compounds of interest with varying concentrations to obtain VLE data over the whole composition range. For each experiment the equilibrium cell was filled with 80 mL of the mixture of components of interest. The pressure was set and the mantle temperature was adjusted. After 30-90 minutes, depending on the system, the equilibrium (overhead) temperature was recorded and samples of the liquid phase and the condensed vapour phase were taken. In the case of an experiment with a solvent this solvent was also added to the equilibrium cell, keeping the total liquid volume at approximately 80 mL. The cooling bath temperature for the experiments with DEMA and DIPE was lowered to  $6^\circ\text{C}$  for binary experiments and  $14-17^\circ\text{C}$  for solvent screening experiments. For the experiments with the acids the cooling bath temperature was set to  $11.1^\circ\text{C}$ . Also regeneration VLE experiments were performed in the ebulliometer with the most promising solvents, using only the solvent and the preferentially entrained component from the original mixture in varying amount. For the solvent screening experiments an equimolar composition of the close-boiling compounds was used. For the case with the acids the solvent-to-feed ratio was 1 for the liquid solvents (octanoic acid, TBP, TOA, DEGDBE and dodecane). A lower molar solvent-to-feed ratio of 0.2 was used for the solvents that are solid at room temperature (Proton Sponge and 18-crown-6) and the solvent-to-feed ratio was only 0.1 for tribenzylamine. For the case with DEMA/DIPE the solvent screening was performed with equimolar mixtures of DEMA and DIPE and solvent-to-feed ratios of 1 and 3. For the detailed study of solvent the pseudo-binary mixtures had a mole fraction of DEMA of 0.05 and 0.95.

### 2.3 Analysis

#### GC, GC-MS and HPLC

Samples for the case of DEMA/DIPE separation were analyzed by gas chromatography (GC) with a Varian CP-3800 GC with FID (error  $\leq 2\%$ ). Samples were prepared using 100  $\mu\text{L}$  of the original sample, 100  $\mu\text{L}$  dodecane as internal standard and 1.5 mL of acetone. From each sample 1  $\mu\text{L}$  was injected 3 times. The column applied was an Agilent DB-WAX column (60m\*0.25mm\*0.25 $\mu\text{m}$ ). The injection and FID temperatures were set to  $280^\circ\text{C}$  and the measurement temperature started at  $40^\circ\text{C}$  and after 1 minute it was increased to  $50^\circ\text{C}$  in 2 minutes, again after 1 minute it was increased in 3 minutes to  $250^\circ\text{C}$  for 3 minutes. Another analysis that was applied for DEMA/DIPE samples was GC-MS, for which samples were diluted to 5 wt% in

methyl isobutyl ketone (MIBK). Measurements were done on a 7890A Ms 5975C Agilent GC-MS with FID (error  $\leq 2\%$ ) and Agilent HP-5Ms, HP19191S-433 column with helium as the carrier gas. The measurement temperature started at 45 °C and started to increase after 4 minutes to 160 °C in 28 minutes, again after 2 minutes it was increased in 13 minutes to 250 °C for 2 minutes. For the acid analysis, the samples of binary VLE experiments were analysed by HPLC with a HPLC 1200 series with RID (error  $\leq 1\%$ ). The columns used were an Agilent Hi-plex H+ Column (300\*7.7 mm) and GROM Resin H+ IEX (250\*8 mm) with a mobile phase of 5 mM H<sub>2</sub>SO<sub>4</sub> at a flowrate of 0.6 mL/min. Samples of experiments that included solvents were analysed using GC with the previously mentioned method of the Varian GC, with the exception that the column used is a VF1701ms (60m\*0.25mm\*0.25 $\mu$ m).

The performance of the ebulliometer and subsequent GC(-MS) analysis was verified by measuring the boiling temperature of the pure components DEMA and DIPE at different pressures after which these results were confirmed by literature data. Furthermore, six identical experiments were performed in the ebulliometer and resulting samples were analysed in GC. The standard deviation in the equilibrium temperature was 0.44°C. The relative volatility of the equimolar mixture of DEMA and DIPE that was calculated based on GC results had a standard deviation of 0.026 and for GC-MS this was 0.041.

### 3. Theory

The extractive distillation process with a binary mixture to which a solvent is added, consists of two columns. In the first column component A is separated from B and the solvent S. The second column is used for regeneration of the solvent. The solvent is added in the top for increased solvent concentration at the different stages where vapour and liquid can interact with the solvent. (Doherty and Knapp, 2000)

#### Vapour-liquid equilibrium

In industry, vapour-liquid systems are the most commonly encountered two-phase systems. (Smith et al., 2005) In the process of (extractive) distillation there is a vapour-liquid system and for a successful separation by distillation a sufficiently high relative volatility ( $\alpha_{i,j} > 1.4$ ) of the components is required. Thereby the vapour phase will become more enriched in the more volatile component. The solvent selectivity  $S_{ij}$  is shown in Equation 1, where  $\alpha_{ij}$  is the relative volatility,  $\gamma_i$  is the liquid activity coefficient of component  $i$  and  $P_i^{sat}$  is the saturated partial vapour pressure of  $i$ , which is assumed to be constant in the presence of the solvent. (Doherty and Knapp, 2000)

$$S_{ij} = \frac{(\alpha_{ij})_s}{\alpha_{ij}} = \frac{\left(\frac{\gamma_i P_i^{sat}}{\gamma_j P_j^{sat}}\right)_s}{\frac{\gamma_i P_i^{sat}}{\gamma_j P_j^{sat}}} \cong \frac{\left(\frac{\gamma_i}{\gamma_j}\right)_s}{\frac{\gamma_i}{\gamma_j}} \quad (1)$$

An extractive distillation process is usually applied in the case of either a maximum-boiling azeotrope, a more common minimum boiling azeotrope or a close-boiling mixture. For both the minimum-boiling azeotrope and the close-boiling mixture an effective high-boiling solvent has a high affinity for component  $j$  and low affinity for  $i$  ( $\gamma_{i,S} > 1$ ), thereby increasing the relative volatility. A good solvent or entrainer should not form an azeotrope, should be completely miscible, easily regenerated, thermally stable, not reactive with the components, non-toxic, non-corrosive, inexpensive, easily available and should have a reasonable low heat of vaporization. (Doherty and Knapp, 2000)

### 4. Results and Discussion

For both of the separation cases that were studied, binary VLE data were measured and the effect of different types of solvent were tested. Regeneration of the most promising solvents of the DEMA/DIPE case was also studied.

#### 4.1 Valeric acid and its isomers

From the mixture of valeric acid (HVal) and 2-methylbutyric acid (2MBA), binary VLE data were obtained at 300, 600 and 900 mbar. For 300 mbar the results are shown in Figure 1a, the average relative volatility is approximately  $1.35 \pm 0.02$ . The VLE data at higher pressures were similar, although the relative volatility is lower in those cases, i.e.  $1.32 \pm 0.04$  at 600 mbar and  $1.30 \pm 0.03$  at 900 mbar. In each of the cases the VLE data have the typical shape of ideal binary data where no azeotrope is present, unless the azeotropic point is very close to the composition of  $x_{2MBA} = 0$  or 1.

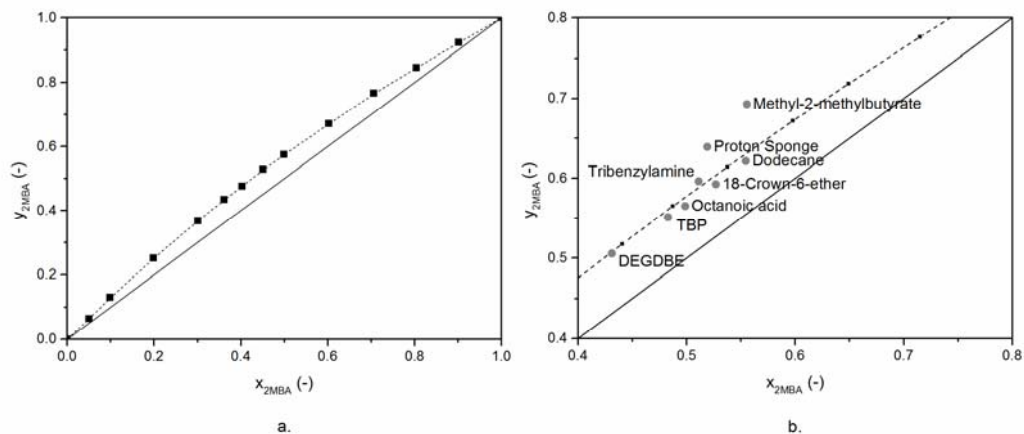


Figure 1: a) Binary VLE data for the system valeric acid and 2-methylbutyric acid (2MBA) at a pressure of 300 mbar, b) Solvent effect on pseudo-binary VLE data for the same system at 300 mbar. Symbols represent experimental data, the line represents ideal VLE behaviour with  $\alpha = 1.35$ .

The solvents that were investigated can be subdivided in the categories basic solvents, acidic solvents, solvents based on similarity with one of the components and apolar solvents. These experiments were also performed at 300, 600 and 900 mbar and the results for 300 mbar are shown in Figure 1b. Most of the solvents are not capable of increasing the relative volatility, except for the Proton Sponge and methyl-2-methylbutyrate. However, for the Proton Sponge the thermal stability was low during experiments as a result of the strong interactions with the acids. In the research of Jongmans et al. (2012) it was also found that strong bases as a solvent were unsuccessful because of too strong interactions. The second most promising solvent was methyl-2-methylbutyrate, a solvent that is based on similarity with 2-methylbutyric acid. This solvent increased the relative volatility to  $\alpha = 1.84 \pm 0.18$ , which is a significant improvement, as in the range between  $\alpha = 1.35$  and 1.84 as measured here, the reduction in heat duty is typically large (Blahusiak et al. (2018)). It was validated that this result could never have been the result of reactivity of the ester with the small amounts ( $\sim 0.5$  wt%) of water in the system, and therefore, it was concluded that with methyl-2-methylbutyrate a good solvent was found.

#### 4.2 Separation of DEMA and DIPE

The binary VLE data as well as the  $T_{x,y}$ -diagram of the two components DEMA and DIPE are shown in Figure 2a and 2b, respectively. It can be seen that the relative volatility is very low,  $\alpha = 1.20$  at 300 mbar. Based on the  $T_{x,y}$ -diagram, the existence of a minimum-boiling azeotrope was also a possibility, as can be seen in Figure 2b.

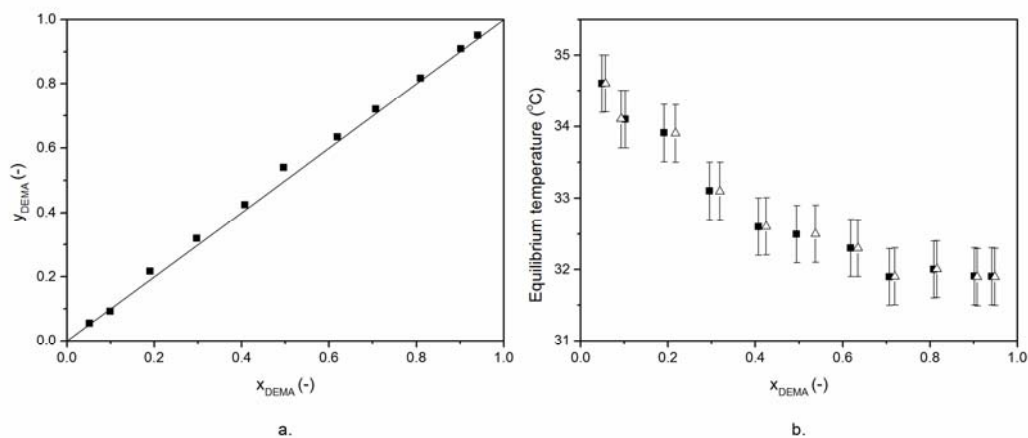


Figure 2: a) Binary VLE data for the system DEMA and DIPE at 300 mbar and b)  $T_{x,y}$ -diagram for the system at 300 mbar, closed symbols represent the liquid phase, open symbols represent the vapour phase.

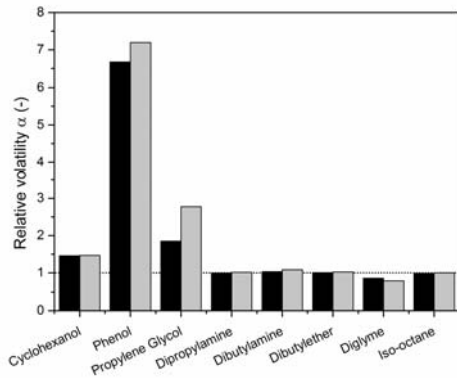


Figure 3 Solvent effect on the relative volatility for the equimolar mixture of DEMA and DIPE. (Black columns: S/F = 1, Grey columns: S/F = 3)

The solvent screening focused on different types of solvents, that are carboxylic acids, glycols, cyclohexanol, ethers, secondary amines, m-cresol, phenol and alkanes, all applied in S/F = 1 and S/F = 3. The carboxylic acids acetic acid, valeric acid and oleic acid had a too strong interaction with the amine, preventing the mixture from reaching an equilibrium. The solvent m-cresol appeared not to be fully miscible with the mixture. The relative volatility of DIPE over DEMA in the presence of the other solvents is shown in Figure 3. Secondary amines, ethers and alkanes did not increase the relative volatility significantly. When using diglyme, DEMA is more volatile. The three most promising solvents were cyclohexanol, phenol and propylene glycol. These solvents are all hydrogen bond forming compounds. Detailed experiments with these three solvents were performed at a solvent-to-feed ratio of 1 and 3, see Table 1. For these experiments pseudo-binary mixture compositions were applied with a DEMA mole fraction of  $x_{DEMA} = 0.05$  and  $x_{DEMA} = 0.95$ . The relative volatility was measured at 1000 mbar and at reduced pressure of 300 mbar at two solvent-to-feed ratios. The results for phenol show the largest relative volatility. Especially at a higher solvent-to-feed ratio miscibility became problematic and no equilibrium was reached in some experiments. The immiscibility limits the application in extractive distillation processes and its effect on the regeneration should be taken into account.

Table 1: VLE data (relative volatility  $\alpha$  and selectivity  $S$ ) for the three most promising solvents for separation of DEMA and DIPE. (n.e. = no equilibrium achievable)

Mole fraction of DEMA (-)	Solvent	1000 mbar		1000 mbar		300 mbar		300 mbar	
		S/F = 1		S/F = 3		S/F = 1		S/F = 3	
		$\alpha$	$S$	$A$	$S$	$\alpha$	$S$	$\alpha$	$S$
0.05	-	1.3	-	-	-	1.1	-	-	-
	Propylene glycol	3.7	2.9	n.e.	-	4.0	3.6	n.e.	-
	Cyclohexanol	1.5	1.2	n.e.	-	1.8	1.6	n.e.	-
0.95	Phenol	7.6	6.0	8.0	6.3	15	14	58	52
	-	1.0	-	-	-	1.1	-	-	-
	Propylene glycol	n.e.	-	n.e.	-	n.e.	-	n.e.	-
	Cyclohexanol	1.6	1.5	1.1	1.1	1.9	1.7	1.8	1.6
	Phenol	3.6	3.5	n.e.	-	5.0	4.5	n.e.	-

Table 2: Overview of relative volatility in solvent regeneration experiments with DEMA and solvent. (n.s. = no solvent in sample)

Solvent	S/F	$\alpha$		$T$ ( $^{\circ}C$ )	
		1000 mbar	300 mbar	1000 mbar	300 mbar
Propylene glycol	1:1	-	-	-	n.s.
	9:1	n.s.	66.7	n.s.	45.7
Cyclohexanol	1:1	172	94.5	650	61.2
	9:1	n.s.	66.5	n.s.	35.1
Phenol	1:1	n.s.	77.8	n.s.	43.9
	1:9	n.s.	120.5	n.s.	90.7

### 4.3 Regeneration

Regeneration experiments were performed with the three most promising entrainers propylene glycol, cyclohexanol and phenol. Experiments with all three solvents show a very high relative volatility of DEMA and solvent, see Table 2. For several systems no solvent peak in the GC analysis of the vapour phase was found. This implies that the separation between DEMA and the solvents is very good and the recovery of the solvents should not be problematic.

### 5. Conclusions

For both of the cases studied, binary VLE data were measured and solvents were selected with the potential to improve the relative volatility of the components. For the case with valeric acid and the isomer 2-methylbutyric acid the relative volatility equals  $1.35 \pm 0.02$  at 300 mbar. Several solvents were applied of which the one that most increased the relative volatility appeared to be thermally unstable, most probably because of too strong interaction. Apparently, the difference in acidity of the acids  $\Delta pK_a$  is too small to allow for a successful extractive distillation process with regenerable solvents that address the difference in acidity, i.e. weaker bases. The solvent methyl-2-methylbutyrate that is based on similarity with 2-methylbutyric acid could increase the relative volatility to  $1.84 \pm 0.18$  and was considered the solvent of choice.

In the second case, the goal was to select an appropriate solvent for extractive distillation of a mixture of DEMA and DIPE. The relative volatility of DEMA and DIPE varies with the applied pressure, from 1.05 at 1000 mbar to 1.20 at 300 mbar. In the solvent screening it was found that carboxylic acids formed too strong complexes with the amine. Furthermore, glycols and m-cresol may cause immiscibility with DIPE, and secondary amines, primary ethers and alkanes do not cause an appreciable increase in relative volatility, even at higher solvent-to-feed ratios. The most promising solvents were phenol, propylene glycol and cyclohexanol. Phenol showed the higher increase of relative volatility, which was up to 8. These solvents all contain hydroxyl groups, by which they can interact with DEMA. All promising solvents could be easily regenerated. However, in detailed experiments miscibility gaps were found in mixtures of the solvent with the components, especially at higher solvent-to-feed ratios. These miscibility gaps should be taken into account for the final design of the extractive distillation process. This indicates that next to the importance of experiments on the possibility to regenerate the solvent, detailed experiments at various solvent-to-feed ratios are important.

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