

Aniline-Driven Liquid-Liquid Extraction for Methylamine-Water Separation: Process Simulation and Performance Evaluation

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Abstract

Methylamines are toxic with ammonia-like odor while aniline has a fishy odor. Both aniline and methylamines affect aquatic life and water quality if present in large concentrations in water. Nevertheless, the later, with solubility of 1120 g/L is more soluble in water than the former with solubility of 3.6 g/L at 25°C. Based on their differences in solubilities, liquid-liquid extraction (LLE) technique can be used to separate or remove the presence of any one of the two pollutants in water. The UNIQUAC property method in Aspen Plus V8.8 was proven to be the best method for the LLE of a water-aniline-methylamine ternary mixture after a single stage partition coefficient analysis with a mixing tank. Adopting the best model for a two-stage separation using 'Extract' and 'RadFrac' Aspen Plus model units, yielded three separate product streams that are 95.5% methylamine, 86.5% aniline and 100% water. The phase boundary, diagonal tie lines and a constant boiling point of 372.505 K showcased by the ternary phase diagram, demonstrated the presence of an azeotrope and the ability of the RadFrac model to separate the mixture easily. Future demonstration on how to separate numerous ternary mixtures is recommended, as the need to treat effluents of many industries containing compounds of varying solubilities may warrant the setting up of an LLE unit.

1. Introduction

Liquid-liquid extraction (LLE) or solvent extraction is a technique for separating compounds based on their relative solubilities in two dissimilar immiscible liquids, typically water and an organic solvent (Ghasem, 2021; Pizzirusso & Brasiello, 2022). Such a mixture is called ternary mixtures (Salih, 2017), referring to a mixture consisting of three components. Example includes, water-ethanol-acetone, nitrogen-oxygen-argon, water-sugar-salts, oil-water-surfactant, hexane-toluene-ethanol, ethanol-water-glycerol and water-methanol-ethanol, acetone-methanol-water, benzene-toluene-xylene, acetonitrile-methanol-water, ethyl acetate-acetic acid-water, hexane-ethanol-water, water-methanol-methyl acetate, water-methanol-chloroform, n-octanol-methyl ethyl ketone-water, ethanol-water-isopropanol, acetic acid-water-isopropyl butyl ether and dichloromethane-methanol-water (Choi et al., 2000; Hilal et al., 2002; Laitinen et al., 2021; Pandurang et al., 2016; Pham et al., 2015; Shangraw et al., 2020). Noticeable drawback of the LLE process is the requirement of a solvent to extract one of the liquids from the mixture. A chosen solvent for a particular LLE may be expensive, corrosive or explosive and hence becomes a basis for numerous other problems; for instance, storage (Bhandari et al., 2016). LLE finds application in diverse fields, including pharmaceutical plant, petroleum industries, environmental analysis, chemical engineering and the extraction of natural products (Bhandari et al., 2016; Caravella et al., 2014; Zaiz et al., 2013). In chemical engineering, several modelling and simulation software including Aspen Plus (Table 1) and Thermo-Calc, have been used to separate ternary mixtures or used for equilibrium and phase diagram calculations (Azevedo & Flower, 2014; Espada et al., 2007; Horsak & Slama, 1987; Ilaiah et al., 2021; Prakash, 2004; Shangraw et al., 2020). Ternary phase diagram (TPD) can also be generated using some simulation software, which give insights into the behavior of multi-component systems (Ghosh, 2018; Graff, 2017). TPD are widely used in fields such as metallurgy, materials science, geology, pharmaceutical, and chemistry to predict and understand phase equilibria, phase transitions and the formation of various phases under different conditions (Dhoot et al., 2018; El-Gendi et al., 2012).

Table 1 Ternary mixtures separated using Aspen Plus or Aspen Hysys

S/No.	Ternary mixtures	Method	Author
1	Butanol/Water/Ethanol	WILSON	Thermo-018 (2012),
2	Water/Acetic acid/MTBE	UNIQUAC & NRTL	Caravella et al. (2014)
3	Ethanol/Water/Cyclohexane	UNIQUAC	Thermo-016 (2012)
4	Triglycerides/Calophyllum inophyllum oil/n-Hexane	UNIQUAC & NRTL	Pizzirusso & Brasiello (2022)
	Triglycerides/Calophyllum inophyllum oil/Methanol		
5	Acetone/Water/3-Methylhexane	PRSV	NCHU (2012)
6	Water/Acetone/Acetic acid/Chloroform	UNIQUAC PR	Zina (2019)
7	Water/Furfural/P-xylene	UNIQUAC & NRTL	Kennedy & Costa (2020)
	Water/Furfural/Toulene		
8	Water/Aniline/Methylamine	UNIQUAC, WILSON, UNIFAC & NRTL	Present work

Aniline ($C_6H_5NH_2$ or C_6H_7N) is an organic aromatic amine compound produced through benzene nitration and hydrogenation of the generated nitrobenzene (Hartwig et al., 2009; Hutník, 2014). Its synonyms include phenylamine, aminobenzene, benzenamine and aminophen (BASF, 2022). Main applications of the substance are in rubber manufacture, plastics, chemical synthesis, oil paints, medicine, pharmaceuticals, pesticides, dyes, defense products and polymer chemistry (Anjalin et al., 2020). When aniline is released into bodies of water, it frequently affects the water ecosystem, causing severe water pollution and even the death of aquatic animals and plants. Because aniline is widely utilized in numerous industries, it can be found in several types of industrial and municipal effluent. When the concentration of aniline in wastewater surpasses a particular threshold, it has a negative impact on microorganisms in the treatment process. As a result, it must be eliminated or converted into biodegradable compounds before biological treatment activities may begin (Jing et al., 2015). Another chemical, methylamine ($MAN - CH_5N$) are offshoots of ammonia with 1, 2, or all 3 hydrogen atoms substituted by methyl groups (Ronny et al., 2019). MANs are colorless gases or compressed liquids, toxic, highly flammable, soluble in various organic solvents and have a strong fishy odor. They are used as intermediates in the manufacture of surfactants, solvents, pharmaceuticals, rubber, agricultural and water treatment chemicals (CGA, 1990; Turcotte & Hayes, 2001).

Extensive study has shown that MAN is soluble in water but insoluble in aniline. In addition, Aspen Plus has not been used to model and simulate the separation of the mixture in question. Therefore, the aim of this work is to extract MAN from water using aniline. The specific objective of the work is to demonstrate the use of four

property methods in Aspen Plus: namely, Non-Random Two Liquid (NRTL), Weighted Integral Low-Order Solubility On Nonrandomness (WILSON), named after Grant Wilson, Universal Quasi Chemical (UNIQUAC) and UNIQUAC Functional-group Activity Coefficients (UNIFAC) for a single stage extraction simulation, compare their respective estimates of the partition coefficients and use it to select the best property method for a multi-stage separation process. Furthermore, adequate block specification was done to finally separate a mixture of MAN-Water-Aniline using the most appropriate thermodynamic property model selected. The underlying reasons for the choice of aniline is because it is moderately soluble in both organic solvents and water and thus, gives a very crucial property for LLE. Furthermore, aniline's low vapor pressure and favorable distribution coefficient make it feasible for extraction procedures (BASF, 2022; Garrick & Gray, 1927; William, 1951).

2. Methodology

2.1 Properties Setup

Under the 'Properties' panel in Aspen Plus V8.8, aniline, water and methylamine, which are the main components of this simulation, were selected. Free water option 'Dirty water' and the base method 'NRTL' were initially chosen. A new Property Set, 'MOLECONC' or MCMAN (mol/L), which stands for molar concentration of MAN in a liquid mixture, was also chosen. Under the 'Qualifiers' tab, MAN was selected as the desired component, before running the properties setup. The thermodynamic property method, NRTL, was changed after running the simulation with the next property method defined in the objective, successively till all property models are tested.

2.2 Single Stage Extraction Simulation

In the simulation environment, feed streams and output streams for a mixing tank model in Aspen Plus was modelled as shown in Fig. 1.

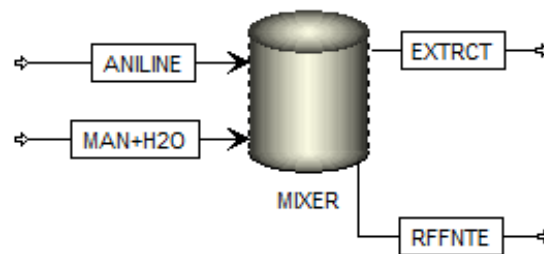


Fig. 1 Single stage liquid-liquid extraction process

Both the ANILINE and MAN+H₂O streams were operating at 1 atm and 25°C. Total mass flow of the ANILINE stream was specified 100 kg/h pure C₆H₇N component stream (mass fraction = 1). For the MAN+H₂O stream, 68.57143 kg/h H₂O and 27.42857 kg/h MAN equivalent to a stream total mass flow of 96 kg/h was specified. Basically, aniline was chosen as absorbent in the separation of MAN from water because it forms a two-phase system with water. It has a relatively high solubility in both organic solvents and water, which makes it a suitable extractant for this type of separation. Additionally, it has the ability to form hydrogen bonds with polar compounds like methylamine. This hydrogen bonding interaction between aniline and MAN aids in the selective extraction of MAN from the aqueous phase into the organic phase, allowing effective separation. Aniline's ability to form a stable emulsion with water also enhances its efficiency in LLE procedures.

The partition coefficient, denoted as 'P', needs to be determined for the liquid-liquid extraction system. P is a measure of the distribution of a compound between two immiscible phases, typically a hydrophobic solvent and water. It represents the ratio of the compound's concentration in one phase to its concentration in the other phase at equilibrium. In the literature, $P \approx 3.35$ at 25°C for MAN, which implies that MAN is roughly 3.35 times more soluble in the organic phase than in water. In this simulation, P of MAN was determined by setting the MCMAN property set, to be calculated by Aspen Plus sensitivity analysis.

An 'S1' new sensitivity set was therefore defined. According to Chemical Book data, ChemBK (2023), maximum solubility of MAN in water at 25°C is 40 wt%. That is, for every 100 g of H₂O, there contain 40g of MAN at equilibrium. This amounts to 40 wt% x 96 kg/h = 38.4 kg/h. Solubility of MAN in water, as observed from literature sources increases with temperature. It is 50g/100 mL at 0°C ; 70g/100 mL at 25°C and; 90g/100 mL at 50°C. Thus, mass flow of MAN lower and upper limits in MAN+H₂O stream under 'S1' Vary tab was set at 0.00001 to 38 kg/h. MCMANR = MCMAN in the raffinate stream and MCMANE = MCMAN in the extract stream were defined under the 'Define' tab. To define P and its logarithmic mean value (log P), Equations 1 and 2 were typed in separate lines inside the 'Fortran' tab in Aspen Plus.

$$\text{DKOW}=\text{MCMANE}/\text{MCMANR} \quad (1)$$

$$\text{DLOGKOW}=\text{LOG10}(\text{DKOW}) \quad (2)$$

Where, $\text{KOW} = P$, $\text{LOGKOW} = \log P$, and the prefix 'D' makes them double integer values. To enter Equations 1 and 2 correctly, first line of code was left empty before writing it in the 3rd column or after pressing the keyboard spacebar 3 times. Inside the 'Tabulate' tab 'Fill Variable' boxes, MCMANR, MCMANE, DKOW and DLOGKOW were selected in that order to be computed by Aspen Plus. The simulation was then re-initialized and re-run to obtain the 'S1' sensitivity result table.

S2, S3 and S4 similar sensitivity analysis was carried out using the same specification but in different Aspen Plus files by selecting the UNIQUAC, WILSON and UNIFAC property models respectively to obtain similar sensitivity result table for comparison. After comparison, the best property method was then selected to run a multi-stage extraction process.

2.3 Multistage Extraction Simulation

The property method that best estimate the partition coefficient (K) under the single-stage system was adopted for a multi-stage model. 'Tank' mixer in Fig. 1 was replaced with the 'Extract' unit from 'Columns' tab in the Aspen Plus 'Model Palette'. All inputs and output streams to this column remains the same. The following 'Extract' unit specifications were used:

- Unit is an adiabatic extractor with 10 stages
- Under 'Key Components' tab, a key component for RFFNTE (1st liquid phase) stream is H₂O and EXTRCT (2nd liquid phase) stream is aniline.
- Stage 1 pressure is 1 atm
- Stage 1 temperature is 25°C

After specifying the block operating conditions, the simulation was reset and re-run. Components mass fraction in the product streams of the 'Tank' and 'Extract' units were compared. Further purification, to obtain a separate pure output stream of aniline and MAN in the EXTRCT stream using a RadFrac distillation column was carried out as described in Brondani et al. (2015) and Zina (2019). This is the beginning of the multistage process simulation. Small amount of water still present in the EXTRCT stream was made to be part of the RadFrac top stream as condensed water (COND-H2O). RadFrac operating conditions specified were as follows:

- A kettle reboiler and a total condenser
- Valid phase is 'Vapor-Liquid-FreeWaterCondenser'
- Number of stages is 10
- Reflux ratio and distillate-to-feed ratio (mass basis) are respectively 0.8 and 0.19
- Feed stream is 'Above-Stage' 6
- For the product stream, COND-H2O is at stage 1 with Free water phase; TOPSTRM is at a stage 1 with 1st liquid valid phase and BTMSTRM is at stage 10 with liquid as valid phase.
- Stage 1 (top stage) condenser pressure is 0.9 atm
- Stage pressure drop across the rest of the column is 0.005 atm

Afterwards, the simulation was reinitialized and re-run to obtain the mass fractions in the second unit of the multistage process shown in Fig. 2. The 'Extract' unit model with feed as MAN and water and solvent as aniline was in accordance with Kennedy & Costa (2020), who had used the same unit.

2.4 Implementing a Ternary Diagram

Under "Properties" environment in Aspen Plus V8.8, we navigate through the "Home" ribbon | "Analysis" group | "Ternary Diag" button and then clicked on 'Continue to Aspen Plus Ternary Diag' button under 'Distillation Synthesis' window to open up the "Ternary Map" tab to select the three components. 'Run Analysis' button was clicked for the 'Ternary Diag' tab window to be displayed.

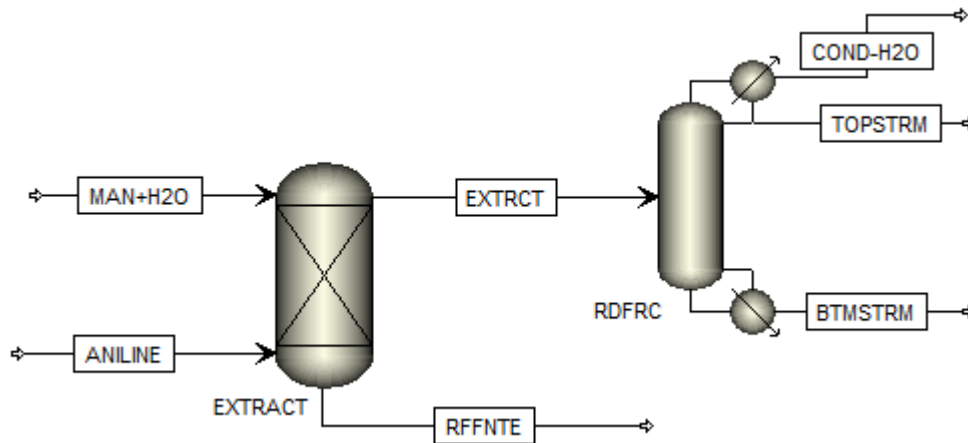


Fig. 2 Multistage extraction process for MAN-water-aniline mixture

3. Results and Discussion

3.1 Property Model Selection

Since $P = 3.35$ for MAN, the recommended equilibrium value of $\log P = 0.525045$. In Table 2, the lowest value of $\log P$ is -0.44266 , which is less than the equilibrium value.

Table 2 Sensitivity report for DLOGKOW under the NRTL model

No. of Point	MAN mass flow (kg/h) in MAN + H ₂ O	MCMANR (mol/L)	MCMANE (mol/L)	DKOW	DLOGKOW
1	1.00E-05	3.11E-06	1.12E-06	0.360863	-0.44266
2	2.000009	0.598701	0.224904	0.375653	-0.42521
3	4.000009	1.153683	0.451112	0.391019	-0.4078
4	6.000008	1.667817	0.678855	0.407032	-0.39037
5	8.000008	2.143624	0.908408	0.423772	-0.37287
6	10.00001	2.583313	1.140098	0.441332	-0.35523
7	12.00001	2.988766	1.374372	0.459846	-0.33739
8	14.00001	3.361969	1.611699	0.479391	-0.31931
9	16.00001	3.703458	1.852759	0.500278	-0.30079
10	18.00001	4.014572	2.09831	0.522673	-0.28177
11	20	4.295865	2.34955	0.546933	-0.26207
12	22	4.547498	2.607617	0.573418	-0.24153
13	24	4.768889	2.874547	0.602771	-0.21985
14	26	4.958443	3.153132	0.635912	-0.1966
15	28	5.112783	3.447752	0.67434	-0.17112
16	30	5.22495	3.767264	0.721014	-0.14206
17	32	5.27884	4.134098	0.783145	-0.10616
18	34	5.205571	-	1.92E+34	34.28353
19	36	5.435352	-	1.84E+34	34.26477
20	38	5.658796	-	1.77E+34	34.24728

Hence, NRTL model is not the best property method for the extraction of MAN from water using aniline. Based on S2 sensitivity report or Table 3, UNIQUAC is not the best property method, since the lowest value of $\log P$ in the table (-0.18575) is below the equilibrium value.

Table 3 Sensitivity report for DLOGKOW under the UNIQUAC model

No. of Point	MAN mass flow (kg/h) in MAN + H ₂ O	MCMANR (mol/L)	MCMANE (mol/L)	DKOW	DLOGKOW
1	1.00E-05	2.46E-06	1.60E-06	0.652009	-0.18575
2	2.000009	0.48032	0.316548	0.659035	-0.18109
3	4.000009	0.93967	0.625896	0.666081	-0.17647
4	6.000008	1.379164	0.928383	0.673149	-0.17189
5	8.000008	1.79984	1.224323	0.68024	-0.16734
6	10.00001	2.202626	1.51405	0.687384	-0.1628
7	12.00001	2.58841	1.797858	0.69458	-0.15828
8	14.00001	2.958014	2.076042	0.701836	-0.15376
9	16.00001	3.312191	2.348882	0.709163	-0.14925
10	18.00001	3.651988	2.616648	0.7165	-0.14478
11	20	3.977361	2.879614	0.724001	-0.14026
12	22	4.289201	3.138115	0.731632	-0.13571
13	24	4.588138	3.392311	0.739365	-0.13114
14	26	4.87464	3.642508	0.747236	-0.12654
15	28	5.133814	3.89027	0.757774	-0.12046
16	30	5.367999	4.135678	0.770432	-0.11327
17	32	5.588488	4.378305	0.783451	-0.10599
18	34	5.795806	4.618317	7.97E-01	-0.09863
19	36	5.990189	4.856214	8.11E-01	-0.09114
20	38	5.052387	6.144451	1.22E+00	0.084986

Log P for the WILSON property method after S3 sensitivity analysis is shown in Table 4. Obviously, WILSON property method failed to partition MAN between the two phases, which practically ended up with huge values of DLOGKOW. In fact, the molar concentration value of MAN in “EXTRCT” stream (i.e., “MCMANE”) could not be calculated by WILSON property method, unlike the two previous activity-coefficient-based methods.

Table 4 Sensitivity report for DLOGKOW under the WILSON model

No. of Point	MAN mass flow (kg/h) in MAN + H ₂ O	MCMANR (mol/L)	MCMANE (mol/L)	DKOW	DLOGKOW
1	1.00E-05	2.00E-06	-	5.00E+40	40.69859
2	2.000009	0.393251	-	2.54E+35	35.40533
3	4.000009	0.772775	-	1.29E+35	35.11195
4	6.000008	1.139259	-	8.78E+34	34.94338
5	8.000008	1.49334	-	6.70E+34	34.82584
6	10.00001	1.835619	-	5.45E+34	34.73622
7	12.00001	2.166657	-	4.62E+34	34.66421
8	14.00001	2.486982	-	4.02E+34	34.60433
9	16.00001	2.797089	-	3.58E+34	34.55329
10	18.00001	3.097447	-	3.23E+34	34.509
11	20	3.388492	-	2.95E+34	34.46999
12	22	3.67064	-	2.72E+34	34.43526
13	24	3.944281	-	2.54E+34	34.40403
14	26	4.209782	-	2.38E+34	34.37574

15	28	4.467491	-	2.24E+34	34.34994
16	30	4.717737	-	2.12E+34	34.32627
17	32	4.960831	-	2.02E+34	34.30445
18	34	5.197065	-	1.92E+34	34.28424
19	36	5.42672	-	1.84E+34	34.26546
20	38	5.650059	-	1.77E+34	34.24795

This is consistent with Thermo-018 (2012), where WILSON's weakness is previously demonstrated during the liquid-liquid extraction of butanol-water-ethanol mixture using the property model. Lowest value of Log P (-0.49265) in Table 5 based on the UNIFAC method, is the lowest estimate obtained which is still lower than 0.525045 equilibrium value.

Table 5 Sensitivity report for DLOGKOW under the UNIFAC model

No. of Point	MAN mass flow (kg/h) in MAN + H ₂ O	MCMANR (mol/L)	MCMANE (mol/L)	DKOW	DLOGKOW
1	1.00E-05	3.43E-06	1.10E-06	0.322	-0.49265
2	2.000009	0.656689	0.223904	0.341	-0.4673
3	4.000009	1.262379	0.452797	0.359	-0.44529
4	6.000008	1.824272	0.684809	0.375	-0.42552
5	8.000008	2.347532	0.918814	0.391	-0.40738
6	10.00001	2.8361	1.154135	0.407	-0.39047
7	12.00001	3.293138	1.390345	0.422	-0.37449
8	14.00001	3.721272	1.627169	0.437	-0.35926
9	16.00001	4.122727	1.864443	0.452	-0.34464
10	18.00001	4.499414	2.10208	0.467	-0.33051
11	20	4.852985	2.34006	0.482	-0.31678
12	22	5.184885	2.578403	0.497	-0.30339
13	24	5.496377	2.817175	0.513	-0.29026
14	26	5.788556	3.056491	0.528	-0.27735
15	28	6.062372	3.296493	0.544	-0.26459
16	30	6.318628	3.5374	0.560	-0.25194
17	32	6.558008	3.779433	0.576	-0.23935
18	34	6.781041	4.022913	0.593	-0.22676
19	36	6.98812	4.268248	0.611	-0.21411
20	38	7.179476	4.515945	0.629	-0.20134

In the absence of any lower value of log P in all the model that is above the equilibrium value, log P values that is much closer to this value can be selected as the best property method. In view of that, the lowest value of log P in Table 3 is -0.18575, which is nearer to the equilibrium value of 0.525045. Hence, UNIQUAC property model is recommended as the property method for extraction of MAN from water using aniline. Log P is typically a positive value, as P itself is a ratio of concentrations or activities. If log P is negative, it implies that the concentration or activity of the solute in the second phase is greater than its concentration or activity in the first phase. This indicates that the solute has a higher affinity for phase 2 and tends to accumulate or distribute more in that phase. In practical terms, a negative log P suggests that the solute is less soluble or less favorably distributed in the first phase compared to the second phase.

According to Kennedy & Costa (2020), UNIQUAC model is a method of determining the activity coefficient used to describe the phase equilibrium, also based on the theory of statistical mechanics used by Guggenheim et al. (1950) in his quasi-chemical theory for non-random molecules of mixtures containing components of different sizes.

3.2 Tank and Extract Unit Products

The dirty water option, as earlier chosen, is used in applications relating the solubility of organic phase in water; even though the solubility is not substantial. Dirty water method uses the distinct water solubility methods to compute solubility of water in the organic phase similar to the free-water method. As well, it uses special method to estimate the quantity of organics permissible in the water phase (Byluppala, 2010).

Using the UNIQUAC property method, the result summary of the single stage tank model and the 'Extract' unit were obtained, as displayed in Fig. 3 and Fig. 4.

Display		All streams	Format	CHEM_M	Stream Table	Copy All
		ANILINE	EXTRCT	MAN+H2O	RFFNTE	
▶	Mass Flow kg/hr					
▶	WATER		12.801	68.571	55.771	
▶	METHY-02		13.682	27.429	13.747	
▶	ANILI-01	100	87.361		12.639	
▶	Mass Frac					
▶	WATER		0.112	0.714	0.679	
▶	METHY-02		0.12	0.286	0.167	
▶	ANILI-01	1	0.767		0.154	

Fig. 3 Mass fraction of the extract and raffinate streams – single stage (MIXER)

Display		All streams	Format	CHEM_M	Stream Table	Copy All
		ANILINE	EXTRCT	MAN+H2O	RFFNTE	
▶	Mass Flow kg/hr					
▶	ANILINE	100	96.006		3.994	
▶	METHYLAM		26.516	27.429	0.912	
▶	WATER		23.883	68.571	44.689	
▶	Mass Frac					
▶	ANILINE	1	0.656		0.081	
▶	METHYLAM		0.181	0.286	0.018	
▶	WATER		0.163	0.714	0.901	

Fig. 4 Mass fraction of the extract and raffinate streams – multi-stage first unit (EXTRACT)

It is observed that the RFFNTE stream is pure water while the EXTRCT stream is mainly aniline and MAN. There was serious increase in water fraction in the RFFNTE stream in the 'Extract' column, as well as the aniline and MAN in the EXTRCT stream, as evidenced in Figure 4. This shows the superiority of the 'Extract' column over the tank mixer. Pure components of all 3 compounds in the products can be recovered by bringing additional separation column (second unit 'see Fig. 2' – forming a multistage process). Purities of all 3 components recovered from the RadFrac unit are as shown in Fig. 5.

Display	Streams	Format	CHEM_M	Stream Table	Copy All
	EXTRCT	COND-H2O	TOPSTRM	BTMSTRM	
▶ Mass Frac					
▶ ANILINE	0.656		0.04	0.865	
▶ METHYLAM	0.181		0.953	880 PPB	
▶ WATER	0.163	1	0.007	0.135	

Fig. 5 Stream fraction or purity of MAN-water-aniline separation system

From Fig. 5, the top stream is mainly MAN (95.3 wt%), the condensed stream is 100% water and the bottom stream of the RadFrac column is 86.5% aniline, which clearly depicts the occurrence of liquid-liquid splitting. In a similar venture to improve the quality (or purity) and efficiency of a LLE technique, Bhandari et al. (2016) moved from a single stage process to a two-stage process using Aspen Plus, obtaining a high product quality. This study observed that changing the number of stages from 10 to 8, 12, 14 and 15 does not affect the percent purity of the product streams result (Fig. 5) of the 'RadFrac' unit.

3.3 Ternary Phase Diagram

A graphical representation of the behavior of three components in a system at different compositions and temperature was carried out using the TPD in Figure 6. It provides a visual understanding of the phases that exist and the regions in which they are stable within the ternary diagram (Fahrenholtz et al., 2001; Salih, 2017). In TPD, the three components are typically represented on the axes of the diagram, where the composition of each species can vary from 0-100% along the respective axis (Campbell, 2012; Cornish, 2005; Pandurang et al., 2016).

With the UNIQUAC model, two liquid phases are expected in the area defined by the blue curve and the water axis, in the ternary map shown in Fig. 6.

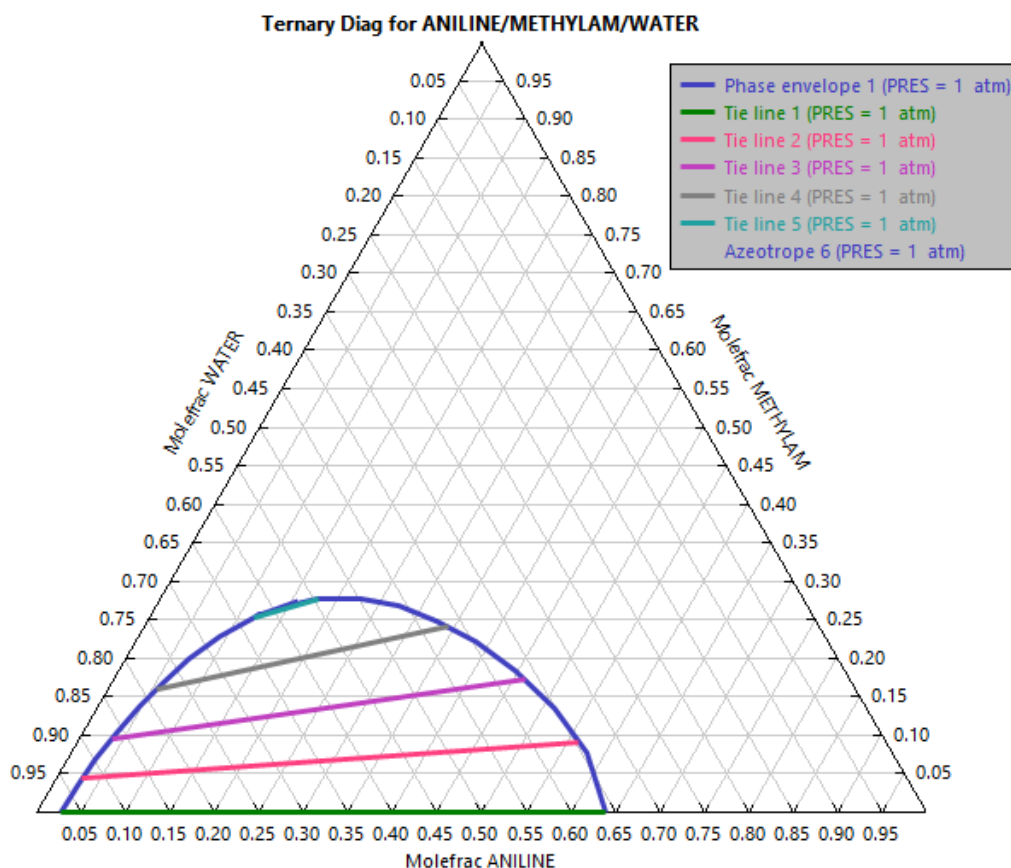


Fig. 6 Aniline/MAN/water ternary diagram

The working principle of the two-stage LLE process is explained using the TPD shown in Figure 6. Composition of Aniline/MAN/Water mixture is marked inside the equilibrium-curve. After phase equilibrium, extract phase and raffinate phase separated across the tie line and their compositions lie on the equilibrium-curve as shown in Figure 6. The extract phase was a mixture of aniline and MAN whereas the raffinate phase was rich in water. The 5 tie lines are straight lines that connect two-phase compositions within a three-component system at a constant temperature (25°C) and pressure (1 atm). These lines represent the coexistence of two different phases in equilibrium with each other. The length of the tie line between two phases indicates the relative proportions of each phase in the mixture. Longer tie lines suggest that one phase is more dominant in the mixture, while shorter tie lines indicate a more even distribution of the two phases.

In Fig. 6, every corner of the triangle represents a pure component, which are 100% A (water), 100% B (MAN) and 100% C (aniline). Each side represents one binary mixture and area in this triangular diagram represents ternary components. Each of the triangle's three corners or apexes represents 100% of one component (A, B, or C). As a result, that same apex will account for 0% of the other two components. The three lines connecting the corner points represent two-component mixtures of the three potential combinations of A, B, and C. Thus, the lines AB, BC, and CA are used for two-component combinations of A and B, B and C, and C and A, respectively. The region within the triangle depicts all of the conceivable combinations of A, B, and C to produce three-component systems. The addition of the third component into one pair of miscible liquids can change their solubility. If the third component is more soluble in any of the two components, the solubility of both decreases. However, if the third component is soluble in two components simultaneously, the solubility increases (Pandurang et al., 2016). This is not the case when aniline is added to a mixture of MAN and water. When the two compounds are mixed, the overall solubility of MAN in water will not experience a significant increase because the solubility of aniline itself is not high enough to enhance the solubility of MAN.

The 'Phase envelope' (in thick blue lines) was drawn using data shown in Fig. 7.

Phase envelope compositions

NUMBER	MOLEFRAC ANILINE	MOLEFRAC METHYLAM	MOLEFRAC WATER
1	0.0274455	0	0.972554
1	0.029011	0.0363437	0.934645
1	0.0330265	0.0696374	0.897336
1	0.0392445	0.103445	0.857311
1	0.0477013	0.136778	0.815521
1	0.0587494	0.168985	0.772266
1	0.0729521	0.199342	0.727705
1	0.0916452	0.22741	0.680945
1	0.118963	0.253588	0.62745
1	0.122966	0.256268	0.620766
1	0.124267	0.257724	0.618009
1	0.132174	0.26262	0.605206
1	0.15452	0.27187	0.57361
1	0.155942	0.271194	0.572864
1	0.176189	0.277258	0.546553
1	0.179369	0.277526	0.543105
1	0.226033	0.277725	0.496242
1	0.274015	0.26803	0.457955
1	0.326785	0.249358	0.423858
1	0.38439	0.221406	0.394204
1	0.446999	0.183728	0.369273
1	0.513469	0.135699	0.350832
1	0.579038	0.077477	0.343485
1	0.639481	0	0.360519

Fig. 7 Phase envelope compositions

Phase envelopes are graphical representation that shows the regions of stability for different phases of a substance or mixture under specific temperature and pressure. Drawing a phase envelope often requires a good understanding of the thermodynamics and phase behavior of the system. Additionally, experimental data or reliable equations of state can be essential for constructing an accurate phase envelope. Phase envelope is a valuable tool in thermodynamics, material science and process engineering for predicting and understanding phase transitions and the behavior of complex systems (Deiters & Bell, 2019; Lindeloff & Michelsen, 2003).

Azeotropy (Rios et al., 2018) refers to a special case of mixture behavior where the vapor phase and the liquid phase have the same composition, resulting in a constant boiling point or a constant composition during the distillation process, as if it were a pure substance (Fig. 8). If there are no azeotropic compositions in the ternary diagram, it implies that the mixture does not exhibit constant boiling points at any specific composition. In such cases, the mixture will show varying compositions of the vapor and liquid phases during the distillation process.

Phase Envelope		Equilibrium Composition		Azeotrope	Status
Azeotrope compositions and temperature					
NUMBER	MOLEFRAC ANILINE	MOLEFRAC METHYLAM	MOLEFRAC WATER	TEMP	
1	0.043098	0	0.956902	372.505	K

Fig. 8 Azeotropic composition and temperature

Without azeotropy, it may be possible to separate the components of the mixture more easily, as there are no fixed boiling points that hinder the separation. Figure 8 points to the existence of a single azeotrope at 372.505 K. As shown, the azeotropic composition of MAN in the ternary mixture is zero. It implies that this component does not participate in the azeotropic behavior. There was only an azeotropic behavior between aniline and water. When one component's azeotropic composition is zero, it means that its presence in the vapor phase is negligible, and its concentration in the liquid phase is constant during distillation. This does not hinder the existence of azeotropy. The presence or absence of azeotropy can vary with changes in temperature and pressure, as well as the specific components in the mixture (Abildskov & O'Connell, 2014; Gibbard & Emptage, 1975). Additionally, not all ternary mixtures exhibit azeotropic behavior, and azeotropy is relatively rare and specific to certain systems.

4. Conclusion

It is very imperative to hand-pick the most fitting property method when simulating real processes, if it has been proven to be so, after series of test or analysis. Here, the logarithm of the partition coefficient of MAN (i.e., 0.525045) is the basis under which the best property model for the LLE method was selected. NRTL, UNIFAC and UNIQUAC's lowest value of $\log P$ falls below the equilibrium value of 0.525045, of which a property method with higher estimate above this value would have been the best model. WILSON activity coefficient model is not suitable for modeling systems consisting of more than one liquid phase, especially in LLE, even though it has the highest value of $\log P$; simply because they are too high and atypical of $\log P$ values of equilibrium mixtures. Thus, UNIQUAC is next in line to satisfy the selection criteria because its $\log P$ value is very much closer to the equilibrium value and hence taken as the best model for a two-stage separation of water/aniline/MAN mixture. Therefore, in order to purify water and get rid of either aniline or MAN from it, UNIQUAC model and a two-stage 'Extract' and 'RadFrac' Aspen Plus models can be used, by forming a ternary mixture of the 3 components to be separated into raffinate and extract streams. The quest to determine the best property method to be used for variety of ternary mixtures is seriously stressed in this study by testing only few common Aspen Plus models. Upcoming studies need to look at additional model's effect on $\log P$ for this particular mixture and others already exemplified, as well as utilizing a different simulation tool.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: **study conception and design:** Abubakar, A.M., Marvin, M.K., & Saad, M.; **data collection:** Wali, S.A., Waziri, A.Y., Abdul. A.Z., Abubakar, M.A., & Yusuf, A.A.; **analysis and interpretation of results:** Coto, B., & Abubakar, A.M.; **draft manuscript preparation:** Yunus, M.U., Baka, Z.M.S., & Ngulde, A.B. All authors reviewed the results and approved the final version of the manuscript.

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