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**RECOVERY OF CARBOXYLIC ACIDS FROM
AQUEOUS STREAMS BY EXTRACTION AND BACK
EXTRACTION**

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Tiivistelmä

Karboksyylihappojen erottaminen vesivirroista on tärkeä osa niiden valmistusta. Vesiliuokset ovat yleensä laimeita sisältäen alle 10 % happoja. Happojen erottaminen tislamalla on hankalaa, sillä niiden kiehumispisteet ovat vain hieman veden kiehumispistettä suurempia. Tämän takia tislaminen on paitsi hankalaa, myös kannattamatonta suurien vesimäärien höyrystämisen takia. Happoja on perinteisesti saostettu kalsiumsuoloina. Näiden prosessien saannot jäävät kuitenkin pieniksi ja kemikaalikulutukset ovat suuria. Etenkin kalsiumsuolojen hajottaminen rikkihapolla tuottaa suuria määriä kalsiumsulfaattilietettä.

Neste-nesteuuttoa on tutkittu vaihtoehtoisena tapana karboksyylihappojen talteenotossa. Uutto perustuu kahden toisiinsa liukenemattoman faasin sekoittamiseen, jolloin halutut komponentit siirtyvät liuksesta toiseen tasapainoeroon perustuen. Karboksyylihappojen tapauksessa hapot siirtyvät vesifaasista orgaaniseen faasiin fysikaalisten ja kemiallisten ilmiöiden vaikutuksesta. Hapot muodostavat yhdessä uuttoaineen kanssa orgaaniseen faasiin liukenevia komplekseja. Uuttotehokkuuteen vaikuttaa moni tekijä, muun muassa alkuperäinen happokonsentraatio, uuttoaineen tyyppi ja konsentraatio, pH, lämpötila sekä uuttoaika. Tässä työssä tutkittiin ennen kaikkea vesifaasin alkuperäisen happokonsentraation, uuttoaineen ja lämpötilan vaikutusta uuttotehokkuuteen.

Koska karboksyylihapot ovat yleensä prosesseissa tuotteita, jotka halutaan saada talteen, on ne uuton jälkeen poistettava orgaanisesta liuottimesta. Happojen poistaminen orgaanisesta faasista myös regeneroi uuttoaineen jolloin sitä voidaan kierrättää prosessissa. Uuttoaineiden regenerointia tutkittiin takaisinuuuttamalla eli strippaamalla hapot orgaanisesta faasista laimeaan natriumhydroksidiliuokseen. Regenerointikokeissa tutkittiin eri uuttoaineiden regeneroitavuutta sekä alkuperäisen happokonsentraation ja lämpötilan vaikutusta.

Hakusanat: karboksyylihappo, neste-nesteuutto, takaisinuuutto, uuttoaineen regenerointi, strippaus.

Abstract

Separation of carboxylic acids from aqueous streams is an important part of their manufacturing process. The aqueous solutions are usually dilute containing less than 10 % acids. Separation by distillation is difficult as the boiling points of acids are only marginally higher than that of water. Because of this distillation is not only difficult but also expensive due to the evaporation of large amounts of water. Carboxylic acids have traditionally been precipitated as calcium salts. The yields of these processes are usually relatively low and the chemical costs high. Especially the decomposition of calcium salts with sulfuric acid produces large amounts of calcium sulfate sludge.

Solvent extraction has been studied as an alternative method for recovery of carboxylic acids. Solvent extraction is based on mixing of two immiscible liquids and the transfer of the wanted components from one liquid to another due to equilibrium difference. In the case of carboxylic acids, the acids are transferred from aqueous phase to organic solvent due to physical and chemical interactions. The acids and the extractant form complexes which are soluble in the organic phase. The extraction efficiency is affected by many factors, for instance initial acid concentration, type and concentration of the extractant, pH, temperature and extraction time. In this paper, the effects of initial acid concentration, type of extractant and temperature on extraction efficiency were studied.

As carboxylic acids are usually the products of the processes, they are wanted to be recovered. Hence the acids have to be removed from the organic phase after the extraction. The removal of acids from the organic phase also regenerates the extractant which can be then recycled in the process. The regeneration of the extractant was studied by back-extracting i.e. stripping the acids from the organic solution into diluent sodium hydroxide solution. In the solvent regeneration, the regenerability of different extractants and the effect of initial acid concentration and temperature were studied.

Keywords: carboxylic acid, solvent extraction, back extraction, solvent regeneration, stripping.

NOMENCLATURES

A^-	negative ion of acid
$[A^-]$	concentration of negative ion of acid, mol/dm ³
c	concentration, g/g(solution)
c_0	initial concentration, g/g(solution)
$E\%$	extraction efficiency, %
H^+	hydrogen ion
$[H^+]$	concentration of hydrogen ions, mol/dm ³
HA	carboxylic acid
$[HA]$	concentration of acid, mol/dm ³
K_a	dissociation constant, -
m	mass, kg
n	stoichiometric coefficient, -
pK_A	acid dissociation constant, -
R_3N	amine
x	mass fraction, %
∞	infinitely soluble

Subscripts

aq	aqueous phase
org	organic phase

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1. Introduction

Carboxylic acids are recovered as a product for instance from fermentation broths and waste waters (Yang *et al.* 1990). Acids are present in low concentration in aqueous streams, the concentration of acids is usually less than 10 wt%. The industries where recovery by solvent extraction is applied are for instance food, plastics, pharmaceutical and biotechnology. (Morales *et al.* 2003; Keshav and Wasewar 2010.)

Carboxylic acids are difficult to separate by distillation due to small differences in boiling points between acids and water and as the acids are often nonvolatile (Ki Hong *et al.* 2001). The boiling point of water is lower than that of carboxylic acids which leads to expensive water evaporation. The conventional method used in separation of acids is precipitation of the acid as calcium salt with calcium hydroxide. The drawbacks of precipitation are chemical consumptions and costs, low yields and losses. (Ki Hong *et al.* 2001.) It is also environmentally unfriendly as it produces calcium sulfate sludge when sulfuric acid is used to decompose calcium salts in the process (Keshav and Wasewar 2010). Solvent extraction has been studied as a substitutive method for distillation and precipitation.

The factors that were studied in this thesis were the type of acid in the solution, the initial concentration of the acid, the extractant and temperature. Two common carboxylic acids, formic and acetic acids were extracted with three extractants, called here extractants 1, 2 and 3.

The regenerability of extractant is an economically and environmentally important factor. The carboxylic acids have to be recovered from the organic solution as products. The acids can be removed from the loaded organic solvent by for instance back extraction. This also regenerates the solvent. The extractants are quite expensive substances and it is thus crucial to use them as efficiently as possible. If the extractant can be regenerated i.e. the acid can be backextracted from the organic phase, the extractant can be reused. This decreases the amount of extractant needed in process

and can have great effect on process economy and profitability as well as environmental issues.

Recovery of carboxylic acids can be studied by laboratory scale measurements. The acids that were studied in these experiments were formic acid HCOOH and acetic acid CH_3COOH .

The regenerability of extractants was studied in a similar way as the extraction. The regeneration was done with sodium hydroxide solution using the organic solution obtained from extraction tests. The factors that were studied were the type and the concentration of acid, temperature and the type of extractant.

2. Solvent extraction

Solvent extraction is a chemical separation process which is used to transfer the wanted compounds or impurities from aqueous phase to organic phase (Habashi 1999). The organic phase contains extractant and solvent. According to Habashi (1999) solvent extraction can only be used for clear solutions with no solid material. Solvent extraction is used also widely in metallurgical industry to transfer metals from aqueous leach solution into organic solvent to be further processed into pure metal.

2.1. Solvent extraction of carboxylic acids

Carboxylic acids are extracted from many sources of aqueous solutions, for instance in food, plastics, pharmaceutical and biotechnological industries (Morales *et al.* 2003; Keshav and Wasewar 2010). Fermentation broths and waste waters are often the sources of dilute, less than 10 %, solutions (Yang *et al.* 1990).

The separation of carboxylic acids by distillation is difficult as the solutions are often nonvolatile (Ki Hong *et al.* 2001). Especially for dicarboxylic acids distillation is not effective either chemically or economically (Poole and King 1991). The conventional method used in separation of acids is precipitation of the acid as calcium salt with

calcium hydroxide. The disadvantages of this method are chemical consumptions and costs, low yields and losses. (Ki Hong *et al.* 2001.) It is also environmentally unfriendly as it produces much waste in the form of calcium sulfate sludge when acid is formed by reaction of calcium salt with sulfuric acid (Keshav and Wasewar 2010). The mentioned two methods, distillation and precipitation, are hence not effective for separation and, therefore, solvent extraction has been studied as an alternative method for recovery of carboxylic acids.

Carboxylic acids are a group of organic molecules that have a carboxylic group COOH. Carboxylic acids ionize partially in aqueous solutions according to reaction



HA carboxylic acid
 H^+ hydrogen ion
 A^- negative ion of acid

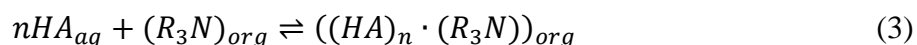
The dissociation constant is hence

$$K_a = [H^+]_{aq}[A^-]_{aq}/[HA]_{aq} \quad (2)$$

K_a dissociation constant
 $[H^+]$ concentration of hydrogen ions
 $[A^-]$ concentration of negative ion of acid
 $[HA]$ concentration of acid
 aq aqueous phase

Extraction of carboxylic acids is both a physical and a chemical phenomenon. The chemical interactions happen between the acid and the extractant forming, for instance, acid-amine complexes which dissolve in the organic diluent (Ki Hong *et al.* 2001). The reaction between acid in aqueous phase and solvent produces a complex

that is solubilized into organic phase. The extractants that are used in reactive extraction are divided into three categories: carbon-bonded oxygen-bearing extractants, phosphorus-bonded oxygen bearing extractants and high molecular weight aliphatic amines. Two first mentioned are based on solvation while amine extraction is based on proton transfer. (Ki Hong *et al.* 2001) Uslu (2009) represents the complexation reaction of formic acid with tertiary amines as



n stoichiometric coefficient

R_3N amine

org organic phase

Aliphatic amines are reported to be the most effective ones, especially tertiary amines. Tertiary amines extract only the undissociated acids while for example quaternary amines extract dissociated forms as well which lead to difficulties in stripping. Han *et al.* (2000) studied phosphorus-bonded and amine extractants. The extraction efficiencies in that study were 45-50 % for phosphorus-bonded and 60-90 % for amine based extractants. In this study, it was also seen that the extractability of amines increase when the number of carbons in the amine increases. However, if the amount of carbons in one chain is higher than eight, the extractability decreases. This means that the best tertiary amine for extraction could be trioctylamine. (Han *et al.* 2000.)

According to Morales *et al.* (2003) the diluent removes the acid by physical extraction. The behavior of these systems is very non-ideal (Uslu 2009). The physical forces have a less significant role in the extraction but they may differentiate the test results as both chemical and physical interactions happen simultaneously and are difficult to separate. When active diluent, for instance methylene chloride or chloroform is used in reactive extraction, it affects the solubility of the acid-complex

in the organic phase. With higher active diluent concentrations the solubility is higher. This helps both the extraction and the stripping process. (Han *et al.* 2000.)

2.2. Factors affecting the extraction

The main factors affecting the extraction are the nature of acid, concentration and type of the extractant, type of diluent and pH (Yang *et al.* 1990; Qin *et al.* 2003; Ki Hong *et al.* 2001). The most important properties of the acids are the strength of the acid and hydrophobicity (Qin *et al.* 2003). Tamada *et al.*(1990) have studied the effects of these factors (Yang *et al.* 1990; Tamada *et al.* 1990). Ki Hong *et al.* (2001) have studied the effect of pH, which they state to have the biggest effect of dissociation rate of acids in the aqueous phase. This affects the equilibrium in the extraction.

2.2.1. Effect of acid concentration

Ki Hong *et al.* (2001) and Tamada and King (1990b) have stated that more acidic acids can be extracted more efficiently. Tamada and King (1990b) also stated that the hydrogen bonding between the acid molecules affects complex stoichiometry and the amount and rate of different complexes is different to each acid. According to Tamada and King (1990b) the effect of hydrophobicity is relatively small compared to that of acidity. In the experiments of Tamada and King (1990b) malonic acid is extracted more than succinic acid although malonic acid is less hydrophobic. The predictability of the effects of acidity and hydrophobicity are difficult as acidity is an aqueous-phase property and complex formation takes place in the organic phase (Tamada and King 1990b).

2.2.2. Effect of pH

Ki Hong *et al.* (2001) studied the effect of pH on solvent extraction of carboxylic acids. The concentration of the undissociated acid is a function of pH, so extraction is influenced by pH in the aqueous phase. Ki Hong *et al.* (2001) used succinic acid and formic acid when studying the effect of pH, and concluded that the loading of the extractant increased when pH decreased leading to better extraction, especially when

the extractant extracts only the undissociated acid, like for instance Extractant 3 does. The extraction was found to be more effective with more acidic acids.

2.2.3. Effect of extractant and diluent

According to Yang *et al.* (1990) solvents used in extraction of carboxylic acids can be divided into three major groups: conventional oxygen bearing and hydrocarbon extractants, phosphorus-bonded oxygen bearing extractants and high molecular weight aliphatic amines. This division of extractants is used in many other sources as well. From these groups, the aliphatic amines are the most effective ones and especially tertiary amines are widely seen as the best extractants for carboxylic acids (Ki Hong *et al.* 2001). Primary and secondary amines can react irreversibly which leads to problems in product recovery. Quaternary amines have also problems as they extract the dissociated acids as well. Tertiary amines extract only the undissociated acids and are easier to strip. (Ki Hong *et al.* 2001.) Especially extractant 3, used in this study, is very powerful extractant. According to Han *et al.* (2000) long chained tertiary amines, such as extractant 3 give the highest extraction efficiencies (Uslu 2009).

Extractants are usually not used as pure compounds but they are dissolved in a suitable organic diluent. Wide variety of different diluents are used, such as kerosene, ketones, alcohols and aromatic solvents. Qin *et al.* (2003) state that polar diluents are more favorable than non-polar as they can form hydrogen bonds with the oxygen in the acid and enhance the extraction. According to Han *et al.* (2000) the extraction efficiency increases when the tertiary amine concentration increases. However, the amines are highly corrosive in high concentrations and the concentration has to be selected appropriately to avoid corrosion. (Han *et al.* 2000.)

2.3. Solvent recovery by back extraction

The carboxylic acids have to be removed from the organic phase after extraction to obtain pure carboxylic acid products. When stripping the acids from the solvent, the solvent is recovered as well and can be re-used. The extractants are often relatively expensive so the recovery of the extractant is an economically important factor when

selecting the extractant. Solvent extraction processes are often done in ambient temperatures meaning that the majority of costs come from chemicals and mixing. The circulation of the extractant affects remarkably the economy of the process. When selecting the appropriate extractant to a process, the recovery properties must be examined carefully.

The back extraction process can be understood as reversal reaction compared to the extraction stage. The acid is recovered as a product and the extractant can be recycled. Keshav and Wasewar (2010) studied different methods for back extraction: back extraction using NaOH, trimethyl amine, temperature swing and diluent swing. Back extraction with NaOH and trimethyl amine are based on the higher solubility of the acids in these substances compared to organic phase. In temperature and diluent swing the extraction is based on the change in the extraction equilibrium. Type of organic phase and acid concentration affect to all of these methods. Both NaOH and trimethyl amine extractions can result in 100 % regeneration. (Keshav and Wasewar 2010.)

In this study, back extraction with NaOH was studied with respect to the type and concentration of acid, type of organic solvent and temperature. Keshav and Wasewar (2010) have stated that solvent can be entirely regenerated with NaOH when using NaOH/organic ratio over 1 with contact time of 24 hours.

Tertiary amines are the best extractants also when concerning back-extraction. Primary and secondary amines form stable amides and the back-extraction process becomes difficult. (Poole and King 1991.)

3. Experimental

The extraction experiments consisted of three parts: extraction, settling and analyses. The effect of organic solvent, acid concentrations, mixing rates and times and aqueous/organic –ratio were studied.

The solvent regeneration experiments consisted of six parts: extraction, settling, analyses, back extraction, settling and analyses.

3.1. Chemicals and methods

Two carboxylic acids, formic acid and acetic acid were used in the experiments. Formic acid and acetic acid are both colorless liquids which are entirely soluble in water.

Formic acid, also known as hydrogen carboxylic acid is a medium strong acid which reacts strongly with oxidants and strong bases. Formic acid consists of hydrogen bonded dimers as shown in Figure 1 (Uslu 2009). In liquid phase, which is the case in these study, formic acid can be thought as an infinite network with hydrogen bonds (Uslu 2009). The purity of formic acid was 98 %.

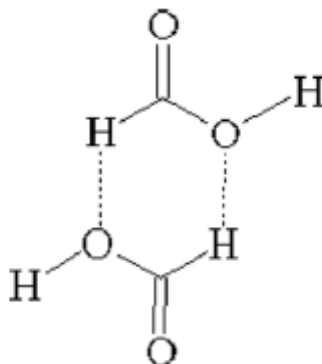


Figure 1. Dimeric structure of formic acid. (Uslu 2009)

Acetic acid, also known as methanecarboxylic acid is a weak acid which reacts strongly with strong acids and strong bases. The purity of acetic acid was 99.8 %. The physical properties of formic and acetic acid are shown in Table I.

Table I. Physical properties of formic acid and acetic acid. (Perry 1997, Evans' pKa table)

	Formic acid	Acetic acid
Molecular formula	HCOOH	CH ₃ COOH
Molecular weight (g/mol)	46,03	60,05
Specific gravity	1,220 ^{20/4}	1,049 ^{20/4}
Melting point (°C)	8,6	16,7
Boiling point (°C)	100,8	118,1
Solubility in water	∞	∞
pK _A	3.77	4.76

Three organic extractants, namely extractant 1, extractant 2 and extractant 3 were used. Extractant 3 and extractant 2 were used as pure, unused solutions. Extractant 1 contained some acids as it was regenerated after using it in previous experiments. The acidic content was determined to be about 7-8 wt-% and the exact concentration was taken into account when determining the extractions. However, this might have affected the results as the extraction efficiency with non-pure solvent is not as good as that of pure solvent.

Sodium hydroxide was used as 0,05 mol/L solution in titration to determine acid concentrations after extraction and as 0,1 mol/L solution in solvent regeneration. 99 % solid NaOH was used for solutions. Phenolphthaleine solution was used as indicator in acid-base titrations.

3.2. Solution preparation

Acid concentrations that were used in the initial equilibrium curve determination tests were 3 wt%, 15 wt%, 25 wt% and 35 wt% both for formic and acetic acid. The solutions were prepared in 1000 ml bottles and the same solution was used in all tests concerning the same concentration. This way the initial concentration of acid and possible impurities were the same in the corresponding tests with different extractants. These concentrations were used to determine the equilibrium curves and extraction efficiencies. The exact properties of the acidic solutions are shown in Table II where also the solutions used in solvent regeneration part are shown.

Table II. Initial acidic solution for all phases of experiments.

Solution	Acid	m (acid) (g)	m (solution) (g)	x (wt-%)
1	Formic	30.31	1000.00	0.0303
2	Acetic	30.01	1000.44	0.0300
3	Formic	50.06	1000.22	0.0500
4	Acetic	50.02	1000.02	0.0500
5	Formic	150.05	1000.16	0.1500
6	Acetic	150.00	1000.00	0.1500
7	Formic	200.06	200.06	0.2001
8	Acetic	200.15	200.15	0.2001
9	Formic	250.03	1000.05	0.2500
10	Acetic	249.98	1000.03	0.2500
11	Formic	349.97	1000.06	0.3499
12	Acetic	349.98	1000.01	0.3500

Sodium hydroxide solutions were made by dissolving solid NaOH into water. Phenolphthaleine solution was made by mixing solid phenolphthaleine in water. Three NaOH solution were made for titrations. Properties of NaOH solutions are presented in Table III.

Table III. Sodium hydroxide solutions used in experiments.

Solution	m (NaOH) (g)	V (solution) (L)	c (mol/L)
NaOH 1	2.1407	1.0	0.0535
NaOH 2	0.1968	0.1	0.0492
NaOH 3	2.0101	1.0	0.0503
NaOH BE	4.0285	1.0	0.1007

3.3. Extraction and settling

The solutions, extractants and conditions in each experiment in the first phase are shown in Table IV.

Table IV. Extraction tests in first phase: solutions, extractants, and conditions.

No	Acid	x(init), wt%	Solvent	m initial (g)	m solvent (g)	Mixing (min)	Mix rate (rpm)	T °C	Settling (min)
1	FA	3.03	Ext 3	100.28	80.28	30	750	22	150
2	FA	3.03	Ext 3	100.28	80.22	30	750	37	120
3	FA	15.00	Ext 3	51.69	39.93	30	500	22	60
4	FA	15.00	Ext 3	51.57	39.53	30	500	38	150
5	FA	25.00	Ext 3	52.81	39.97	30	500	22	90
6	FA	25.00	Ext 3	52.7	39.82	30	500	38	90
7	FA	34.99	Ext 3	53.78	39.72	30	500	22	70
8	FA	34.99	Ext 3	53.85	39.72	30	500	38	45
9	AA	3.00	Ext 3	49.9	40.23	30	500	21	40
10	AA	3.00	Ext 3	49.84	40.03	30	500	38	40
11	AA	15.00	Ext 3	50.72	40.04	30	500	21	50
12	AA	15.00	Ext 3	50.59	39.98	30	500	38	50
13	AA	25.00	Ext 3	51.27	39.89	30	500	21	50
14	AA	25.00	Ext 3	51.17	40.13	30	500	38	30
15	AA	35.00	Ext 3	51.75	40.17	30	500	21	50
16	AA	35.00	Ext 3	51.79	40.03	30	500	38	50
17	FA	3.03	Ext 2	50.05	42.41	30	500	21	70
18	FA	3.03	Ext 2	50.07	42.36	30	500	38	40
19	FA	15.00	Ext 2	51.47	42.35	30	500	21	45
20	FA	15.00	Ext 2	51.49	42.32	30	500	38	30
21	FA	25.00	Ext 2	52.64	42.38	30	500	21	35
22	FA	25.00	Ext 2	52.63	42.36	30	500	38	35
23	FA	34.99	Ext 2	53.85	42.36	30	500	21	45
24	FA	34.99	Ext 2	53.81	42.37	30	500	38	65
25	AA	3.00	Ext 2	49.85	42.34	30	500	21	105
26	AA	3.00	Ext 2	49.8	42.35	30	500	38	40
27	AA	15.00	Ext 2	50.69	42.37	30	500	21	30
28	AA	15.00	Ext 2	50.58	42.33	30	500	38	65
29	AA	25.00	Ext 2	51.28	42.35	30	500	21	40
30	AA	25.00	Ext 2	51.28	42.42	30	500	38	45
31	AA	35.00	Ext 2	51.73	42.7	30	500	21	30

Acidic solution was mixed with organic solvent in a 250 mL Erlenmeyer flask. The volumes of both phases were 50 mL except in the first two tests where the volumes were 100 mL. The exact masses were measured for mass balance calculations. The phase ratio O/A was 1:1 in all cases. Mixing time was 30 minutes and mixing rate

varied between 500 rpm and 700 rpm. Mixing rate was adjusted so that no foam was formed during mixing but the mixing was still thorough. After the mixing the solution was left to settle in a separating funnel. Settling time was between 30 minutes and 150 minutes. In some experiments, emulsion- like layer was formed in the boundary of the phases. The settling time was selected individually for each case so that the separation was complete and the emulsion- like boundary had disappeared. In all cases this was not possible to achieve as the boundary phase was stable. According to Tamada (1990) this so called third phase contains the most of the extracted acid. Because of this, the phases were separated so that the emulsion- like phase was taken with the organic phase. The phases were taken into sample bottles and they were weighted for mass balance and distribution calculations.

3.4. Analysis

A sample of 120-150 mg was taken from both organic and aqueous phase. The exact masses were used to calculate the acid content of the sample. The samples were mixed with about 150 mL of water and soluted phenolphthaleine indicator in a 250 mL flask and mixed with a magnetic stirrer. The dispersion of organic solvent had to be complete and foam formation avoided.

The total acidic content of the samples were determined by titration. Titration was done using 0,05 molar NaOH. The exact volume of NaOH consumed were used to calculate the amount of acids in the samples

3.5. Solvent regeneration

The main methods in solvent regeneration tests were similar to those in the first part. Therefore only the differences are explained in this chapter.

In solvent regeneration experiments, the extractions were made using 5 wt% and 20 wt% solutions of both formic and acetic acid. The solutions were prepared in similar way as in the first part. The preparation of these solution are shown in Table II.

Mixing was done similarly and 50 mL of both liquids were used. Settling and separation were done similarly as well. The solutions, extractants and conditions are shown in Table V.

Table V. Solution, extractants and conditions in extraction experiments in solvent regeneration phase.

No	Acid	x(HA) , wt%	Solvent	m initial (g)	m solvent (g)	Mixing (min)	Mix rate (rpm)	T °C	Settling (min)
S1	AA	5.00	Ext 3	49.83	40.01	30	500	20	30
S2	AA	20.01	Ext 3	50.89	40.11	30	500	20	30
S3	FA	5.00	Ext 3	50.12	40.20	30	500	20	30
S4	FA	20.01	Ext 3	52.04	40.04	30	500	20	30
S5	AA	5.00	Ext 3	49.86	39.90	30	500	40	30
S6	AA	20.01	Ext 3	50.80	39.88	30	500	40	30
S7	FA	5.00	Ext 3	50.17	39.84	30	500	40	30
S8	FA	20.01	Ext 3	52.00	39.87	30	500	40	30
S9	AA	5.00	Ext 2	49.84	45.52	30	500	20	30
S10	AA	20.01	Ext 2	50.93	42.48	30	500	20	30
S11	FA	5.00	Ext 2	50.17	42.47	30	500	20	30
S12	FA	20.01	Ext 2	51.95	42.53	30	500	20	30
S13	AA	5.00	Ext 2	49.89	42.42	30	500	40	30
S14	AA	20.01	Ext 2	50.87	42.35	30	500	40	30
S15	FA	5.00	Ext 2	50.19	42.54	30	500	40	30
S16	FA	20.01	Ext 2	51.95	42.50	30	500	40	30

Analyses in extraction part were similar to those in the first part.

In solvent regeneration, the organic solutions obtained from previous extractions were regenerated using 0,1 molar NaOH solution. All of the solutions were not used and the used solutions and conditions of the experiments are shown in Table VI.

Table VI. Solutions and conditions of solvent regeneration experiments.

No	Acid	Solvent	m NaOH (g)	m solvent (g)	Mixing (min)	Mix rate (rpm)	T (°C)	Settling (min)
B1	3.00 % AA	Ext 3	20.08	20.08	30	450	20	30
B2	17.24 % AA	Ext 3	21.2	21.15	30	450	20	30
B3	2.75 % FA	Ext 3	20.29	20.25	30	450	20	30
B4	18.26 % FA	Ext 3	20.28	20.21	30	450	20	30
B6	16.68 % AA	Ext 3	21.23	20.94	30	450	40	30
B8	18.40 % FA	Ext 3	21.47	21.34	30	450	40	30
B10	13.80 % AA	Ext 2	22.15	22.38	30	450	20	30
B12	13.06 % FA	Ext 2	22.58	22.61	30	450	20	30
B14	14.11 % AA	Ext 2	22.53	22.52	30	450	40	30
B16	12.58 % FA	Ext 2	22.5	22.58	30	450	40	30

About 20 g of an organic solution was mixed with similar mass of NaOH solution for 30 min in a 250 mL flask. After this the phases were separated in a separating funnel for at least 30 min. In this case the separation was quite fast and the 30 min separation time was sufficient. The separated phases were taken into sample bottles and weighted for mass balance calculations.

The acid content was determined by titration with 0,05 molar NaOH solution from the organic phase. The determination was done in similar manner as before. The properties of NaOH solutions are shown in Table III.

4. Results and discussion

In the first part, the extraction efficiencies and equilibrium curves were determined for each extractant; extractant 3, extractant 1 and extractant 2. The effect of extractant was studied for formic and acetic acid in concentration between 3 and 35 wt%. The effect of temperature was studied in 21 °C and elevated temperature at 37 °C.

In the second part, solvent regeneration was studied for extractant 3 and extractant 1. Extractant 2 was excluded as in the first part it was found to be clearly the worst extractant.

4.1. Extraction efficiencies and equilibria

Extraction efficiency $E\%$ and distribution coefficient K_d are used to describe the performance of extraction. Extraction efficiency can be determined as

$$E\% = \frac{c(HA)_{org} \cdot m_{org}}{c_0(HA)_{aq} \cdot m_{0,aq}} \cdot 100\% \quad (4)$$

$c(HA)_{org}$	concentration of acid in organic phase after extraction, g/g solution
m_{org}	mass of organic phase after extraction, g
$c_0(HA)_{aq}$	initial concentration of acid in aqueous phase, g/g solution
$m_{0,aq}$	initial mass of aqueous phase, g

Distribution coefficient is determined as

$$K_d = \frac{c(HA)_{org}}{c(HA)_{aq}} \quad (5)$$

The extraction efficiencies of formic and acetic acids in different extractants are presented in Figure 2, Figure 3 and Figure 4 and the results in Appendix I. When comparing different extractants, it can be seen that extractant 1 has clearly the worst extraction efficiencies. The maximum efficiency achieved with extractant 1 is only 60 % and this is achieved only for 35 % acetic acid in 21 °C. For other experiments, the efficiencies are less than 50 %. The extraction efficiencies of extractant 2 are clearly better. Even the worst efficiencies of these extractants are more than 60 %. The shape of the efficiency curve of extractant 2 is different from that of the other extractants. It is higher with small and high initial concentrations and decreases in the middle. The efficiency is still relatively good especially for small concentrations. The efficiency curve of extractant 3 is somehow opposite from that of extractant 2 as the efficiency is best with the initial concentrations between 15-25 % and worse with small and big concentrations. At low acid concentrations the obtained efficiency is probably too low. This is due to the presence of the third phase which causes

problems in phase separation and sampling. The efficiency is even over 90 % in best cases and smaller than 70 % only with small initial concentrations. According to this data it seems that extractant 3 is the best extractant with intermediate concentrations (10-30 %) and probably also with small and high concentrations.

The separation of phases was not possible to do perfectly as in some cases a third phase was formed between the phases. However, there was not any rule or connection between experiments in which this layer was formed. It occurred with all extractants, acid concentrations and temperatures. This was probably caused by too intense mixing for extractant 2 and extractant 1. With too intense mixing there may be foam forming in the solution which doesn't separate easily. The mixing rate was kept constant in similar experiments so mixing intensity should not have been varied. In the end, there was no clear reason why this emulsion- like layer formed in some cases. For extractant 3 the reasons for third phase formation are the reaction between acid and amine and thermodynamics which separate the organic phase into two phases. This phenomenon made the phase separation more difficult as there was no clear phase boundary. This may affect to the masses of the phases and hence the mass balance calculations as well. According to Uslu (2009) this can modify the reversible complexation stage, which affects the extraction efficiency. Because this third phase is assumed to contain most of the acid and to consist mostly of organic liquid it was separated into organic phase (Tamada *et al.* 1990a).

For solvent regeneration, new extraction tests were made with 5 wt% and 20 wt% formic and acetic acids in extractant 3 and extractant 2. These concentrations were selected to be in between the concentrations used in first phase tests. Two test series were made: one at room temperature 20 °C and one at 40 °C. Equilibrium points for extractant 3 and extractant 2 are illustrated in same equilibrium curves as the initial extraction in Figure 2, Figure 3 and Figure 4. Acid concentration after extraction, extraction efficiencies and distribution coefficients are presented in Appendix I.

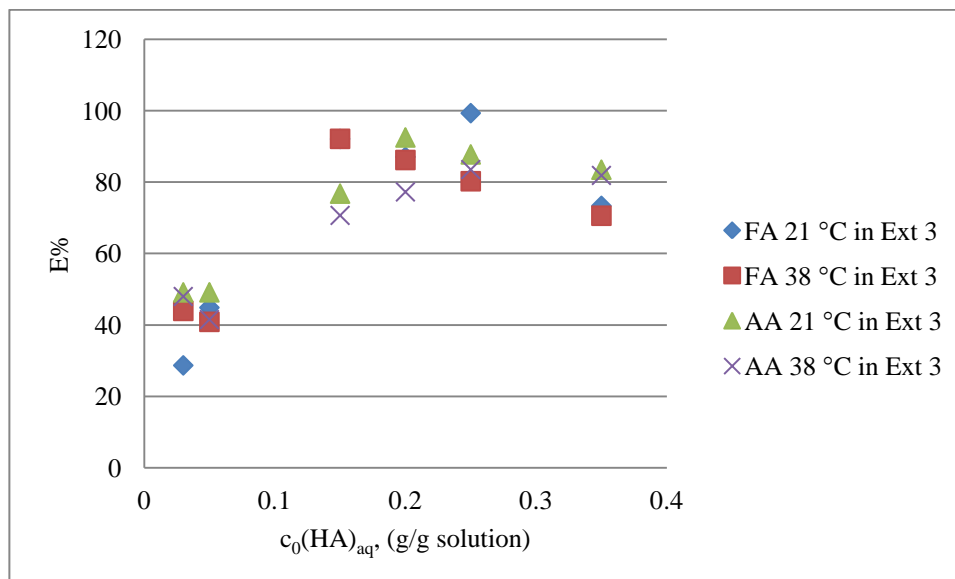


Figure 2. Extraction efficiency of extractant 3 for formic acid (FA) and acetic acid (AA) solutions. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

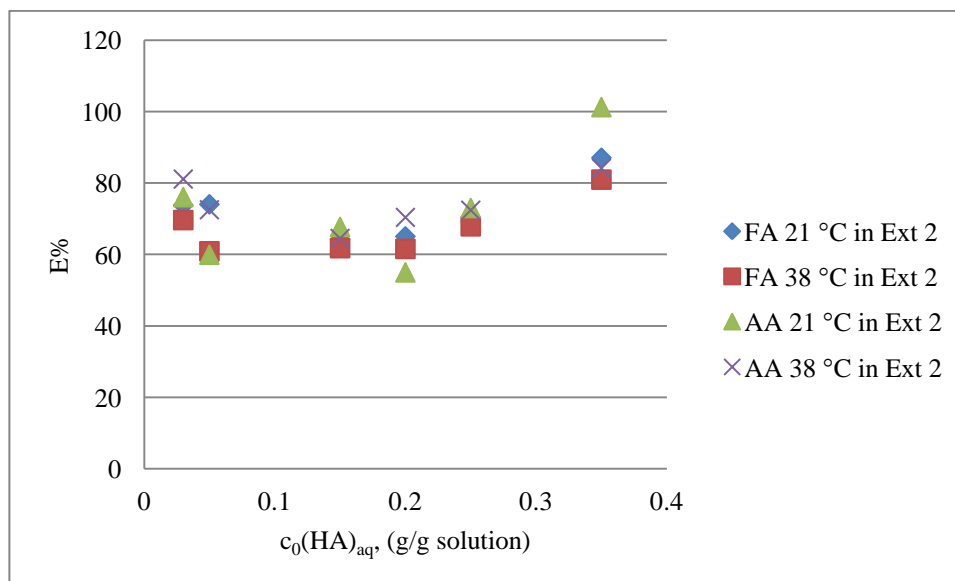


Figure 3. Extraction efficiency of extractant 2 for formic acid (FA) and acetic acid (AA) solutions. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

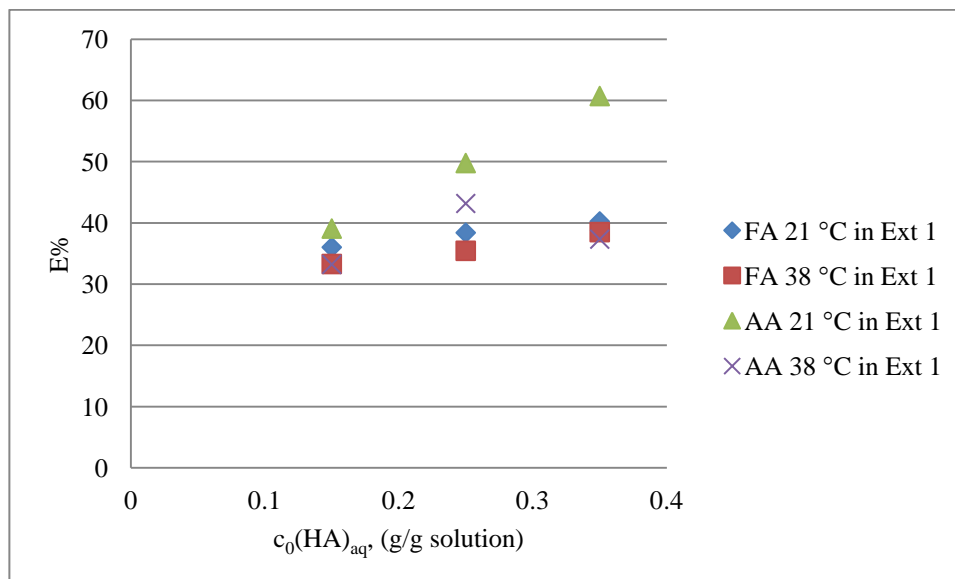


Figure 4. Extraction efficiency of extractant 1 for formic acid (FA) and acetic acid (AA) solutions. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

4.1.1. Effect of temperature

The effect of temperature for extraction was studied in two temperatures: room temperature 21 °C and elevated temperature of 38 °C. The effect can be seen from equilibrium curves for different extractants.

For extractant 3 the effect is difficult to see as the curves are not shaped the same manner as seen in Figure 5. However, for both acids it seems that the extraction is more efficient with the lower temperature 21 °C especially at higher concentrations. For extractant 2 the differences are not significant in either way. The efficiency at lower temperature might be slightly better as seen in Figure 6. For extractant 1 the efficiency with lower temperature is again better for both acids as seen in Figure 7. In summary, it can be said that the extraction is more efficient at lower temperatures but the difference is not significant.

Extractant 3 extracts formic acid better than acetic acid especially at low concentrations. In contrast, extractant 2 and extractant 1 extract acetic acid better than formic acid. The difference in the latter mentioned case is not remarkable. With

extractant 3 the third phase formation affects the results giving worse results at low concentrations.

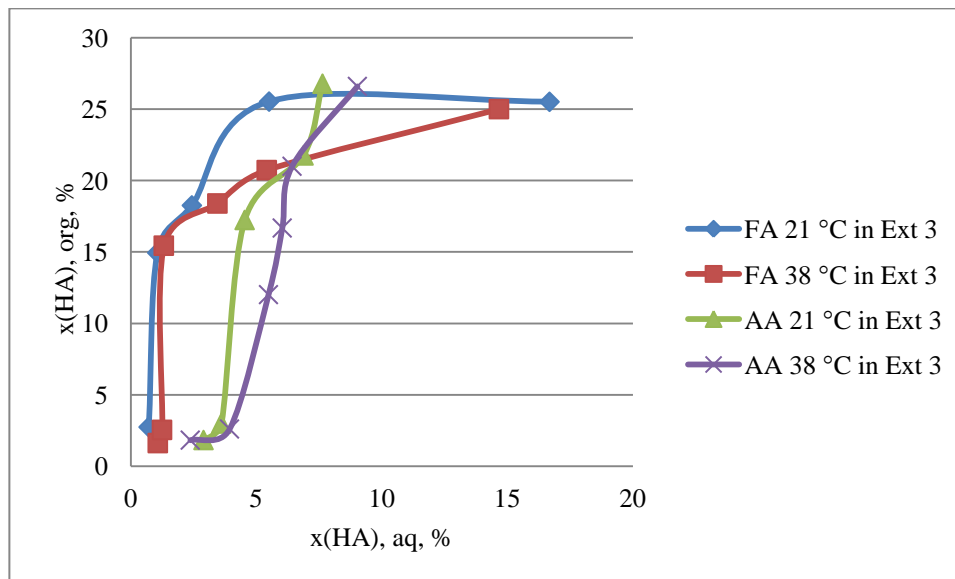


Figure 5. Equilibrium curve for extractions in extractant 3 for formic acid (FA) and acetic acid (AA) solutions. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

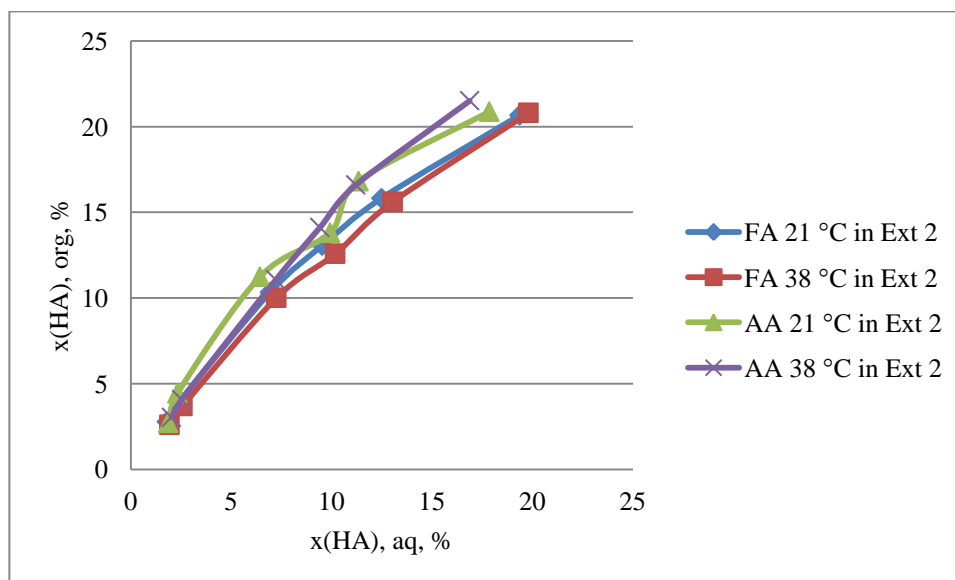


Figure 6. Equilibrium curve for extractions in extractant 2 for formic acid (FA) and acetic acid (AA) solutions. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

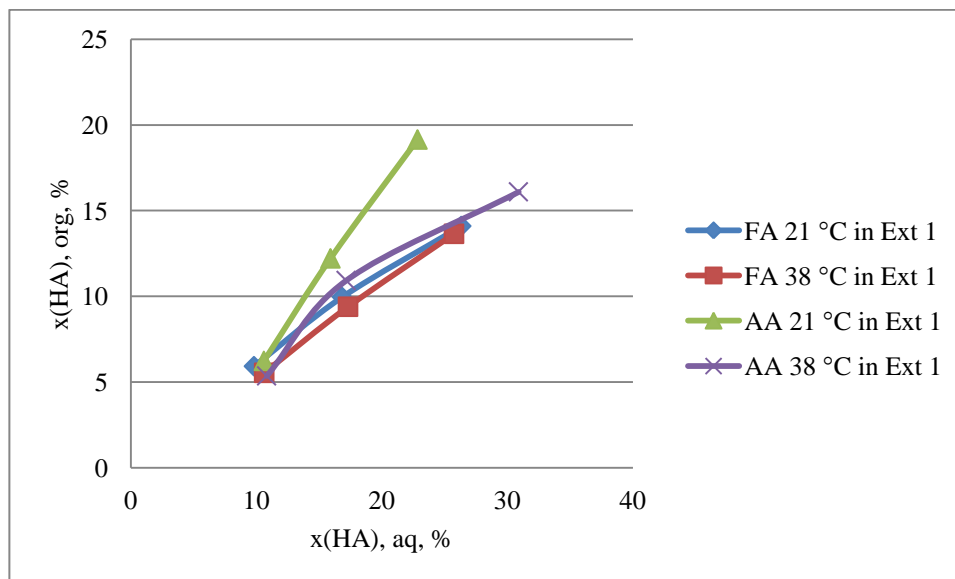


Figure 7. Equilibrium curve for extractions extractant 1 for formic acid (FA) and acetic acid (AA) solutions. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

4.1.2. Effect of extractant

In the experiments, three extractants were used: extractant 3, extractant 2 and extractant 1. The effect of extractant to equilibrium curve is very significant and clear. As it can be seen in all Figure 8, Figure 9, Figure 10 and Figure 11, the efficiency of extractant 3 is the best for both acids in both temperatures. extractant 2 seems to be competitive only in small concentrations for both acids and for acetic acid it is even better in low concentrations. In reality extractant 3 is probably better also at low concentrations but again the third phase formation affects the results and the obtained efficiencies are too low. It was already noticed from efficiency curve in Figure 3 that extractant 2 has good efficiency in low and high concentrations. Overall extractant 3 is the best extractant and extractant 1 has the worst efficiencies in each case for both acids.

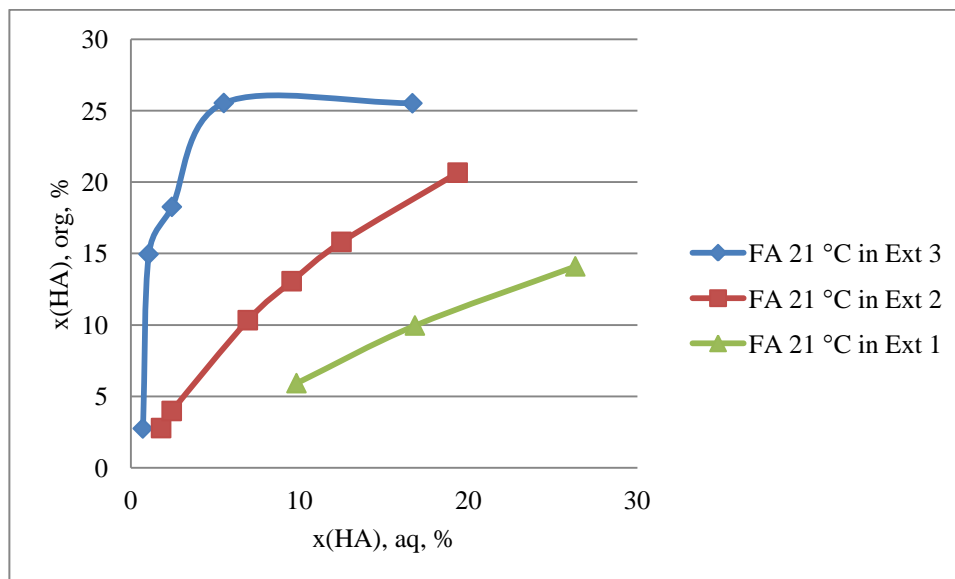


Figure 8. Equilibrium curves for formic acid in 21 °C. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

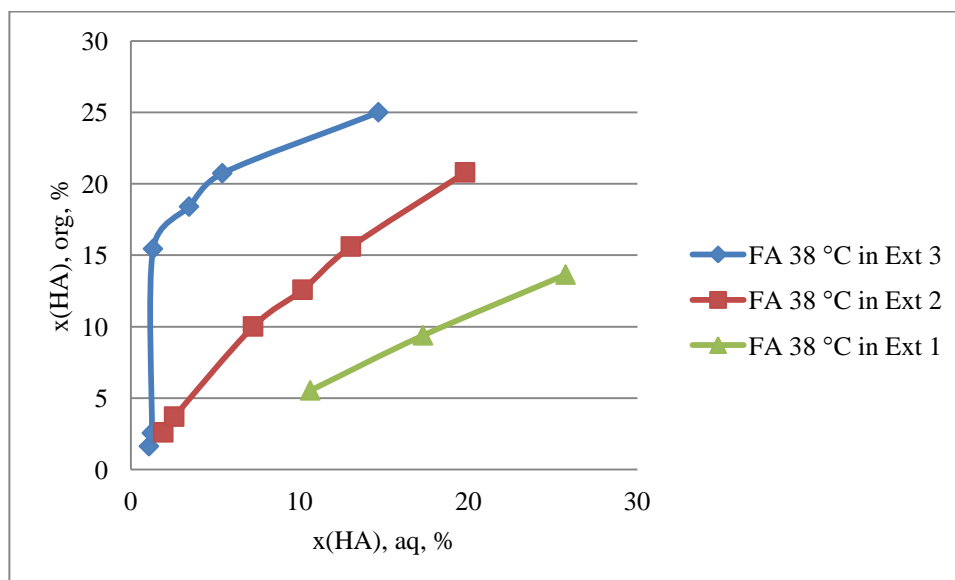


Figure 9. Equilibrium curves for formic acid in 38 °C. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

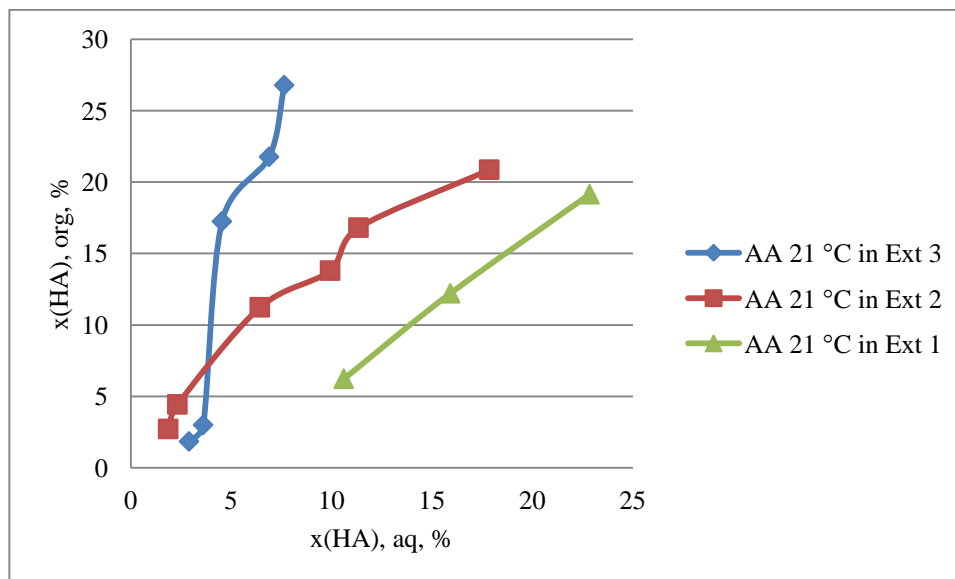


Figure 10. Equilibrium curves for acetic acid in 21 °C. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

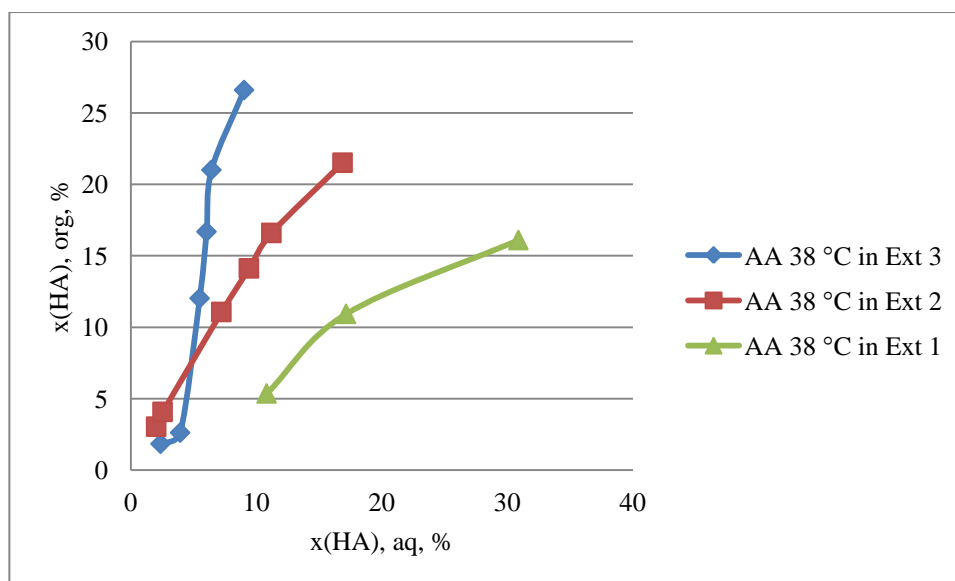


Figure 11. Equilibrium curves for acetic acid in 38 °C. Mixing 30 min with rate 500 rpm in 250 mL flask, O/A 1:1.

4.2. Solvent regeneration

For the solvent regeneration, organic solution which were obtained from initial solutions containing 20 wt-% acid were used. Two solutions with only 5 wt-% acid in initial solutions were used. The solutions are shown in Table VII.

Table VII. Initial solutions used in solvent regeneration.

No	Solvent	Acid	x_0 /wt-%	From test
B1	Ext 3	Acetic	2.998	S1
B2	Ext 3	Acetic	17.244	S2
B3	Ext 3	Formic	2.750	S3
B4	Ext 3	Formic	18.261	S4
B6	Ext 3	Acetic	16.683	S6
B8	Ext 3	Formic	18.400	S8
B10	Ext 2	Acetic	13.802	S10
B12	Ext 2	Formic	13.058	S12
B14	Ext 2	Acetic	14.115	S14
B16	Ext 2	Formic	12.583	S16

The solvent regenerability tests gave more reliable results when extractant 2 was regenerated. From all of the extractant 2 solutions more than 55 % of acids were removed. As seen in Figure 12, there is no difference in extraction between different acids or temperatures. From extractant 3 solutions, the back-extraction efficiency varied from 25 % to over 60 %. The back-extraction of acetic acid was better than that of formic acid. Acetic acid was extracted over 50 % with both lower and higher initial concentration while formic acid extraction was over 20 % smaller in both cases. Especially with higher initial concentrations the results were poor, one test gave extraction efficiency of 24 % and other gave a result that was negative and is excluded from the results. This is most likely caused by too dilute NaOH solution which cannot extract all the acids in the solution. With higher concentration the results would probably have been better. In the test where high concentration acetic acid was extracted at 20 °C, the extraction was only 36 % which differs greatly from the other value at this concentration range. The back-extraction efficiencies of all solvent regeneration tests are shown in Figure 12 and the results are presented in Appendix I.

Compared to results obtained by Keshav and Wasewar (2010) the back-extraction efficiencies are worse but the extraction and settling times used by Keshav and Wasewar were 48 times longer. Compared to this, over 50 % efficiency in much shorter time is relatively good. Keshav and Wasewar also suggested that

NaOH/organic rate should be over 1 and in these experiments rate of 1 was used. With higher NaOH concentration the poor results at high acid concentrations would probably have been better.

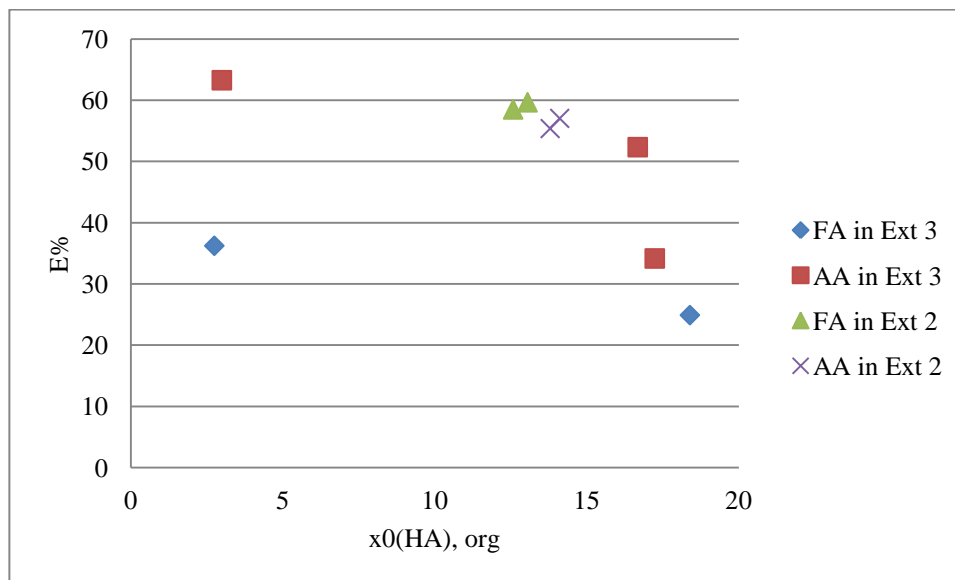


Figure 12. Back extraction efficiencies in solvent regeneration. Organic solutions from extraction tests used as initial solutions, regenerated with 0,1 mol/L NaOH solution. Mixing 30 min with rate 450 rpm in 250 mL flask, O/A 1:1.

5. Conclusions

Solvent extraction of carboxylic acids from aqueous streams and solvent regenerability were studied in laboratory scale. In the first phase, the extraction efficiency of three extractants; extractant 3, extractant 2 and extractant 1 were studied with formic and acetic acid. The factors affecting the extraction were the type and the concentration of the acid in the aqueous solution, the type of extractant and temperature. The extraction was studied with 30 min mixing time with O/A ratio 1.

In the second phase, extraction tests were carried out in a similar way and the extractants were recovered by back extracting the acids to sodium hydroxide solution. The factors that were studied were the type and the concentration of the acid in the solution, and temperature.

5.1. Extraction of carboxylic acids

In the extraction tests it was found out that extractant 3 was the best extractant having extraction efficiencies between 24 and 99 %. Especially with medium concentrations of 15 - 25 % the efficiencies were excellent concerning the extraction time, between 70 and 99 %. extractant 2 had extraction efficiencies between 60 and 90 %. With low and high concentrations of 3 % and 35 % extractant 2 was even better than extractant 3. The result is probably misleading as the third phase formation with extractant 3 caused problems with phase separation and sampling. According to Tamada (1990) the third phase contains most of the extracted acid. This means that the real extraction efficiencies with extractant 3 at low concentrations are higher than the obtained ones. extractant 1 was found to be the worst of the three extractants giving extraction efficiencies of 30 to 60 %. The poor results with extractant 1 were probably affected by non-purity of extractant 1. As it was regenerated from earlier tests it contained some acids already as initial solution. This initial acid content most likely decreased extraction efficiencies. However, any estimate of decrease is impossible to give.

Distribution coefficients with extractant 3 varied between 0.6 and 14.2. Values over ten were obtained only with initial solution containing 15 % formic acid. These values may not be right as other values are between 1.5 and 4.6. The worst distribution coefficients were obtained with 3 % initial formic and acetic acid concentrations and the best with 25 % formic acid and 25 % - 35 % acetic acid concentrations. The distribution coefficients with 3 % concentrations are probably affected again by third phase formation which causes problems in phase separation and sampling. With other extractants there is no sign of this phenomenon. Distribution coefficients with extractant 2 were between 1.0 and 1.75 and there were no remarkable differences concerning initial concentration. With extractant 1 the distribution coefficients were between 0.5 and 0.8 and there is no visible effect of initial concentrations. Due to the third phase formation it is best to exclude the 3% concentrations. If this is done, the distribution coefficients obtained from extractions with extractant 3 are the best. If the third phase formation can be avoided the

distribution coefficients are about 2-4. With extractant 2 the coefficients are about 1-2 and with extractant 1 about 0.5-0.8

The type of acid did not give any remarkable difference in efficiencies. Extractant 3 extracted acetic acid better at low and high concentrations and formic acid better with medium concentrations. Extractant 2 extracted formic acid slightly better with all concentrations and extractant 1 extracted formic acid increasingly better when concentrations were increased. The initial concentration of the acid affected in very different manner with different extractants. Extractant 3 seems to be the best extractant with medium concentrations of 10-30 % and most likely with low and high concentrations as well.

The effect of temperature was not significant. Formic acid was extracted slightly better at room temperature 21 °C than at elevated temperature 38 °C. The extraction efficiencies for formic acid at lower temperature were 1-20 % higher with extractant 3, 2-7 % higher with extractant 2 and 2-3 % higher with extractant 1. Correspondingly, acetic acid extraction efficiencies at lower temperature were 2-15 % higher with extractant 3, 3-15 % higher with extractant 2 and 6-23 % higher with extractant 1. Almost in all experiments the extraction efficiency was higher at lower temperature in otherwise similar conditions. Some exceptions exist but the trend is so clear that these can be neglected. According to Han *et al.* (2000) the complexation reaction in organic phase involves hydrogen bonding or proton transfer which are exothermic reactions. Complex formation makes the system more ordered meaning that entropy decreases. Therefore, when temperature is increased, the amount of acid extracted decreases. (Han *et al.* 2000.) This effect is not large but there is no advantage in using elevated temperatures in the extraction.

Third phase formation affected in some experiments decreasing the extraction efficiencies. According to Pazouki and Panda (1998) the formation of third phase, i.e. emulsification could be inhibited by adding NaCl and activated carbon to the solution.

5.2. Solvent regeneration

Solvent regeneration is done to obtain acid products from organic phase as the acids are used as aqueous solutions and not as organic solutions. Simultaneously the solvent is regenerated to be further used in the process. The back extraction tests were done with 0.1 mol/L NaOH solution.

Extraction efficiencies were relatively good concerning the conditions. The extraction efficiencies in extractant 3 were 25-35 % for formic acid and 35-65 % for acetic acid. In extractant 2 the extraction efficiencies were about 55- 60 % for both formic acid acetic acid. The efficiencies were relatively good especially with extractant 2. With extractant 3 the efficiencies are good for acetic acid but with formic acid the results were not so satisfying.

Keshav and Wasewar (2010) studied the back extraction with NaOH using extraction times of 24 hours and settling times of 24 hours. With molar ratio of NaOH higher than molar ratio of acid, they obtained extraction efficiencies of 100 %. As the extraction times were shorter and NaOH concentration lower in these experiments, over 55 % efficiencies are satisfying. Better results should be easy to achieve with longer contact times and higher NaOH concentrations.

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Results of extraction and back extraction experiments.

Acid concentrations in aqueous and organic phases after extraction, extraction efficiencies and distribution coefficients in primary experiments.

No	Acids	Solvent	wt-% aq	wt-% org	E%	K _d
1	3% FA	EXT 3	1.15	1.08	28.66	0.94
2	3% FA	EXT 3	1.08	1.63	43.92	1.51
3	15% FA	EXT 3	1.06	14.94	92.06	14.16
4	15 % FA	EXT 3	1.32	15.45	92.09	11.73
5	25% FA	EXT 3	5.51	25.53	99.28	4.63
6	25% FA	EXT 3	5.42	20.73	80.21	3.83
7	35% FA	EXT 3	16.69	25.51	73.32	1.53
8	35% FA	EXT 3	14.67	25.00	70.55	1.70
9	3% AA	EXT 3	2.90	1.84	49.10	0.64
10	3% AA	EXT 3	2.37	1.84	47.95	0.77
11	15% AA	EXT 3	5.06	12.76	76.75	2.52
12	15% AA	EXT 3	5.49	12.02	70.65	2.19
13	25% AA	EXT 3	6.89	21.76	87.73	3.16
14	25% AA	EXT 3	6.43	21.00	83.49	3.27
15	35% AA	EXT 3	7.64	26.78	83.45	3.50
16	35% AA	EXT 3	9.03	26.60	81.84	2.95
17	3% FA	EXT 2	1.80	2.78	73.81	1.55
18	3% FA	EXT 2	1.92	2.60	69.64	1.35
19	15% FA	EXT 2	6.93	10.33	64.23	1.49
20	15 % FA	EXT 2	7.25	10.01	61.78	1.38
21	25% FA	EXT 2	12.49	15.81	69.38	1.27
22	25% FA	EXT 2	13.04	15.61	67.90	1.20
23	35% FA	EXT 2	19.37	20.65	87.08	1.07
24	35% FA	EXT 2	19.81	20.80	80.97	1.05
25	3% AA	EXT 2	1.86	2.72	76.06	1.46
26	3% AA	EXT 2	2.02	3.04	81.12	1.50
27	15% AA	EXT 2	6.43	11.23	67.73	1.75
28	15% AA	EXT 2	7.22	11.06	64.51	1.53
29	25% AA	EXT 2	11.34	16.81	73.01	1.48
30	25% AA	EXT 2	11.21	16.60	72.40	1.48
31	35% AA	EXT 2	17.85	20.87	101.25	1.17
32	35% AA	EXT 2	16.88	21.51	84.14	1.27

Acid concentrations in aqueous and organic phases after extraction, extraction efficiencies and distribution coefficients in primary experiments (continued).

No	Acids	Solvent	wt-% aq	wt-% org	E%	K_d
35	15% FA	EXT 1	9.82	5.92	36.01	0.60
36	15 % FA	EXT 1	10.63	5.54	33.28	0.52
37	25% FA	EXT 1	16.84	9.96	38.38	0.59
38	25% FA	EXT 1	17.32	9.39	35.43	0.54
39	35% FA	EXT 1	26.34	14.10	40.22	0.54
40	35% FA	EXT 1	25.76	13.65	38.48	0.53
43	15% AA	EXT 1	10.61	6.23	39.06	0.59
44	15% AA	EXT 1	10.83	5.36	33.21	0.50
45	25% AA	EXT 1	15.92	12.21	49.76	0.77
46	25% AA	EXT 1	17.16	10.93	43.16	0.64
47	35% AA	EXT 1	22.85	19.15	60.71	0.84
48	35% AA	EXT 1	30.89	16.10	37.33	0.52

Acid concentrations in aqueous and organic phases after extraction, extraction efficiencies and distribution coefficients in second phase extractions.

No	Acids	Solvent	wt-% aq	wt-% org	E%	K_d
S1	5% AA	EXT 3	3.60	3.00	49.11	0.83
S2	20 % AA	EXT 3	4.54	17.24	92.47	3.80
S3	5% FA	EXT 3	0.71	2.75	44.85	3.86
S4	20% FA	EXT 3	2.43	18.26	87.03	7.50
S5	5% AA	EXT 3	3.94	2.62	41.49	0.66
S6	20 % AA	EXT 3	6.04	16.68	77.22	2.76
S7	5% FA	EXT 3	1.25	2.55	40.85	2.05
S8	20% FA	EXT 3	3.45	18.40	86.16	5.33
S9	5% AA	EXT 2	2.32	4.44	59.92	1.91
S10	20 % AA	EXT 2	9.93	13.80	55.00	1.39
S11	5% FA	EXT 2	2.43	3.98	74.05	1.64
S12	20% FA	EXT 2	9.53	13.06	65.06	1.37
S13	5% AA	EXT 2	2.53	4.07	72.53	1.61
S14	20 % AA	EXT 2	9.42	14.11	70.39	1.50
S15	5% FA	EXT 2	2.57	3.70	60.89	1.44
S16	20% FA	EXT 2	10.18	12.58	61.56	1.24

Acid concentrations in aqueous and organic phases after back extraction and back-extraction efficiencies.

No	Acid	Solvent	wt-% A	wt-% O	E%	K_d
B1	3.00 % AA	EXT 3	1.00	1.19	63.25	1.189208
B2	17.24 % AA	EXT 3	3.28	13.25	34.14	4.043168
B3	2.75 % FA	EXT 3	0.55	1.87	36.22	3.40115
B4	18.26 % FA	EXT 3	-0.30	21.24	-2.97	-70.8278
B6	16.68 % AA	EXT 3	3.76	9.49	52.32	2.525755
B8	18.40 % FA	EXT 3	2.01	16.11	24.89	8.030991
B10	13.80 % AA	EXT 2	4.02	9.66	55.36	2.400757
B12	13.06 % FA	EXT 2	4.03	8.13	59.65	2.01841
B14	14.11 % AA	EXT 2	4.95	9.10	57.02	1.838628
B16	12.58 % FA	EXT 2	4.39	7.52	58.49	1.711946