CHAPTER IV

RESULTS AND DISCUSSION

4.1 Conversion of Extractant

Extractant A (chloride form) was converted to extractant B (chloride and hydroxide form) by reacting with 2 M sodium hydroxide (NaOH). Ten sequential conversions were performed to achieve the highest conversion. Mohr's method titration was used to determine chloride concentration remaining in extractant B. The average conversion from extractant A to extractant B was 63.45±3 wt%.

4.2 HSS Characterization

4.2.1 HSS without MEA in Solution

Before extraction, the mixture of 1,000 ppm of each, formate, acetate, glycolate, and oxalate in the aqueous phase without MEA was analyzed for the HSS concentrations by HPLC as shown in a chromatogram in Figure 4.1. The retention times of oxalate, glycolate formate, and acetate are 7.7, 9.4, 10.0 and 16.0 minutes, respectively. Calibration curves of each salt were generated from the aqueous standard solution of 5, 10, 50, and 100 ppm as shown in Figures 4.2, 4.3, 4.4, and 4.5, respectively.

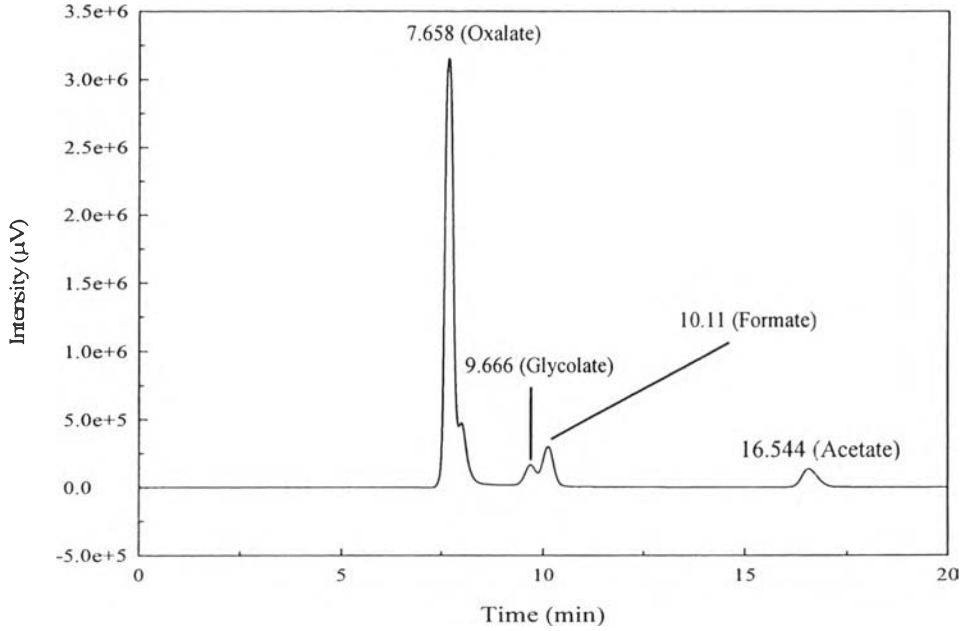

Figure 4.1 Chromatogram of HSS solution without MEA before extraction.

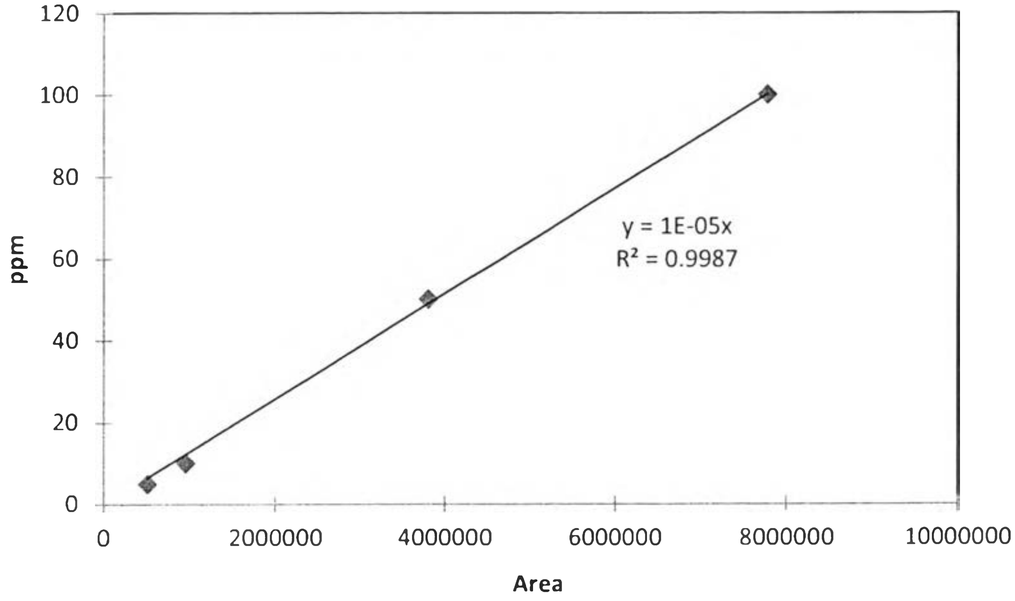

Figure 4.2 Calibration curve of oxalate in aqueous solution.

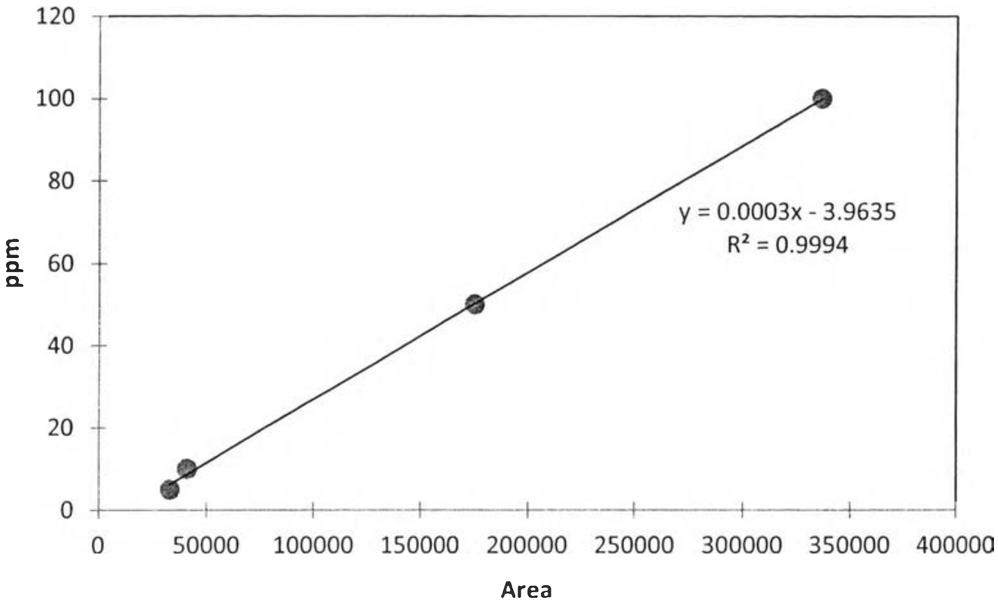

Figure 4.3 Calibration curve of glycolate in aqueous solution.

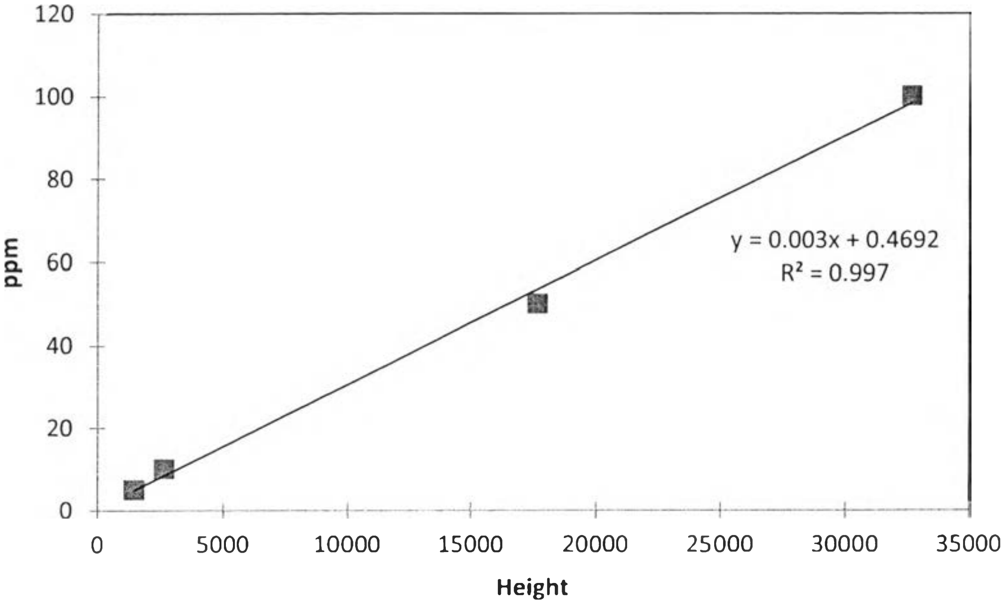

Figure 4.4 Calibration curve of formate in aqueous solution.

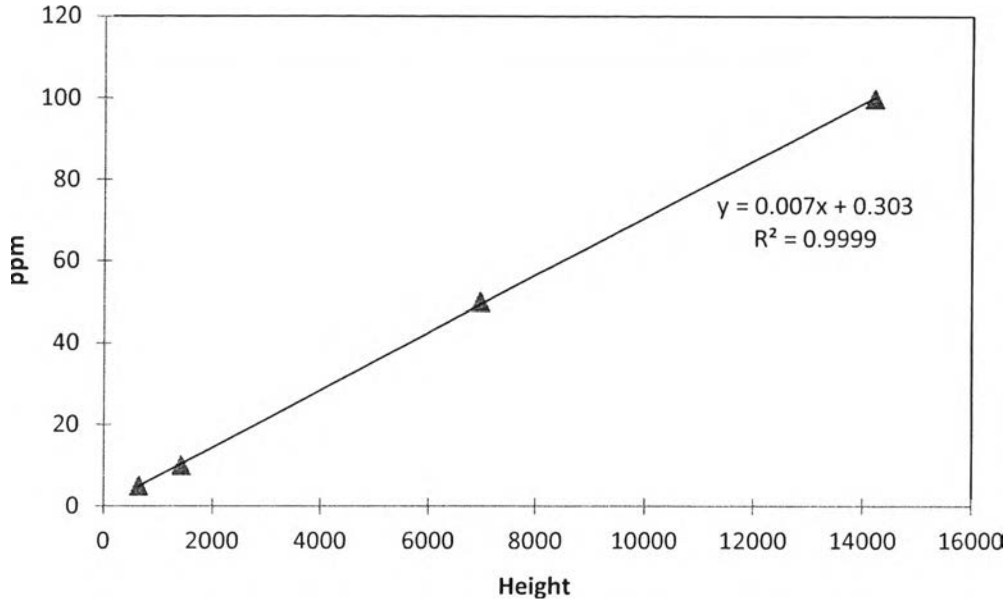

Figure 4.5 Calibration curve of acetate in aqueous solution.

4.2.2 HSS in MEA Solution

For the HSS in the presence of 30 wt% MEA solution, concentration of acetate cannot be measured, due to retention time overlapping with MEA, thus HSS was included only formate, glycolate, and oxalate. When formate and glycolate dissolved in MEA solution, their retention time were overlapped, the extraction of HSS in MEA solution had to perform into two separate aqueous solutions (formate in 30 wt% MEA solution, and glycolate together with oxalate in 30 wt% MEA solution). Figures 4.6 and 4.7 shows the chromatograms of formate in 3 wt% MEA solution and glycolate with oxalate in 3 wt% MEA solution, respectively. The calibration curves are generated as shown in Figures 4.8, 4.9, and 4.10.

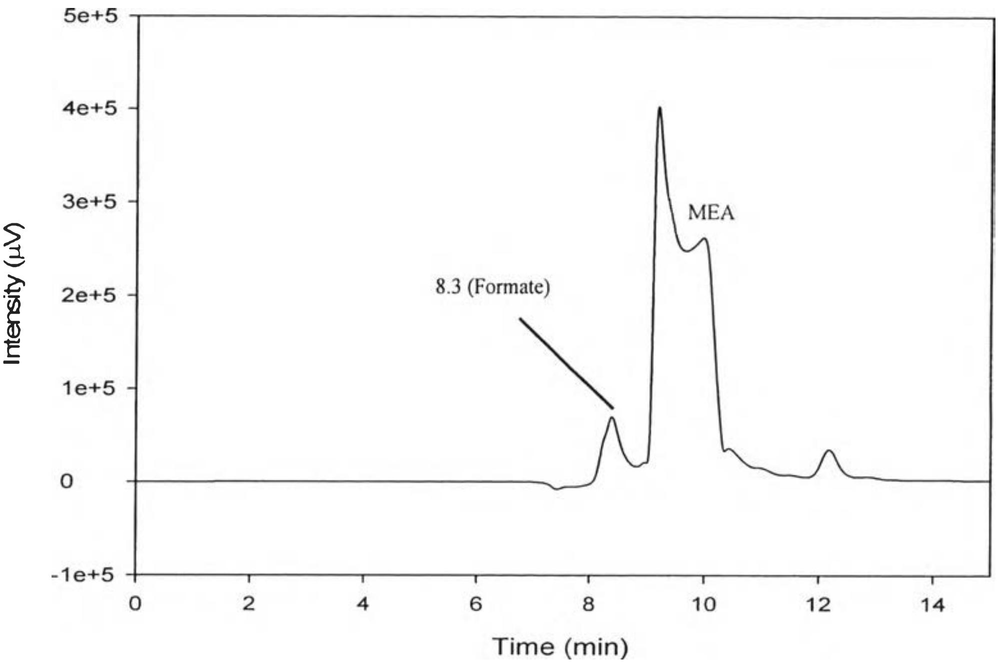

Figure 4.6 Chromatogram of diluted formate solution with MEA before extraction.

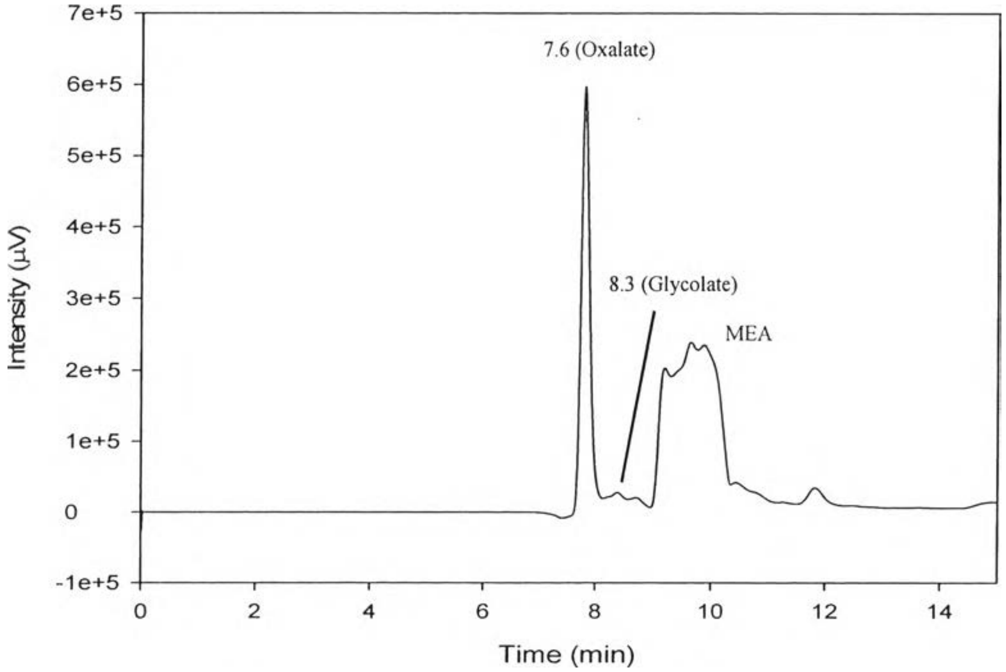

Figure 4.7 Chromatogram of diluted glycolate and oxalate solution with MEA before extraction.

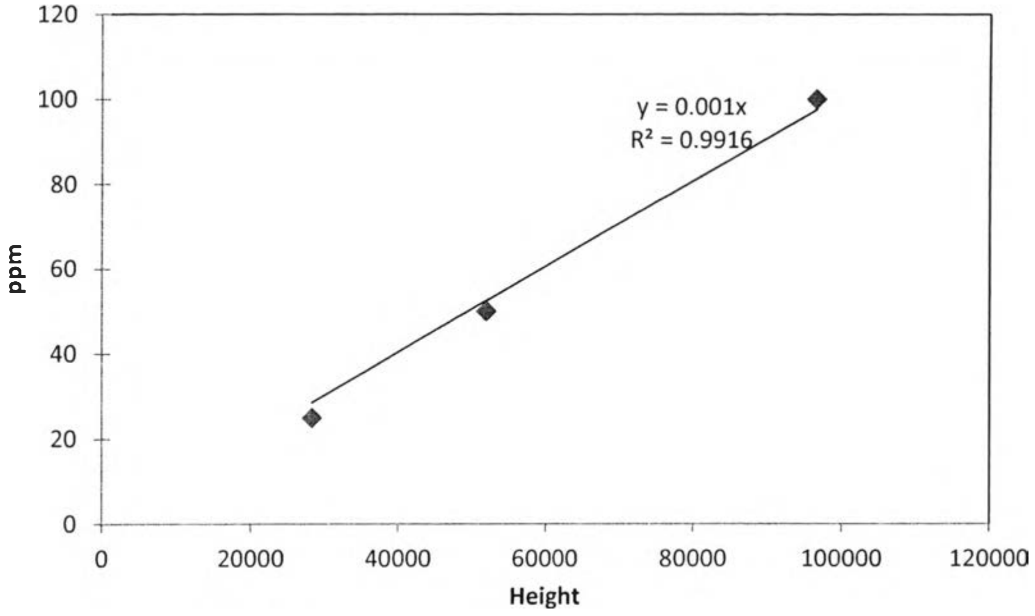

Figure 4.8 Calibration curve of formate in 3 wt% MEA solution.

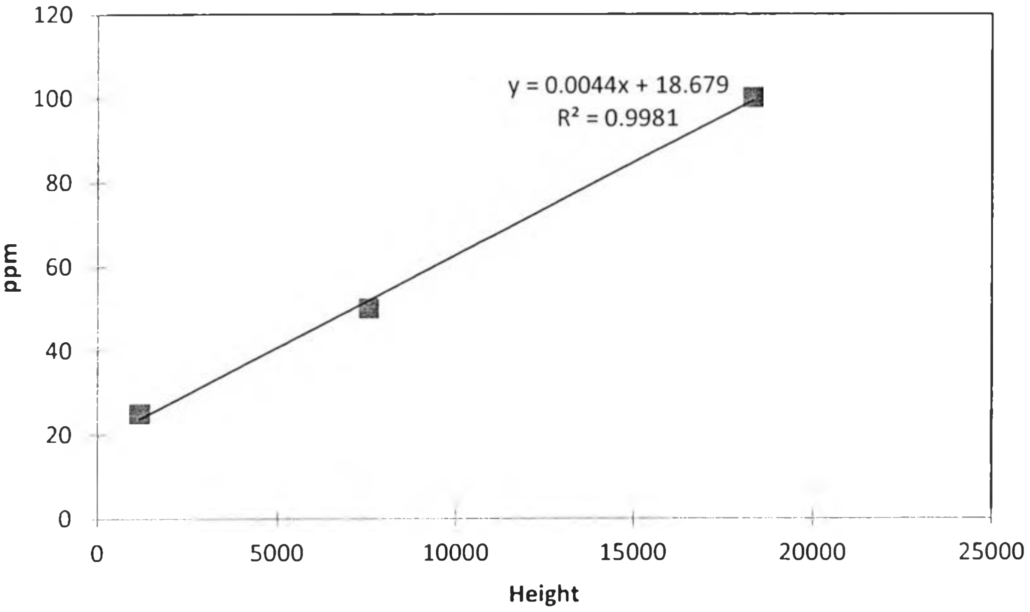

Figure 4.9 Calibration curve of glycolate in 3 wt% MEA solution.

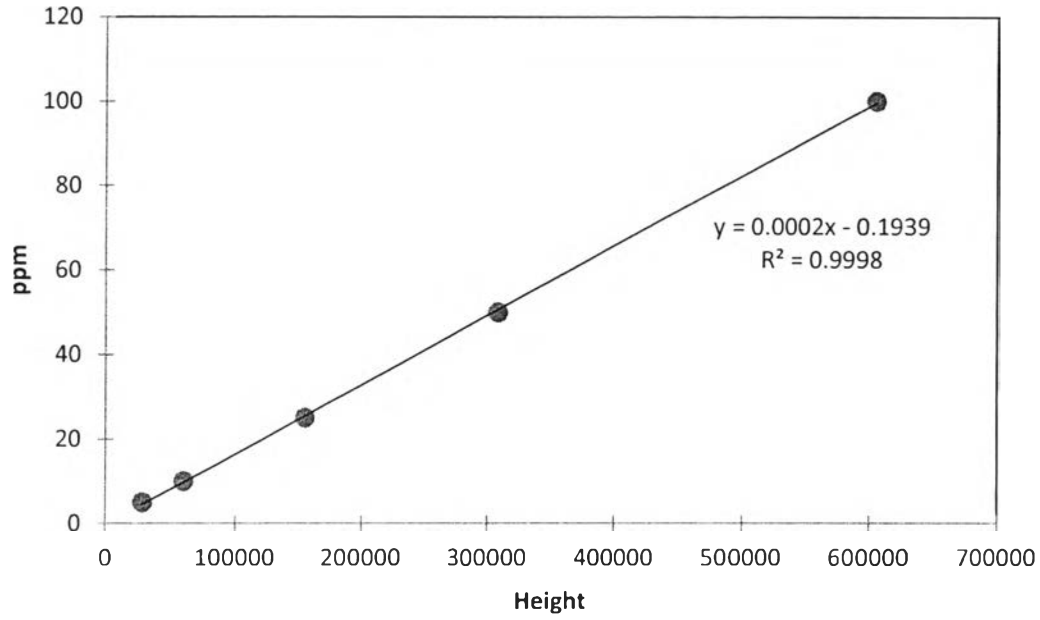

Figure 4.10 Calibration curve of oxalate in 3 wt% MEA solution.

4.3 HSS Extraction

4.3.1 Effect of Diluent Background on HSS Extraction

The HSSs extraction of diluents alone (in the absence of extractant) shows that the alcohol diluents can physically extract HSS into itself.

Figure 4.11 shows that as the number of carbons in the alcohol chain decrease, the diluent extraction increases. Acetate was the most extractable (29.86 – 43.53 %), followed by formate (9.55 – 17.05 %) and glycolate (0.95 – 8.13 %), while the lowest physical extraction efficiency, which unable to be extracted by alcohol diluents was oxalate (0 %).

In Table 4.1 shows viscosity at 25 °C (Lide *et al.*, 2004 *and* Al-Jimaz *et al.*, 2004) and Table 4.2 shows relative polarity (Reichardt, 2003) of each diluent. For the effect of carbon chain length in alcohol diluents, the shorter alcohol chain lengths of 1-pentanol, showed better physical association than longer alcohol chains of 1-octanol with a salt structure. It can be explained by the viscosity of each diluents, the lower viscosity of 1-pentanol has a higher mass transfer between two phases at the same speed of stirring than the higher viscosity diluents, i.e. 1-octanol.

In term of polarity of diluents, the extraction efficiency increased as increasing in polarity of diluents, i.e., 1-pentanol > 1-hexanol > 1-heptanol > 1-octanol. Polarity is dependent of carbon number in a chain length of diluents. The polarity increases with decreasing in carbon number. The extraction efficiency of 1-pentanol to carboxylic acid can be explained according to polarity of diluents in which carboxylic acids are a polar compound, which prefering to dissolve in high polarity solution such water. Thus the higher polarity of diluents is, the higher dissolution of carboxylic acid and extraction efficiency becomes.

Table 4.1 Viscosity at 25 °C of each diluent (Lide *et al.*, 2004 *and* Al-Jimaz *et al.*, 2004)

Diluents	**Molecular Formula**	**Viscosity at 25 °C (cP)**	**Reference**
2-ethyl-1-hexanol	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	6.27	Lide *et al.*
1-ocatnol	$CH_3(CH_2)_7OH$	7.663	Al-Jimaz *et al.*
1-heptanol	$CH_3(CH_2)_6OH$	5.942	Al-Jimaz *et al.*
1-hexanol	$CH_3(CH_2)_5OH$	4.339	Al-Jimaz *et al.*
1-pentanol	$CH_3(CH_2)_4OH$	3.497	Al-Jimaz *et al.*

Table 4.2 Relative polarity of each diluent (Reichardt, 2003)

Diluents	**Molecular Formula**	**Relative Polarity**	**Reference**
2-ethyl-1-hexanol	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	N/A	-
1-ocatnol	$CH_3(CH_2)_7OH$	0.537	Reichardt
1-heptanol	$CH_3(CH_2)_6OH$	0.549	Reichardt
1-hexanol	$CH_3(CH_2)_5OH$	0.559	Reichardt
1-pentanol	$CH_3(CH_2)_4OH$	0.568	Reichardt

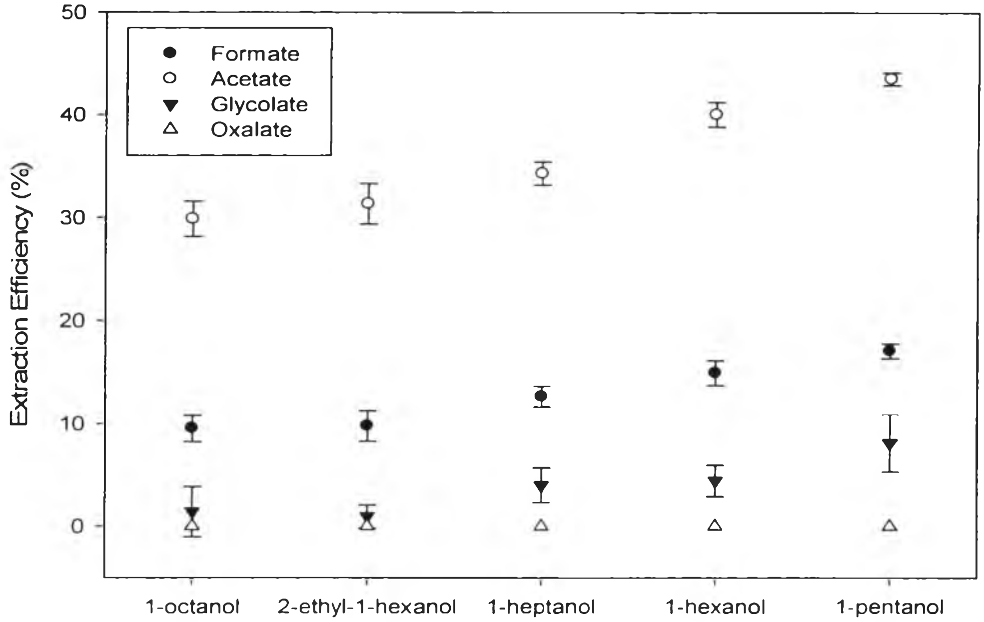

Figure 4.11 An average extraction of HSS with various diluents in the absence of extractant B at room temperature.

4.3.2 HSS Extraction without MEA in Aqueous Solution

In Figure 4.12, in the absence of MEA, the result in various diluents showed that the extraction efficiency of all HSS is higher than 83 %; especially, the extraction of oxalate (99 %). There were slightly decreases in extraction efficiency with decreasing carbon numbers from C8 to C5 of alcohol diluents for glycolate, acetate and formate. 1-octanol yielded an average extraction efficiency of 94.87 %, 93.01 %, 85.97 %, and 99.92 % for formate, acetate, glycolate, and oxalate, respectively. 2-ethyl-1-hexanol yielded an average extraction efficiency of 96.57 %, 96.05 %, 90.43 %, and 99.95 % for formate, acetate, glycolate, and oxalate, respectively; 1-heptanol yielded an average extraction efficiency of 94.84 %, 93.62 %, 85.94 %, and 99.92 % for formate, acetate, glycolate, and oxalate, respectively; 1-hexanol yielded an average extraction efficiency of 95.23 %, 94.75 %, 88.13 %, and 99.87 % for formate, acetate, glycolate, and oxalate, respectively; and 1-pentanol yielded an average extraction efficiency of 93.94 %, 91.78 %, 83.92 %, and 99.77 % for formate, acetate, glycolate, and oxalate, respectively.

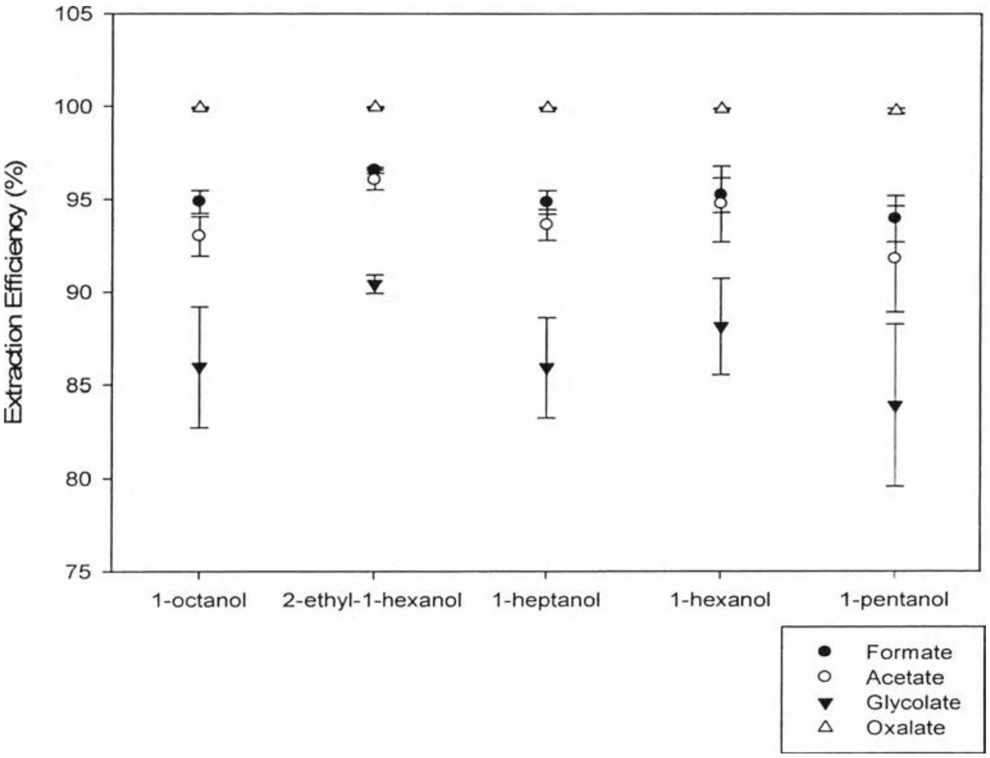

Figure 4.12 An average extraction efficiency of HSS without MEA in aqueous solution by extractant B in various diluents at room temperature (30 °C).

For the same carbon chain length, the branched alcohols (2-ethyl-1-hexanol) showed better extraction than the straight chain alcohols (1-octanol). When the straight chain lengths were compared, the extractant in the longer chain alcohols performed noticeably better than the shorter chain alcohols, i.e. 1-octanol, and 1-heptanol yielded better extraction than 1-hexanol and 1-pentanol. The longer chain diluents shows higher immiscible with aqueous solution than the shorter chain (Grzenia *et al.,* 2008 and Yang *et al.,* 1991), which means that low extracted HSS losses to aqueous solution with the longer chain alcohols. Although 1-octanol are extensively used in many carboxylic acid extraction, but the extraction efficiency of 1-octanol was not outstandingly different from shorter chain diluents (i.e., 1-hexanol, and 1-pentanol) due to its higher viscosity.

When compared with the extraction results of HSS by diluents alone, the extractant can reacts with HSS by acid-base reaction. As described in Eq. 4.1, the extractant can react with both forms of carboxylic acid i.e., undissociated form, and dissociated from (Yang *et al.*, 1991), but it usually forms an ion exchange formation to maintain neutrality in organic phase. Extractant B, which is quaternary amine salt with OH^- ion reacts with MEA-carboxylate salt ($H_2NC_2H_4^+HSS^-$), which appears in the aqueous solution as carboxylate anions (HSS anions), to form carboxylate-amine complexes (RN^+HSS^-) and MEA ($H_2NC_2H_4OH$).

$$RN^+OH^- + HSS^-H_2NC_2H_4^+ \rightarrow RN^+HSS^- + H_2NC_2H_4OH \qquad (4.1)$$

Due to the basic property of extractant, the presence of extractant significantly increases the HSS extraction efficiency as compared to the physical extraction by the diluents alone. Table 4.3 shows the acid strength (pK_a) of each carboxylic acid, which the pK_a value is involved in HSS-extractant interaction. The lower pK_a,, the more acid dissociats leading to more acid strength. The evident can be proved for example, every diluent cannot extract the oxalate (0 %) even it is the strongest acid (the lowest pK_a) in this study, but in the presence of extractant, the oxalate can be extracted up to 99 % in all diluents. Thus, the acid-base interaction of the extractant with HSS dominates the physical extraction of diluents alone.

Table 4.3 Carboxylic acid strength

Acids	**pK_a**
Acetic acid	4.18
Formic acid	3.77
Glycolic acid	3.83
Oxalic acid*	1.25(1), 4.28 (2)

* Oxalate is weak diprotic acid, where $pK_{a1} = 1.25$, $pK_{a2} = 4.28$.

Even though glycolic acid has lower pK_a (stronger acidity) than acetic acid, the extraction efficiencies of glycolate by extractant in every diluent is lower than acetate. It can be explained by the hydroxyl group on glycolic acid that makes the glycolate-extractant complex more hydrophilic, and thus lost in extraction efficiency (Yang *et al.*, 1991).

4.3.3 Extraction of HSS in MEA Solution

Figure 4.13 shows that the extraction efficiency of formate and glycolate in aqueous solution at room temperature (30 °C) decreased with the presence of 30 wt% MEA in the solution. The average extraction of formate and glycolate in every diulent decreases to 68.11±5.13 % and 73.77±1.07 % as compared to 95.09±0.95 % and 86.88±2.48 % in the absence of MEA, respectively. For oxalate, the extraction efficiency is 99.95±0.06 %, not significantly decrease as compared to 99.89±0.07 % in the absence of MEA. The results show that the extraction efficiency is independent of numbers of carbons in alcohol diluents with 5.63 %, 1.07 %, and 0.06 % variation for formate, glycolate, and oxalate, respectively. Each diluent showed that: 1-octanol yielded an average extraction efficiency of 67.43 %, 72.44 %, and 99.98 % for formate, glycolate ,and oxalate, respectively; 2-ethyl-1-hexanol yielded an average extraction efficiency of 67.40 %, 74.81 %, and 99.99 % for formate, glycolate ,and oxalate, respectively; 1-heptanol yielded an average extraction efficiency of 62.04 %, 73.07 %, and 99.96 % for formate, glycolate ,and oxalate, respectively; 1-hexanol yielded an average extraction efficiency of 77.37 %, 73.65 %, and 99.98 wt% for formate, glycolate ,and oxalate, respectively; and 1-pentanol has an average extraction efficiency of 66.29 %, 74.86 %, and 99.84 % for formate, glycolate ,and oxalate, respectively. From the literature review of Tamada *et al.* (1990), the extraction efficiency is dependent of acidity of aqueous solution, means that the lower acidity leads to higher efficiency due to the acid-base interaction between extractant and carboxylate anions. MEA was added into the aqueous solution, which makes acidity of the solution decreased, and then decreasing in extraction efficiency. In case of oxalate extraction, the efficiency did not decreased as expected, which can be explained by the oxalic acid strength. The first dissociation of oxalate (pK_{a1} = 1.25) is the strongest compared to the others. Even though the MEA was added and acidity decreased but the oxalate was still in dissociated form and can form a complex with extractant, which leads to almost the same extraction efficiency as in the absence of MEA in aqueous solution.

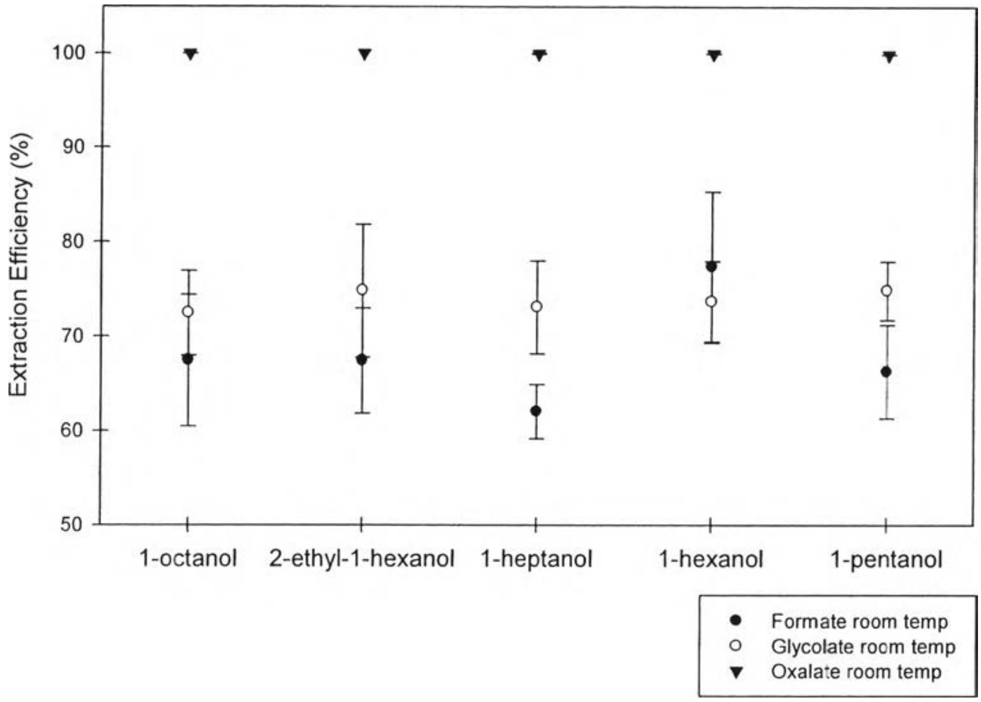

Figure 4.13 An average extraction efficiency of HSS in 30wt% MEA by extractant B in various diluents at room temperature (30 °C).

From previous work done by Akkarachalanont *et al.* (2010), the HSS extraction in MEA solution using extractant in 1-octanol at room temperature (25 °C), the extraction efficiency was 88.76 %, 76.37 %, and 98.56 % for formate, glycolate, and oxalate, respectively. When compare to this work the extraction efficiency of HSS extraction in MEA solution by extractant in 1-octanol at room temperature (30 °C) was decreased to 67.43 %, 72.44 % for formate and glycolate, respectively and for oxalate extraction efficiency was increased to 99.98 %.

4.3.4 Effect of Temperature on HSSs in MEA Extraction

Figures 4.14, 4.15, and 4.16 shows the effect of temperature on extraction of HSS in 30 wt% MEA solution. The previous section was study the extraction of HSS in MEA solution at room temperature (30 °C) for 3 times in each sample to find the deviation and average of extraction efficiency. As the temperature is increased to 45 °C and 60 °C, the efficiency results are still in the deviation range of extraction efficiency at room temperature. 1-octanol yielded an average extraction efficiency of 67.43±6.95 %, 72.44±4.49 %, and 99.98±0.03 % for formate, glycolate, and oxalate, respectively; 2-ethyl-1-hexanol yielded an average extraction efficiency of 67.40±5.54 %, 74.81±7.04 %, and 99.99±0 % for formate, glycolate, and oxalate, respectively; 1-heptanol yielded an average extraction efficiency of 62.04±2.87 %, 73.07±4.94 %, and 99.96 ±0.04 % for formate, glycolate, and oxalate, respectively; 1-hexanol yielded an average extraction efficiency of 77.37±7.93 %, 73.65±4.33 %, and 99.98±0.02 % for formate, glycolate, and oxalate, respectively; and 1-pentanol yielded an average extraction efficiency of 66.29±4.96 %, 74.86±3.11 %, and 99.84±0.15 % for formate, glycolate, and oxalate, respectively.

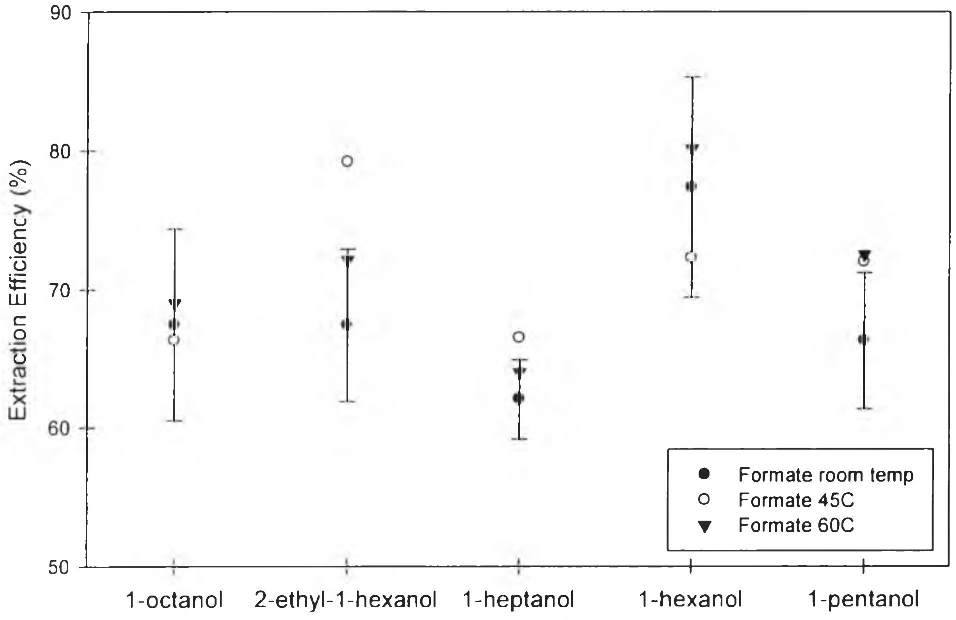

Figure 4.14 Effect of temperature on extraction of formate in 30 wt% MEA solution.

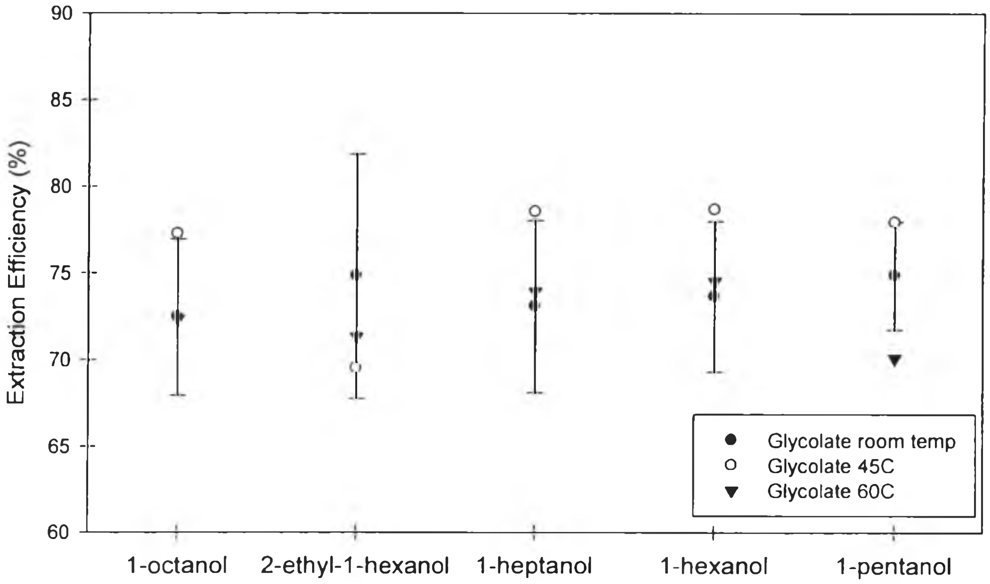

Figure 4.15 Effect of temperature in glycolate with 30 wt% MEA solution extraction.

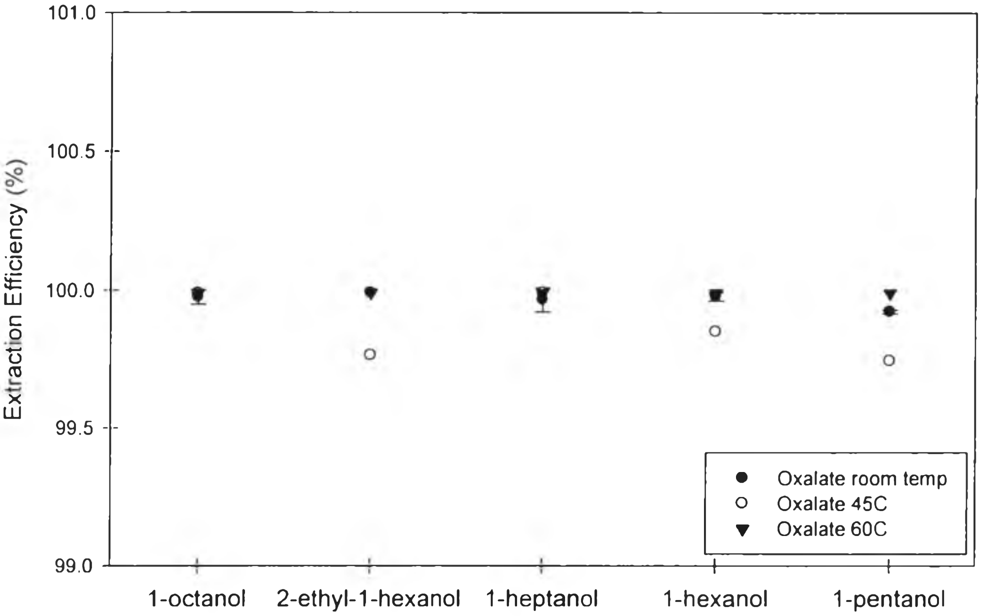

Figure 4.16 Effect of temperature on extraction of oxalate in 30 wt% MEA solution.

When considered the effect of the extraction temperature on the extraction trend for formate, the extraction efficiency of the extractant in 2-ethyl-1-hexanol, 1-heptanol, and 1-pentanol slightly deviated from the deviation range when the extraction temperature increased from 30 °C to 45 °C and then 60 °C. While for glycolate, the extractant in 1-octanol, 1-heptanol, and 1-hexanol slightly deviated from the deviation range when the extraction temperature increased from 30 °C to 45 °C and then 60 °C. On the other hand, the oxalate extraction efficiency appeared to have insignificant effect on an increase in temperature at 45 °C and 60 °C. Thus, the extraction efficiency in every diluent is independent of extraction temperature.

The effect of temperature (40 °C, 50 °C, and 110 °C) done by Akkarachalanont *et al.* (2010), the extraction of HSS (formate, glycolate, and oxalate) in MEA solution using extractant in 1-octanol was independent of temperature.

4.4 Regeneration

Regeneration of extractant in various diluents, which was used in HSS extraction in the presence of MEA solution at different temperature are shown in Table 4.4 to 4.8, shows that many of the results have the efficiency more than 100 wt%. The HSS concentration in the second column of each table is a regenerated HSS, which was back-extracted from extractant used in HSS extraction to 4 M NaOH in an aqueous solution.

The over efficiency which can be explained by the HPLC chromatograms in appendix F, was occurred due to the sensitivity of UV detector to hydroxide ion in the aqueous solution. Due to avoiding the overloading effect, the 4 M sodium hydroxide solution must be diluted 20 times to 0.2 M, thus the HSS also diluted with the aqueous solution. This procedure reduces the HSS peak in the chromatogram, which eventually increase the difficulty in analysis of HSS concentration. The hydroxide has a high sensitivity to UV detector, even used at low concentration as 0.2 M, which caused the interference of hydroxide peak to HSS peak and makes it hard to obtain the exact value of concentration of HSSs. The calculated regeneration efficiencies are shown in Table 4.4 – 4.8.

The regeneration of extractant in the previous work done by Akkarachalanont *et al.* (2010), the extractant dissolved in 1-octanol was reacted with NaOH and analyzed by capillary electrophosis (CE) to measure the concentration of HSS in NaOH. The regeneration efficiency was 32.96 %, 17.16 %, and 20.47 % for formate, glycolate, and oxalate, respectively.

Table 4.4 Regeneration efficiency of 1st HSS extraction with MEA solution at room temperature (30 °C)

Extractant in diluent	**HSS Concentration in rgenerant(ppm)**			**Regeneration Efficiency (%)**		
	Formate	Glycolate	Oxalate	Formate	Glycolate	Oxalate
1-Octanol	510.30	1,515.12	1,054.61	110.53	136.25	86.56
2-ethyl-hexanol	352.46	1,397.28	1,060.15	79.89	126.43	87.01
1-heptanol	370.14	1,305.85	1,046.89	117.47	122.34	85.99
1-hexanol	370.94	1,314.12	1,039.10	81.56	119.26	85.29
1-pentanol	374.02	1,371.06	1,036.59	99.21	118.06	85.14

Table 4.5 Regeneration efficiency of 2nd HSS extraction with MEA solution at room temperature (30 °C)

Extractant in diluent	**HSS Concentration in rgenerant(ppm)**			**Regeneration Efficiency (%)**		
	Formate	Glycolate	Oxalate	Formate	Glycolate	Oxalate
1-Octanol	302.00	1,465.48	1,225.47	88.18	138.40	100.64
2-ethyl-hexanol	297.82	1,350.56	1,208.18	75.97	124.16	99.16
1-heptanol	268.80	1,582.26	1,308.11	78.23	142.19	107.36
1-hexanol	261.28	1,286.93	1,255.64	69.31	116.66	103.10
1-pentanol	305.56	1,744.62	1,362.65	88.85	157.00	112.20

Table 4.6 Regeneration efficiency of 3rd HSS extraction with MEA solution at room temperature (30 °C)

Extractant in diluent	HSS Concentration in rgenerant(ppm)			Regeneration Efficiency (%)		
	Formate	Glycolate	Oxalate	Formate	Glycolate	Oxalate
1-Octanol	326.76	2,984.36	1,524.19	228.50	243.26	127.85
2-ethyl-hexanol	370.82	2,612.21	1,351.88	265.25	207.88	113.39
1-heptanol	377.12	2,694.84	1,726.11	313.22	218.08	144.78
1-hexanol	397.94	2,418.26	1,779.23	272.19	203.63	149.28
1-pentanol	441.46	2,660.26	1,986.15	361.26	223.48	166.74

Table 4.7 Regeneration efficiency of HSS extraction with MEA solution at 45 °C temperature

Extractant in diluent	HSS Concentration in rgenerant(ppm)			Regeneration Efficiency (%)		
	Formate	Glycolate	Oxalate	Formate	Glycolate	Oxalate
1-Octanol	403.84	2,829.22	1,191.54	118.32	169.41	98.34
2-ethyl-hexanol	297.58	1,427.12	1,124.67	92.13	99.64	93.05
1-heptanol	381.50	2,364.93	1,176.72	111.65	139.62	97.13
1-hexanol	296.88	2,408.58	1,297.15	100.67	142.00	107.22
1-pentanol	321.56	2,493.94	1,184.34	109.45	148.21	97.99

Table 4.8 Regeneration efficiency of HSS extraction with MEA solution at 60 °C temperature

Extractant in diluent	HSS Concentration in rgenerant(ppm)			Regeneration Efficiency (%)		
	Formate	Glycolate	Oxalate	Formate	Glycolate	Oxalate
1-Octanol	389.86	1,898.62	1,015.70	138.49	118.55	83.83
2-ethyl-hexanol	405.80	1,931.36	986.97	144.11	121.67	81.46
1-heptanol	479.90	1,686.01	1,161.53	196.20	110.68	95.87
1-hexanol	425.54	1,545.12	1,124.37	133.90	100.64	92.80
1-pentanol	389.86	1,558.41	1,185.82	131.80	107.89	97.87