

CHAPTER VI
RESULTS AND DISCUSSION

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4.1 Conversion of Extractant

Extractant in chloride form was converted to extractant in hydroxide form by reacting with 2 M sodium hydroxide (NaOH). Thirteen conversions were performed to achieve maximum conversion. The conversion efficiency was determined by Mohr's method titration from concentration of chloride remaining. The average conversion was 62.48 ± 0.57 wt% as shown in Figure 4.1. The average conversion was drop because water and NaCl were removed from extractant by rotary evaporation. Therefore, some extractant in OH form can be loss.

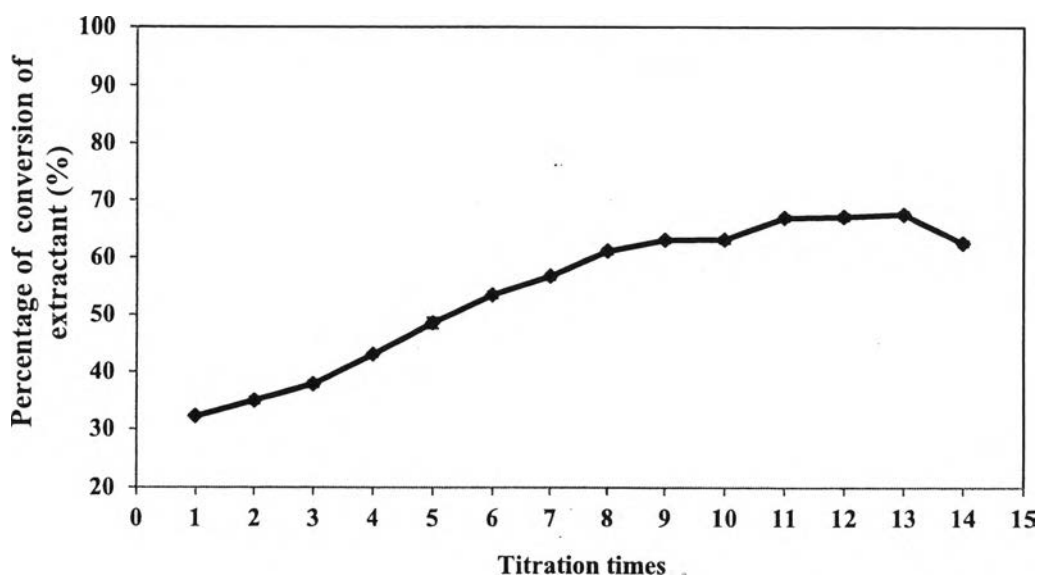


Figure 4.1 Percentage conversion of extractant chloride to hydroxide form.

4.2 Neutral MEA Degradation Products Characterizations

4.2.1 Neutral MEA Degradation Product without MEA in Aqueous Solution

The concentration 1000 ppm of each neutral MEA degradation products, i.e. imidazole, N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxy ethyl)-succinimide was analyzed by GC-FID as a chromatogram shown in Figure 4.2. The retention times of imidazole, N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide are 18.00, 20.40, 23.50 and 27.30 minutes, respectively.

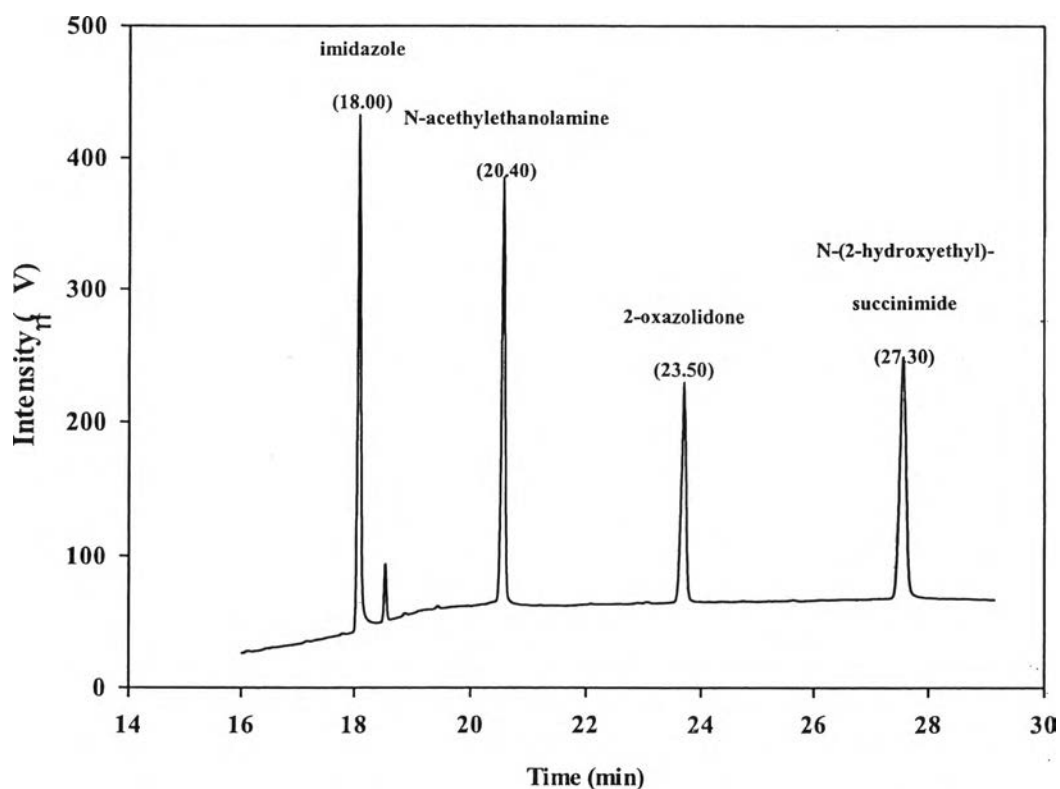


Figure 4.2 Chromatogram of neutral MEA degradation products without MEA in aqueous solution before extraction.

4.2.2 Neutral MEA Degradation Product with MEA in Aqueous Solution

The chromatogram is shown in Figure 4.3. The retention times of monoethanolamine, imidazole, N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide are 5.00, 17.70, 20.10, 23.00 and 26.50 minutes, respectively. The 30 wt% MEA was added into the neutral MEA degradation products solution, the chromatogram shows very large peak of MEA without overlapping with those of the degradation products being studied.

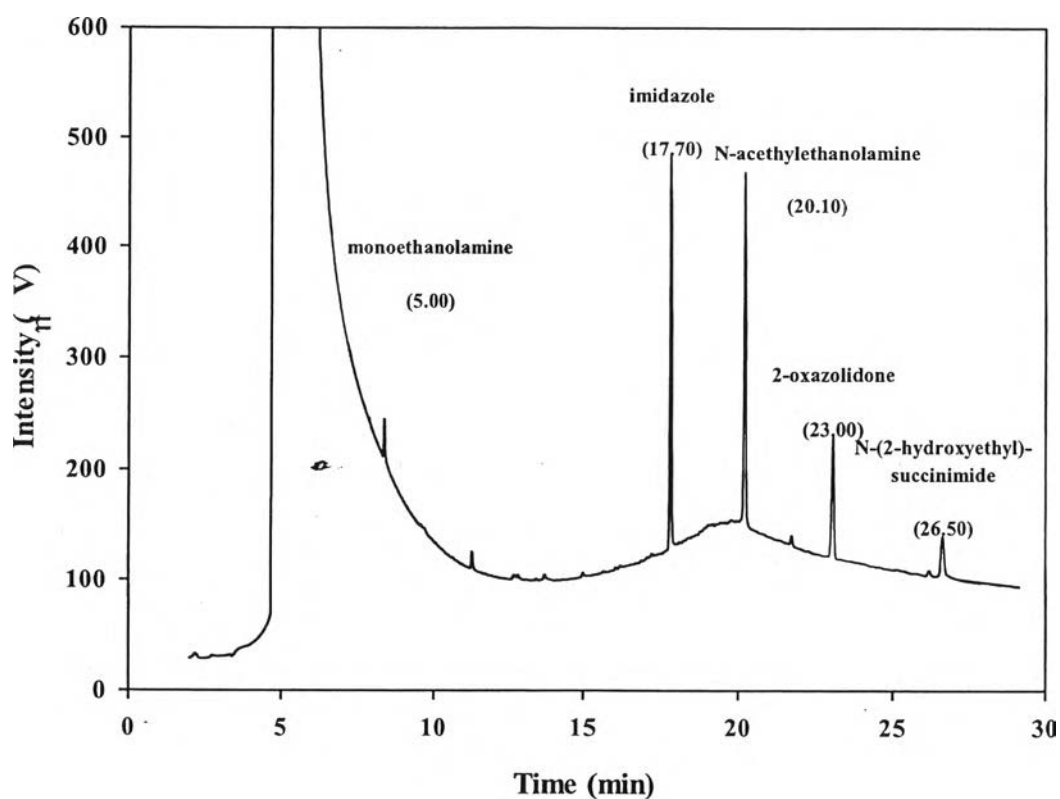


Figure 4.3 Chromatogram of neutral MEA degradation products with MEA in aqueous solution before extraction.

Before extraction of the neutral MEA degradation products with extractant in 2-ethyl-1-hexanol, the mixture of imidazole, N-acetyl ethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide with/without MEA was used to generate a calibration curve from aqueous standard solutions of 5, 10, 50, 100, 500 and 1000 ppm (Appendix C).

4.3 Neutral MEA Degradation Products Extraction

4.3.1 Effect of Diluent Alone

The extraction efficiency of the diluent (2-ethyl-1-hexanol) alone was investigated and results showed that the average extraction efficiency of each neutral MEA degradation products was 41.19 ± 1.49 %, 16.39 ± 3.95 %, 4.55 ± 1.26 % and 2.89 ± 2.64 % for imidazole, N-(2-hydroxyethyl)-succinimide, N-acethylethanolamine and 2-oxazolidone, respectively (Figure 1). The extraction capability of 2-ethyl-1-hexanol was important to know, firstly because it was used as the diluent to reduce the high viscosity of the extractant solution and secondly to determine its contribution to the total extraction efficiency (diluent in extractant). The diluent alone was able to extract neutral MEA degradation products based on their physical solubility in 2-ethyl-1-hexanol. This was as a result of the polarity of the diluent and the neutral MEA degradation products (“like dissolves like” principle). The diluent (2-ethyl-1-hexanol) is a branched long hydrocarbon chain alcohol which is low polar molecule and also insoluble in water.

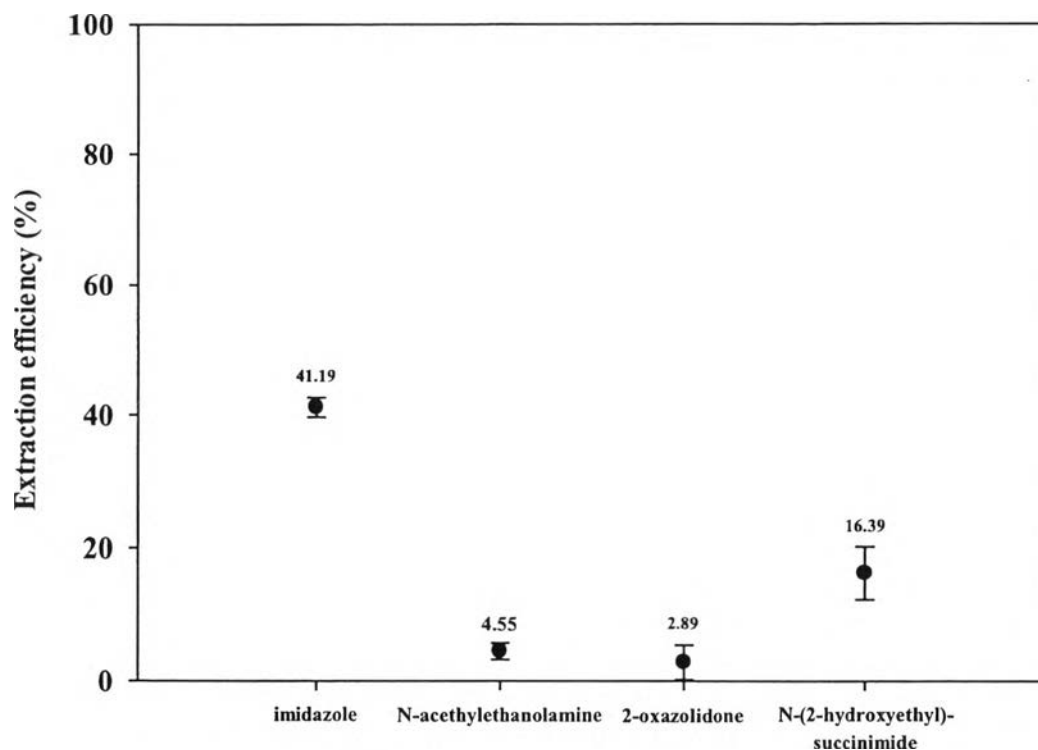
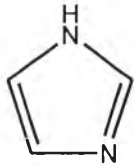
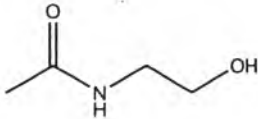
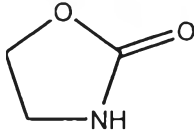
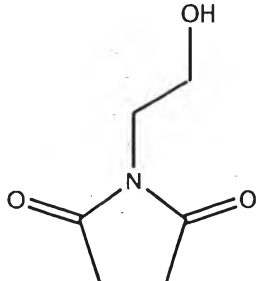


Figure 4.4 Average extraction efficiency of neutral MEA degradation products with 2-ethyl-1-hexanol diluent alone in the absence of extractant at 298 K.

Figure 4.4 shows the average extraction efficiency of neutral MEA degradation products with the diluent alone at 298 K. Anions of weak acid neutral MEA degradation products will preferably dissolve in water than in organic solvent. This phenomenon depends on their dissociation constants (K_a) as shown in Table 4.1. Very low K_a value indicates that the neutral MEA degradation products are considered as very weak acids, and do not readily dissociate. From Table 4.1 it can be seen that imidazole have the lowest K_a (lowest dissociation) when compared with the other neutral MEA degradation products, but it indicated the highest extraction efficiency. This can be attributed to the absence of a hydroxyl group in its structure (hence none of the imidazole dissolved in water) which increased its contact surface area with the diluent. The K_a values of N-acetyethanolamine and N-(2-hydroxyethyl)-succinimide are close to imidazole, but their average extraction

efficiencies are dramatically lower than imidazole. This is due to the presence of hydroxyl group (OH) in both N-acetyethanolamine and N-(2-hydroxyethyl)-succinimide structures which increased its hydrophilicity (Yang *et al.*, 1991) and decreased their contact surface area with the diluent. Hence, N-acetyethanolamine, and N-(2-hydroxyethyl)-succinimide were more soluble in the aqueous phase than in the 2-ethyl-1-hexanol phase. It's also important to note that the average extraction efficiency of N-(2-hydroxyethyl)-succinimide is higher than N-acetyethanolamine (Figure 4.4). This can be attributed to the presence of more carbon atoms attached to the OH group in N-(2-hydroxyethyl)-succinimide which makes it less hydrophilic than N-acetyethanolamine, thereby dissolving more in the diluent. For 2-oxazolidone, it possessed the lowest pK_a hence its lowest extraction efficiency.

Table 4.1 Dissociation constants (K_a) of neutral MEA degradation products

Component	Molecular Formula	pK_a	K_a	Reference
imidazole		14.90	1.26×10^{-15}	Venkatesan <i>et al.</i> (2009); Ullmann, (2000)
N-acetyethanolamine		14.56	2.75×10^{-15}	Zahlsen <i>et al.</i> (2009)
2-oxazolidone		12.78	1.66×10^{-13}	Zahlsen <i>et al.</i> (2009)
N-(2-hydroxyethyl)-succinimide		14.20	6.31×10^{-15}	Zahlsen <i>et al.</i> (2009)

4.3.2 Effect of Extractant in 2-Ethyl-1-Hexanol

Extraction of neutral MEA degradation products without MEA present in aqueous solution .

The results in Figure 4.5 show that the average extraction efficiencies of all neutral MEA degradation products are 39.77 ± 1.12 %, 27.83 ± 1.66 %, 84.09 ± 0.47 % and 99.44 ± 0.02 % for imidazole, N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide, respectively.

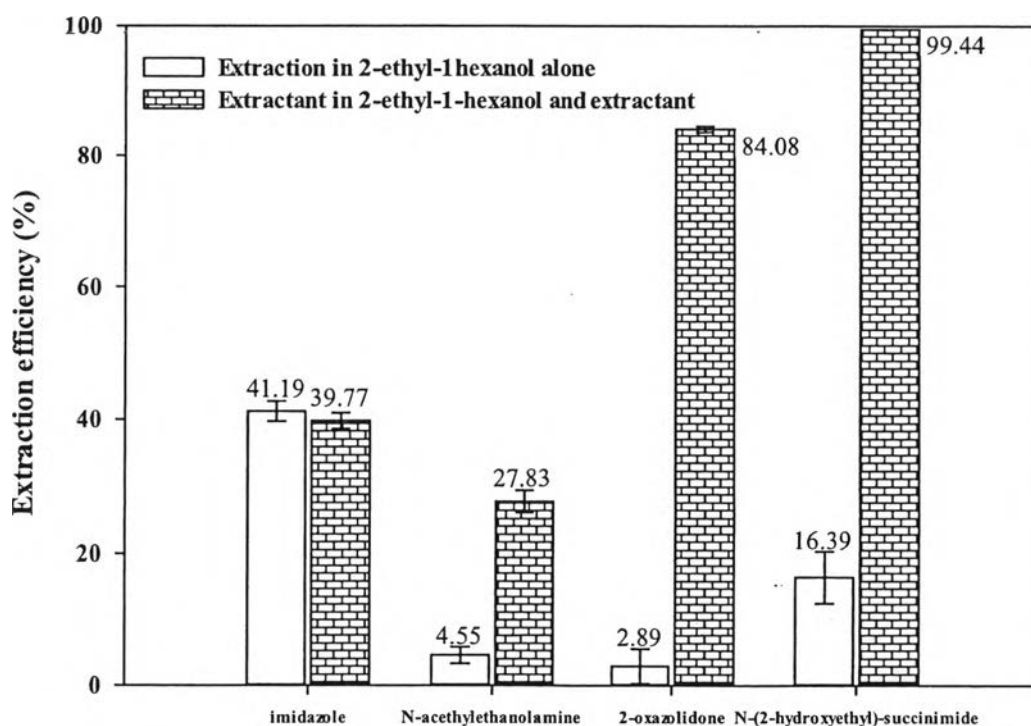
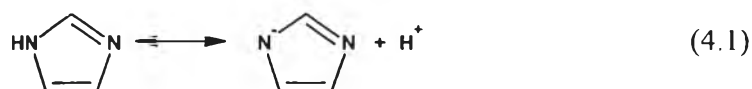


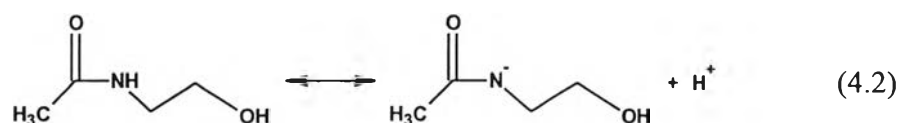
Figure 4.5 Average extraction efficiency of neutral MEA degradation products without MEA by extractant in 2-ethyl-1-hexanol and by 2-ethyl-1-hexanol alone at 298 K.

As previously stated, some of neutral MEA degradation products (imidazole, N-acethylethanolamine and 2-oxazolidone) could act as weak acid in the aqueous solution, which can exist either as un-dissociated (HA) or dissociated anion (A^-) forms depending on its pK_a (Table 4.1). The dissociated fraction (H^+ and A^-) prefer water phase, while the un-dissociated fraction (HA) could be in equilibrium in aqueous and organic phases depending on its solubility in each phase as shown in Equations 4.1, 4.2, and 4.3 for imidazole, N-acethylethanolamine and 2-oxazolidone, respectively.

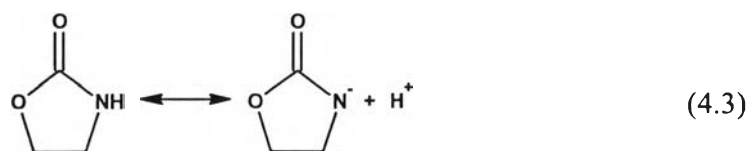
For imidazole,



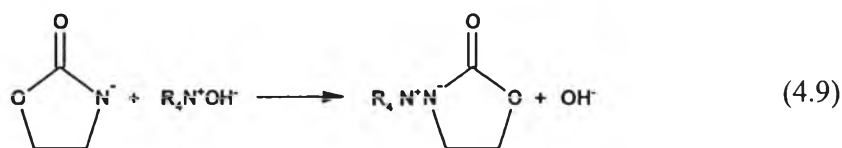
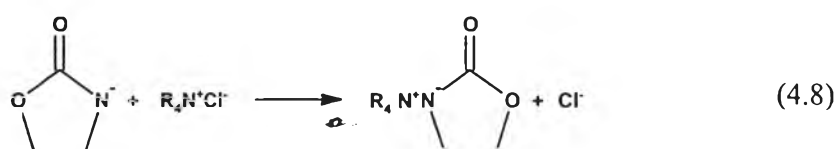
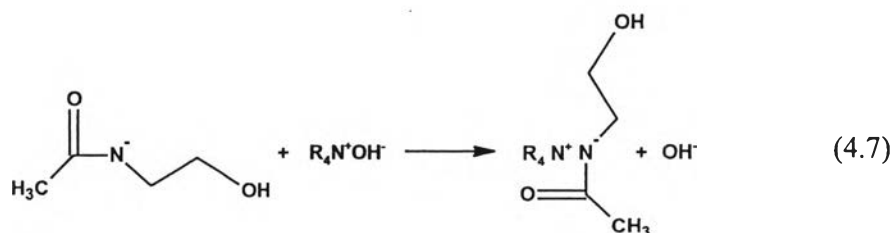
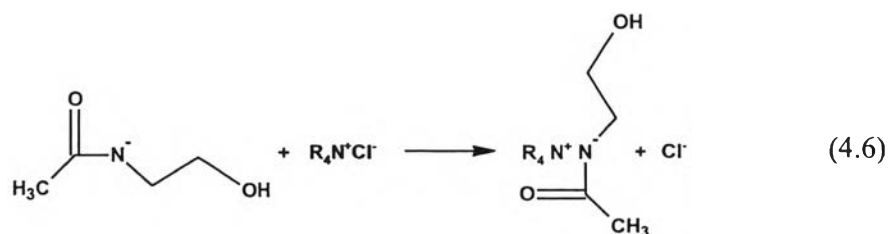
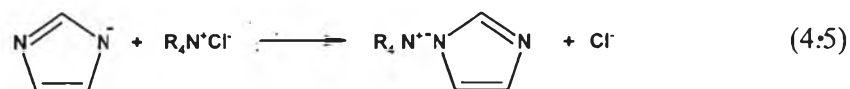
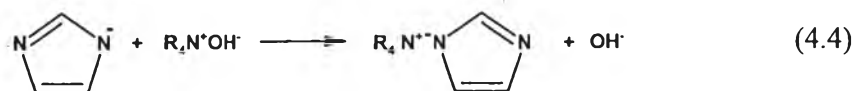
For N-acethylethanolamine,



For 2-oxazolidone,



Thus, the dissociated form of these neutral MEA degradation products that were extracted into the organic phase occurred at the interface by forming acid-base complex with the extractant as represented in Equations 4.4 – 4.9. The extractant (Aliquat-336) that was mixed with the diluent in this current study consists of 37.52 % extractant in chloride form ($R_4N^+Cl^-$) and 62.48 % in hydroxide form ($R_4N^+OH^-$).



Venkatesan and Begum (2009) the extraction of imidazole from dilute aqueous solutions using Aliquat 336 as extractant. Imidazole is an amphoteric molecule so it can act both as a base and an acid depending on its pH. If moderately basic ($\text{pK}_a = 7.0$) it'll act as a hydrogen acceptor and if weakly acidic ($\text{pK}_a = 14.9$) it acts as hydrogen donor, so when the pH of imidazole solution is maintained high ($\text{pH} > 7$), it deprotonates to anionic form. Therefore, in the previous research

carbonate or phosphate was used as a buffer to maintain pH in the imidazole solution (Venkatesan and Begum, 2009). This increased the anionic form of imidazole, and the ion exchange formed acid-base complex with Aliquat 336 at more than 70 %.

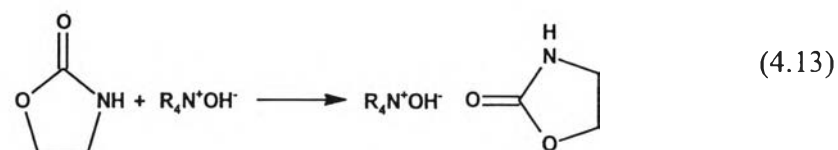
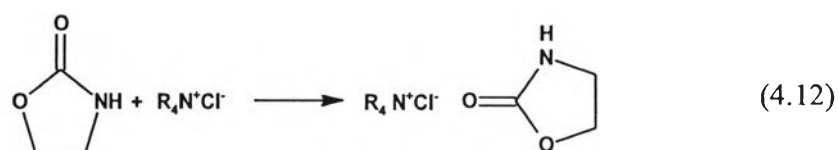
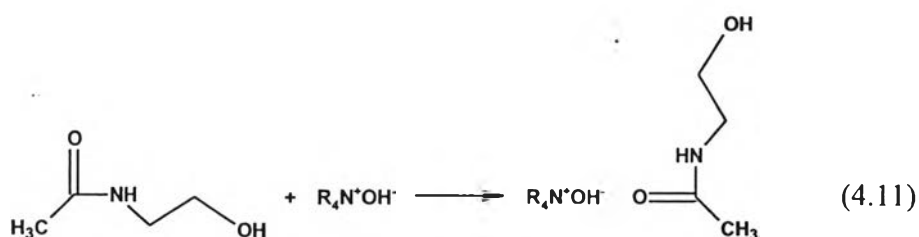
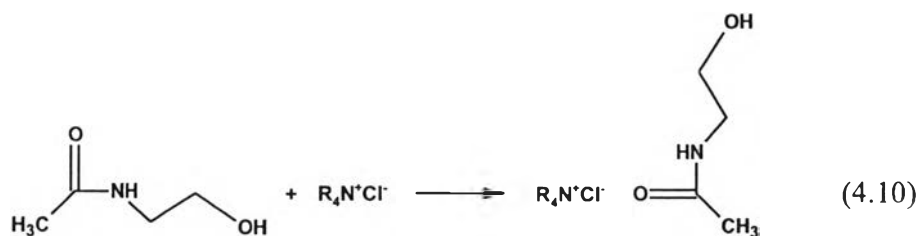
Nevertheless, in this study the pH of imidazole solution was not more than 7 because of the presence of distilled water in aqueous imidazole solution. Thus, imidazole was difficult to deprotonate into anionic form and there was not ion exchange, hence did not form acid-base complex with the extractant. This was the main reason why there was not change in the extraction efficiency of imidazole between diluent alone and extractant in diluent (Figure 4.5).

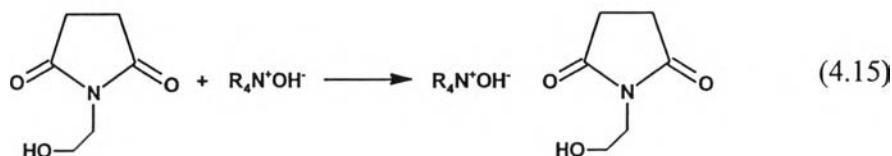
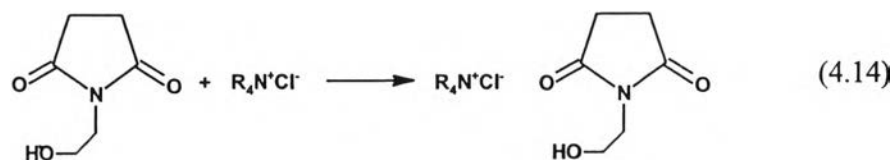
Yang *et al.* (1991) investigated the extraction of carboxylic acids by using Aliquat 336 (a quaternary ammonium chloride) as an extractant. Their result revealed that Aliquat 336 chloride form could extract both un-dissociated and dissociated acids under both acidic and basic conditions. In addition, the interaction between the carboxylic acids (HA) in the aqueous phase and quaternary amine extractant in the organic phase occurs at the interface. The interaction at the interface can lead to increased extraction efficiency. The interaction between Aliquat 336 and carboxylic acids is the reason why the extraction efficiency of N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide greatly increased. The un-dissociated acid of these neutral MEA degradation products binds with extractant in the organic phase as shown in Equations 4.10 – 4.15. The highest extraction efficiency was seen in N-(2-hydroxyethyl)-succinimide, which can be attributed to the presence of two carbonyl groups (C=O) in its structure. The extraction efficiency of 2-oxazolidone was close to that of N-(2-hydroxyethyl)-succinimide due to the presence of carbonyl group in its structure. The least extraction efficiency was noticed for N-acethylethanolamine, and this can be related to the presence of hydroxyl group in its structure which made it a bit soluble in the aqueous phase (hydrophilic) hence reduced its contact surface area with the extractant (Aliquat 336). It's also important to note that the extraction efficiency of N-acethylethanolamine for the extractant in diluent is higher compared to diluent alone because of the presence of carbonyl group in its structure. In addition, N-(2-hydroxyethyl)-succinimide also has hydroxyl group (OH) in its structure but it contains more carbon chains than N-acethylethanolamine, thereby making it more

hydrophobic. On the contrary, imidazole has no C=O in its structure, so there is no interaction with the extractant and complex formation through the ion pair interaction. This is another reason why there was not change in the extraction efficiency of imidazole between diluent alone and extractant in diluent (Figure 4.5). The results indicated that increase in carbonyl groups the structure increases extraction efficiency, while the presence of hydroxyl group was counter-productive.

Another important observation is that the extraction efficiency of the neutral MEA degradation products (using extractant in diluent) was higher with those with cyclic structure than those with straight chain structure. Therefore, It is believed that cyclic structure played a role in the extraction efficiency.

In organic phase:

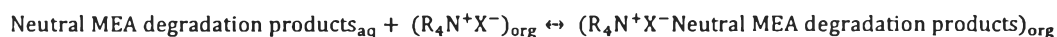




Another important parameter is the distribution coefficient. Marinova et al. (2004) studied the distribution of acid in the organic phase (K_D) that is used to measure the extraction efficiency. The correlation was also applied to this current research seen in Equation 4.16.

$$K_D = \frac{[\text{TA}]_{\text{org total}}}{[\text{TA}]_{\text{aq total}}} \quad (4.16)$$

Where $[\text{TA}]_{\text{org}}$ and $[\text{TA}]_{\text{aq}}$ are total concentration of neutral MEA degradation products in organic phase and aqueous phase, respectively.



When the neutral MEA degradation products were involved equilibrium extraction (K_E). The extraction of the neutral MEA degradation products by extractant as followed in Equation. 4.18.

$$K_E = \frac{[\text{R}_4\text{N}^+\text{X}^- \text{TA}]_{\text{org}}}{\text{TA}_{\text{aq}}[\text{R}_4\text{N}^+\text{X}^-]_{\text{org}}} \quad (4.18)$$

Where $[\text{R}_4\text{N}^+\text{X}^-]_{\text{org}}$ is concentration of amine extractant, which in this work is 1 molar. Thus, it can be assumed that the equilibrium extraction constant (K_E) is equal to distribution coefficient (K_D) as followed in Equation 4.19.

$$K_E = \frac{[R_4N^+X^-TA]_{org}}{TA_{aq}[R_4N^+X^-]_{org}} = K_D \quad (4.19)$$

Table 4.2 shows the result of neutral MEA degradation products distribution at equilibrium extraction. N-(2-hydroxyethyl)-succinimide was highest distribution coefficient to 177.20 and followed by 2-oxazolidone, imidazole and N-acethylethanolamine for 5.22, 0.65 and 0.37, respectively.

Table 4.2 Distribution coefficient of neutral MEA degradation products extraction with 2-ethyl-1-hexanol absent and presence extractant without MEA at 298 K

Components	K _D	
	2-ethyl-1-hexanol	Extractant in 2-ethyl-1-hexanol
imidazole	0.70	0.65
N-acethylethanolamine	0.05	0.37
2-oxazolidone	0.03	5.22
N-(2-hydroxyethyl)-succinimide	0.20	177.20

The result in Table 4.2 indicates that using quaternary ammonium (R_4N^+) in 2-ethyl-1-hexanol enhanced the distribution of the neutral MEA degradation products extraction. The distribution coefficient also followed the same trend of their extraction efficiency.

Extraction of Neutral MEA Degradation Products with MEA Present

The extraction of neutral MEA degradation products in the presence of 5 kmol/m³ MEA by using extractant in 2-ethyl-1-hexanol shown in Figure 3 and they followed this order N-(2-hydroxyethyl)-succinimide > 2-oxazolidone > N-acethyl-ethanolamine > imidazole. Figure 4.6 also reveals that the extraction efficiency of neutral MEA degradation products (using extractant in diluent) without 5 kmol/m³ MEA was higher than those with 5 kmol/m³ MEA. This was due to the

competitive reaction of MEA and the extractant with the neutral MEA degradation products.

The MEA in the aqueous solution increased the pH values which then increased the concentration of neutral MEA degradation product in dissociated form. This dissociation of neutral MEA degradation products into to anion form increased its interaction with MEA, hence making them difficult to extract.

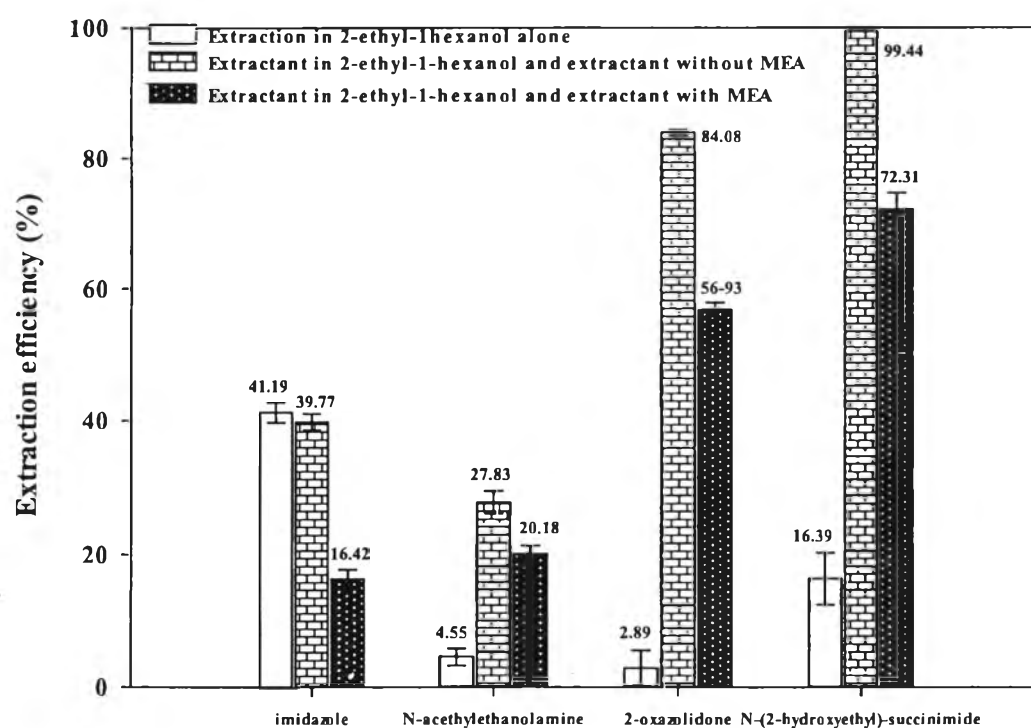


Figure 4.6 Average extraction efficiency of neutral MEA degradation products with and without MEA by extractant in 2-ethyl-1-hexanol and by 2-ethyl-1-hexanol alone at 298 K.

Table 4.3 highlights the distribution coefficient of the neutral MEA degradation products using extractant in diluent both with MEA and without MEA. Results also indicated that the presence of MEA in the aqueous solution reduced the

distribution coefficient of the neutral MEA degradation products, and it followed the same order of their extraction efficiency.

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Table 4.3 Distribution coefficient of neutral MEA degradation products extraction extractant in 2-ethyl-1-hexanol with and without MEA present at 298 K

Components	K_D	
	Without MEA	With MEA
imidazole	0.66	0.20
N-acethylethanolamine	0.39	0.25
2-oxazolidone	5.28	1.32
N-(2-hydroxyethyl)-succinimide	177.52	2.61

4.3.3 Effect of Temperature on Neutral MEA Degradation Product Extraction

Using Extractant in Diluent in the Absence of 5 kmol/m³ MEA

Temperature can have effect in the extraction efficiency of neutral MEA degradation products. Figure 4.7 depicts the effect of temperature (298 K, 313 K and 333 K) in the extraction efficiency (using extractant in 2-ethyl-1-hexanol) of neutral MEA degradation products in the absence of MEA. It was observed that the extraction efficiency had linear relationship with the studied temperatures (298 K, 313 K and 333 K), most especially for imidazole which increased from 39.77 ± 1.12 % to 41.06 ± 0.54 % and 62.59 ± 1.25 %, for N-acethylethanolamine from 27.83 ± 1.66 % to 28.11 ± 0.66 % and 52.23 ± 1.00 % and for 2-oxazolidone from 84.09 ± 0.47 % to 84.24 ± 0.22 % and 97.34 ± 0.24 %. It was also noticed that the increase in the extraction efficiency was more evident at 333 K than in 313 K. Since viscosity of substances reduces with increase in temperature, it can be said that the viscosity of the extractant and diluent reduced at 333 K which led to an increase in contact surface area with the neutral MEA degradation products, hence increase in extraction efficiency. In addition, the temperature increase might have also reduced the interaction between MEA and the neutral MEA degradation products which allowed its increase in extraction efficiency. For the extractability of N-(2-hydroxyethyl)-

succinimide, the efficiency reached maximum 99.44 ± 0.02 % extraction at 298 K and maintained it as temperature increased (99.58 ± 0.05 % at 313 K and 99.65 ± 0.01 % at 333 K). Table 4.4 highlights the distribution coefficients of the neutral MEA degradation products with extractant in 2-ethyl-1-hexanol without 5 kmol/m^3 MEA at 298 K, 313 K and 333 K. The distribution coefficient also followed same trend as the extraction efficiency.

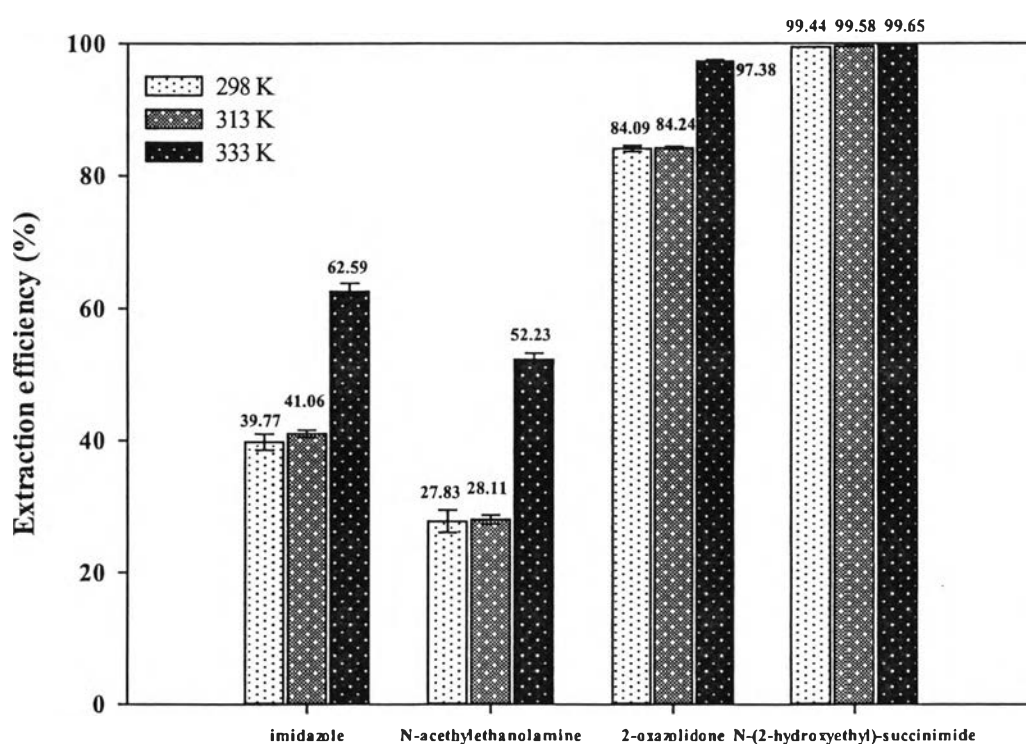


Figure 4.7 Effect of temperature on neutral MEA degradation products extraction efficiency without MEA by extractant in 2-ethyl-1-hexanol at 298 K, 313 K and 333 K.

Table 4.4 Distribution coefficient of neutral MEA degradation products extraction with extractant in 2-ethyl-1-hexanol without MEA at 298 K, 298 K and 333 K

Components	K_D		
	298 K	298 K	333 K
imidazole	0.66	0.70	1.67
N-acethylethanolamine	0.39	0.39	1.09
2-oxazolidone	5.28	5.34	36.64
N-(2-hydroxyethyl)-succinimide	177.52	237.95	284.58

Using Extractant in Diluent in the Presence of 5 kmol/m³ MEA

The effect of temperature (298 K, 313 K and 333 K) on the extractability of neutral MEA degradation products in the presence of MEA is shown in Figure 4.8. As observed in the absence of MEA, extraction efficiency had a linear relationship with temperature. The extraction efficiency was increased from 16.42±1.36 % to 28.90±1.21 % and 45.38±0.25 % for imidazole, from 20.18±1.19 % to 27.94±2.93 % and 46.64±0.54 % for N-acethylethanolamine, from 56.93±1.09 % to 72.14±0.74 % and 79.47±1.99 % for 2-oxazolidone and from 72.31±2.54 % to 79.40±0.43 % and 83.38±2.35 % for N-(2-hydroxyethyl)-succinimide at 298 K, 313 K and 333 K, respectively. The extraction efficiency was lower in the presence of MEA compared to the absence of MEA but increase in temperature up to 333 K increased their extraction efficiency. The Table 4.5 showing the distribution coefficient also followed same order with the effect of temperature.

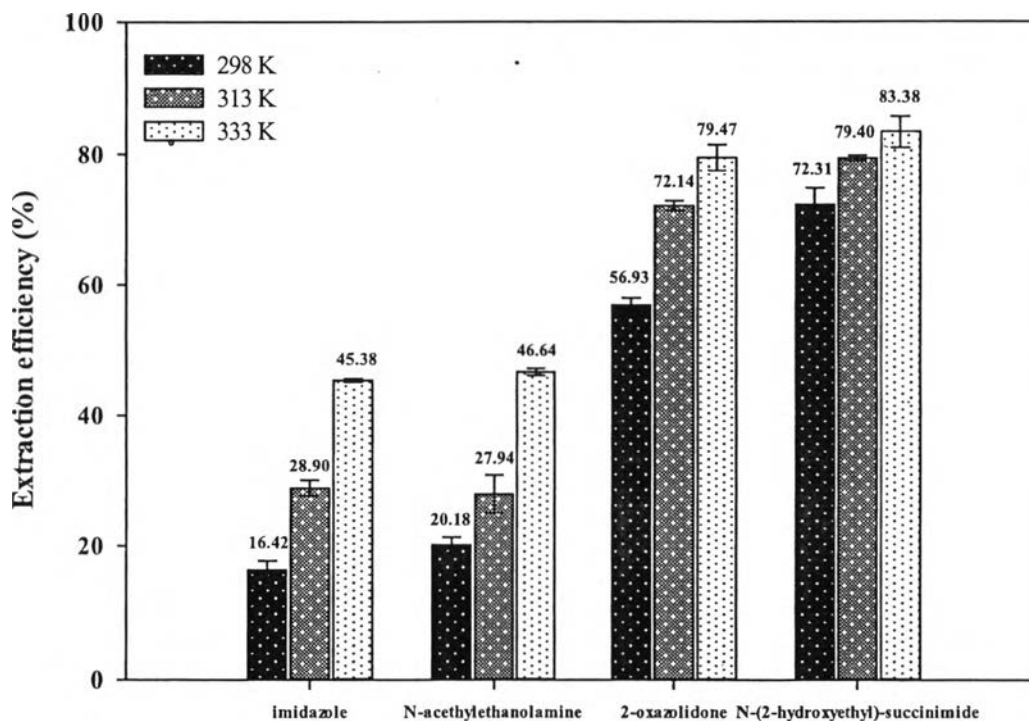


Figure 4.8 Effect of temperature on neutral MEA degradation products extraction efficiency in the presence of MEA by extractant in 2-ethyl-1-hexanol at 298 K, 313 K and 333 K.

Table 4.5 Distribution coefficient of neutral MEA degradation products extraction with extractant in 2-ethyl-1-hexanol with MEA at 298 K, 313 K and 333 K

Components	K_D		
	298 K	313 K	333 K
imidazole	0.20	0.41	0.83
N-acetyethanolamine	0.25	0.39	0.87
2-oxazolidone	1.32	2.59	3.87
N-(2-hydroxyethyl)-succinimide	2.61	3.85	5.02

Taking into consideration the linear relationship between the extraction efficiency of neutral MEA degradation products and temperature (up to 333 K) both in the absence and presence of 5 kmol/m³ MEA (using extractant in diluent), it is believed that liquid-liquid extraction at typical regeneration temperature (393 K – 413 K) is likely give higher extraction efficiency. Additionally, the boiling points of 2-ethyl-1-hexanol (459 K) and Aliquat 336 (498 K) are farther away from the typical regeneration temperature, hence there will be minimized losses through vaporization and increase in the extraction efficiency.

4.3.4 Effect of CO₂ Loading

The effect of CO₂ loading (0.00, 0.05, 0.13 and 0.3 mol CO₂/mol MEA) in 5 kmol/m³ MEA was studied at 298 K. The results in Figure 4.9 showed that the average extraction efficiency of neutral MEA degradation products decreased with increasing the CO₂ loading. The average extraction of 0.00, 0.05, 0.13 and 0.3 mol CO₂/mol MEA were 39.77±1.12 %, 11.88±0.71 %, 10.35±0.79 % and 7.59±1.93 % for imidazole, 27.83±1.66 %, 18.00±0.25 %, 13.70±0.79 % and 10.59±0.73 % for N-acethylethanolamine, 84.09±0.47 %, 38.71±1.89 %, 28.68±0.91 % and 13.50±1.22 % for 2-oxazolidone and 99.44±0.02 %, 53.72±3.28 %, 40.80±2.73 % and 23.97±4.73 % for N-(2-hydroxyethyl)-succinimide, respectively. The same trend was also reflected in their distribution coefficient (Table 4.6).

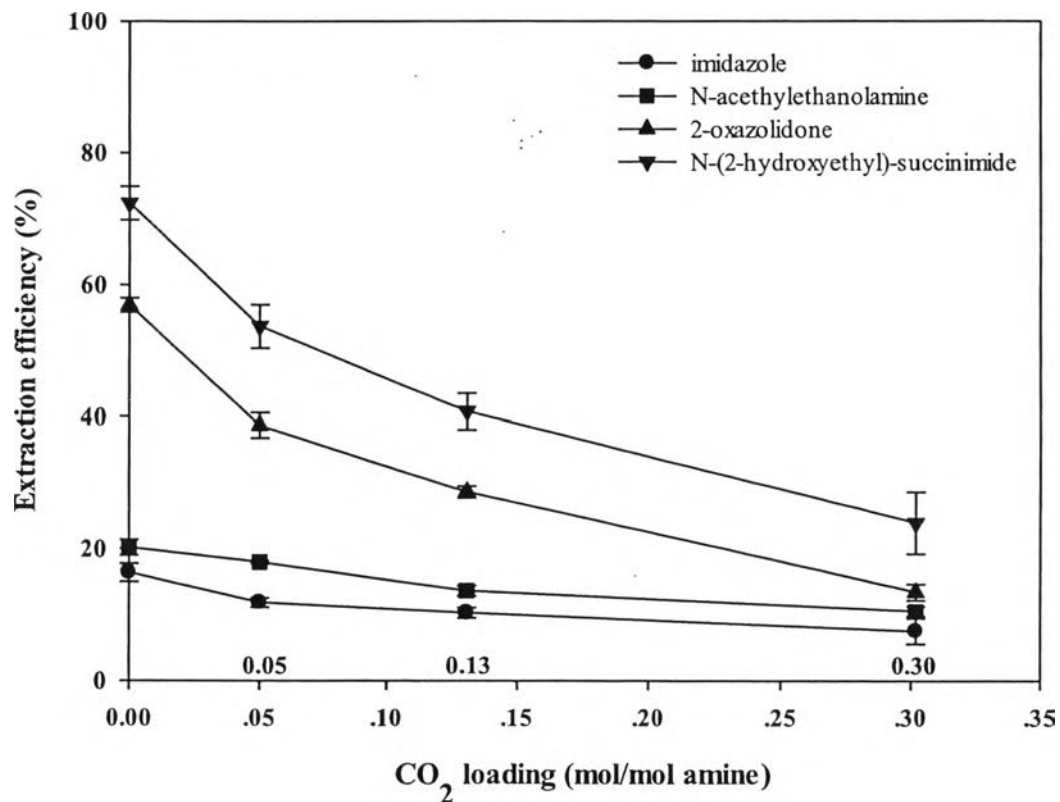
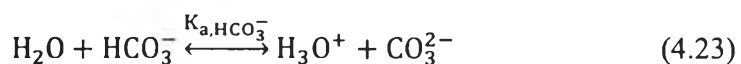
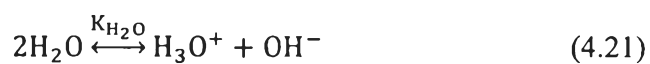
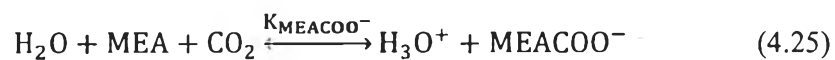
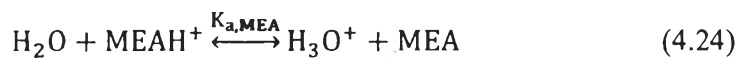


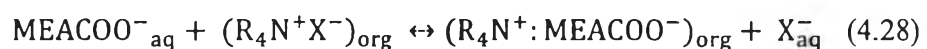
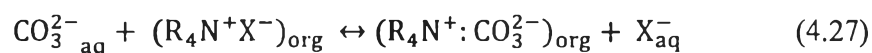
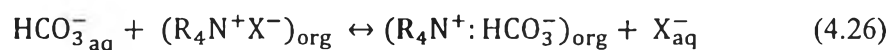
Figure 4.9 Effect of CO₂ loading on extraction of neutral MEA degradation products in the 5 kmol/m³ MEA solution at 298 K (using extractant in diluent).

According to Dang and Rochelle (2001) the chemical reactions of CO₂-MEA-H₂O are represented using Equations 4.20 – 4.25.





The presence of CO₂ in aqueous MEA solution added bicarbonate (HCO₃⁻), carbonate (CO₃²⁻) and carbamate (MEACOO⁻) anions in the system as shown in Equations 23 - 26 (Dang and Rochelle, 2001). This reduced the extraction efficiency because of the competitive extraction (co-extraction) between the anions of HCO₃⁻, CO₃²⁻, and MEACOO⁻ with the anions of the neutral MEA degradation products react with the extractant. Equations 4.26 – 4.28 show the anion exchange of HCO₃⁻, CO₃²⁻, and MEACOO⁻ with the extractant. The extraction efficiency further reduced as CO₂ loading increased, because of the increased concentration of the CO₂ carrying species which increase with CO₂ loading.



This reduction in extraction efficiency followed this order 39.77±1.12 %, 11.88±0.71 %, 10.35±0.79 % and 7.59±1.93 % for imidazole, 27.83±1.66 %, 18.00±0.25 %, 13.70±0.79 % and 10.59±0.73 % for N-acethylethanolamine, 84.09±0.47 %, 38.71±1.89 %, 28.68±0.91 % and 13.50±1.22 % for 2-oxazolidone and 99.44±0.02 %, 53.72±3.28 %, 40.80±2.73 % and 23.97±4.73 % for N-(2-hydroxyethyl)-succinimide, respectively.

The distribution coefficient of the neutral MEA degradation products in the organic phase reduced with increasing CO₂ loading as shown in Table 4.6. This was also due to the competitive reaction between the carbonate/carbamate species and the neutral MEA degradation products with the extractant.

Table 4.6 Distribution coefficient of neutral MEA degradation products extraction with extractant in 2-ethyl-1-hexanol with CO₂ loading at 298 K

Components	K _D		
	0.05 (mol/mol amine)	0.10 (mol/mol amine)	0.30 (mol/mol amine)
imidazole	0.13	0.12	0.08
N-acethylethanolamine	0.22	0.16	0.12
2-oxazolidone	0.63	0.40	0.16
N-(2-hydroxyethyl)-succinimide	1.16	0.69	0.32