THE UNIVERSITY OF CALGARY

DEGRADATION OF MDEA-DEA MIXTURES WITH CO_2

by

ÜLKÜ ERSAN

A THESIS

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DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Degradation of MDEA-DEA Mixtures with CO_2" submitted by Ülkü Ersan in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

Aqueous amine solutions are widely used for the removal of H_2S and CO_2 from raw natural gas. These solutions often break down, as a result of side reactions with CO_2, forming degradation compounds. Degradation causes solvent losses and increased maintenance costs due to operational problems.

Degradation of MDEA-DEA mixtures was studied by contacting the amine mixture with CO_2 under carefully controlled conditions in a batch reactor. Degradation was found to be affected by temperature, pressure and initial solution concentration. It was also shown that H_2S had no effect on degradation. A simple kinetic model was developed to describe the degradation of MDEA-DEA mixture.

Different methods were examined to purify degraded DEA solutions; such as ion-exchange resins, vacuum distillation and reversing the degradation reactions by NaOH treatment. Vacuum distillation was found to be ineffective while the other two methods were partially effective in purification of degraded solutions.

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TO MY FAMILY

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NOMENCLATURE

BHEP	N,N-Bis(hydroxyethyl) piperazine
C	Concentration (M)
C_0	Initial concentration (M)
DEA	Diethanolamine
DMAE	2-(dimethylamino) ethanol
EG	Monoethylene glycol
HEOD	3-(hydroxyethyl)-2-oxazolidone
k	Reaction rate constant
k_1, k_2	MDEA-DEA degradation rate conslants (l /mol hr)
$k_{3\rightarrow 7}$	MDEA-DEA degradation rate constants (hr^{-1})
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
R	Universal gas constant (J / mol K)
T	Absolute temperature (K)
t	Time (hr or min)
THEED	N,N,N-Tris(hydroxyethyl) ethylenediamine

CHAPTER 1

INTRODUCTION

Raw natural gas obtained from a natural underground reservoir generally contains a considerable amount of non-hydrocarbons, such as nitrogen (N_2), hydrogen sulphide (H_2S), carbon dioxide (CO_2) and water. The acid gases (H_2S and CO_2) and water must be removed from the natural gas prior to its industrial or domestic use in order to prevent pipeline corrosion and to avoid health and pollution problems. According to pipeline gas specifications, H_2S content of the natural gas must be reduced to 4 - 16 ppm and CO_2 concentration must not exceed 2 % by volume. Therefore, large quantities of 'sour' natural gas must be 'sweetened' to meet these specifications.

1.1 ACID GAS REMOVAL PROCESSES

There are many commercially available processes for removing acid gases. The selection of the process depends on the specifications to be met, the quantity of the gas to be processed and the composition of the raw gas being treated. Acid gas removal processes may be broadly classified into four main categories:

- Chemical solvent processes
- Physical solvent processes
- Direct conversion processes

- Dry bed processes

Chemical solvent processes are based on chemical absorption and commonly used chemical solvents are amines and promoted hot carbonates. On the other hand, physical solvent processes depend on physical absorption where no chemical reaction takes place. Also, hybrid solvents that are mixtures of physical and chemical solvents, combining the desirable characteristics of both, are used. The basis of direct conversion processes is chemical conversion and dry bed processes are based on chemical or physical adsorption.

Chemical solvents, particularly amines, are by far the most commonly used for acid gas removal. Among amines, monoethanolamine (MEA) and diethanolamine (DEA) have been widely used, but are losing ground to the more modern, energy efficient, methyldiethanolamine(MDEA)-based formulated solvents [6,21]. MDEA-based mixed solvents have many advantages over MEA, DEA and other conventional amines. They provide both a selective removal of H_2S over CO_2, and energy savings due to reduced heat of reaction and reduced CO_2 load. Also, because of their less corrosive character, MDEA-based solvents can be concentrated up to 50 wt% against 15 to 35 wt% of typical MEA and DEA concentrations. This increased concentration allows lower circulation rates to remove the same amount of acid gas which in return can provide capacity increases and energy reduction due to decreased regeneration and pumping energy. Also, the mixed-solvents combine the desirable qualities of individual amines.

1.2 AMINE PROCESS

Amines absorb acid gases by forming ionic salts which release the acid gas and regenerate the solvent on heating. The overall reactions of DEA and MDEA with CO_2 and H_2S can be summarized as follows [2]:

DEA-CO_2

$$2\ R_2NH + H_2O + CO_2 \rightleftharpoons (R_2NH_2^+)_2CO_3^{--} \tag{1.1}$$

$$(R_2NH_2^+)_2CO_3^{--} + H_2O + CO_2 \rightleftharpoons 2\ R_2NH_2^+ + 2\ HCO_3^- \tag{1.2}$$

MDEA-CO_2

$$R_2NCH_3 + H_2O + CO_2 \rightleftharpoons R_2NHCH_3^+ + HCO_3^- \tag{1.3}$$

DEA-H_2S

$$R_2NH + H_2S \rightleftharpoons R_2NH_2^+ + HS^- \tag{1.4}$$

MDEA-H_2S

$$R_2NCH_3 + H_2S \rightleftharpoons R_2NHCH_3^+ + HS^- \tag{1.5}$$

where R represents $-C_2H_4OH$

The equilibria of the above reactions lie to the right at low temperatures and high acid gas partial pressures. However, the equilibrium can be shifted to left by increasing the temperature at reduced acid gas partial pressures, which is the basic idea behind the amine process.

Figure 1.1 shows a simplified process flow sheet for a typical industrial amine sweetening unit. The raw natural gas entering the unit, is contacted with a counter-current stream of aqueous amine solution in the absorber at 30-50 °C. The acid gases are absorbed by the amine and the sweetened gas leaves the top of the absorber. The rich amine solution is reduced in pressure in a flash tank where most of the absorbed hydrocarbons are flashed off. Then, the rich amine solution, containing the acid gases, passes through a heat exchanger where it is heated by the hot, lean amine solution. It is, then pumped to the top of the stripper where it is regenerated at 100-120 °C by contacting with a counter-current flow of vapor generated in the reboiler. The acid gases are removed by the stripping vapour which is generally steam. The lean amine solution is cooled and recycled back to the absorber.

1.3 AMINE DEGRADATION

Although, CO_2 reacts reversibly with the amines at low temperatures, amines also undergo irreversible reactions with CO_2 at high temperatures in the stripper forming undesirable compounds which cannot be regenerated [8,58]. This phenomenon is called "degradation". Most plants experience loss of amine due to degradation in varying quantities depending on raw gas composition and plant operation.

Degradation is undesirable since the accumulation of degradation products causes operating problems. The main disadvantages of degradation can be summarized as follows [11,58,63]:

- Loss of valuable solvent

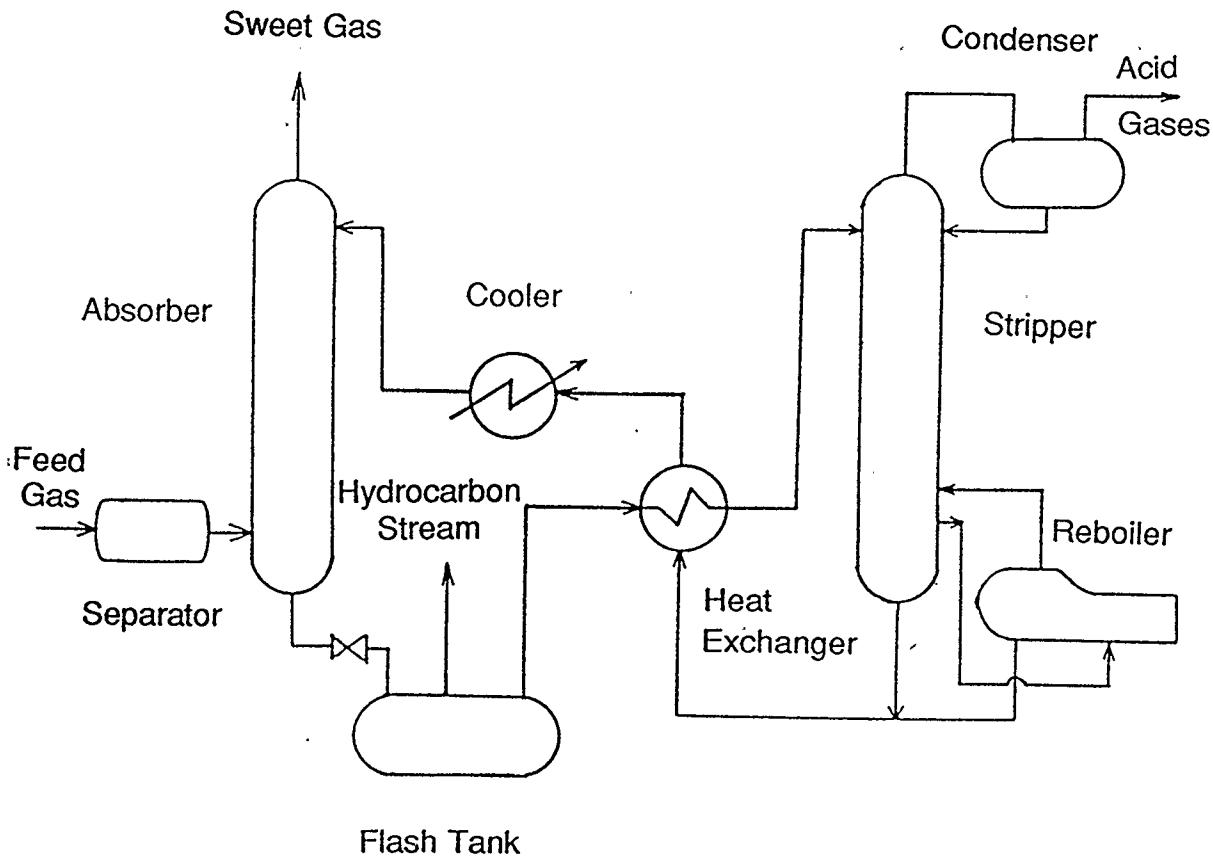


Figure 1.1 Simplified flow sheet of a typical amine unit

- Corrosion
- Equipment fouling
- Foaming

Amine degradation and purification have been investigated by many researchers since it is an industrially important problem (see Chapter 2). However, there is still need for further exploration, especially on the degradation of the newer MDEA-based mixed solvents which have gained an increasing share of the gas treating market over the recent years.

1.4 OBJECTIVES OF THE PRESENT STUDY

The main objectives of the present study are:

- To examine the degradation of MDEA-DEA mixtures at different temperatures, pressures and initial solvent concentrations.
- To develop a simple kinetic model able to predict the degradation of MDEA-DEA mixtures with CO_2 and the production of the major degradation compounds.
- To explore different methods suitable for the purification of the degraded amine solutions.

CHAPTER 2

LITERATURE REVIEW

2.1 AMINE DEGRADATION

The alkanolamine process for acid gas removal from natural gas streams began in 1930 with the first licensed amine plant [44].

Organic bases for gas sweetening were first studied by Bottoms [8] who stated in his work that the ethanolamines (diethanolamine and triethanolamine) were found to be the most satisfactory compounds for this purpose. He also observed that the ethanolamines were stable at low temperatures, but when the pure compounds or the water solutions were heated to above 150 °C, some decomposition was noticed. This was the first reported observation of amine degradation.

2.1.1 DEA DEGRADATION WITH CO_2

The most widely used amine solvent for gas sweetening is diethanolamine (DEA). However, on prolonged use, it can undergo "degradation" which is a complex phenomenon.

In 1955, Henry and Grennert [31] investigated some heat stable diethanolamine salts formed by the reaction of DEA with some acidic constituents stronger than H_2S and CO_2 and stated that DEA would not be liberated during the regeneration process. Those constituents were reported to be organic acids

(shown by Norris and Clegg [52] to be mainly acetic and formic acids); chloride; cyanide and thiocyanate; sulphite, sulphate and thiosulphate. Also, Waterman et al. [66] reported the presence of heat stable anions in gas treating DEA solutions such as acetate, formate, oxalate and thiosulphate.

The degradation of DEA is mainly due to irreversible reactions of DEA with CO_2. The first major work on DEA degradation was published by Polderman and Steele [58] in 1956. Their experimental procedure was to saturate a 25 % DEA solution with CO_2 at 25 °C and to seal it in a stainless steel pressure autoclave. Then the autoclave was heated to a temperature ranging from 100 °C to 175 °C for 8 hours under a pressure range of 1.24 MPa - 4.14 MPa. After cooling to 25 °C, the contents were analyzed by fractional distillation and crystallization. DEA losses were found to range from 0 % at 100 °C and 1.24 MPa to 97 % at 175 °C and 4.14 MPa. They identified one of the degradation compounds to be N,N-bis(hydroxyethyl)piperazine (BHEP) and suggested that it was formed from the reaction of an intermediate compound, 3-(2-hydroxyethyl)-2-oxazolidone (HEOD) with carbon dioxide. Other degradation compounds were characterized as linear polycarbamides containing polyalkylene-amine structures, but could not be identified due to the lack of suitable analytical techniques.

In a following study, Hakka et al. [29] isolated and identified N,N,N'-tris(2-hydroxyethyl)ethylene diamine (THEED) as another degradation product of DEA by more sophisticated chemical and spectroscopic techniques. They found that THEED frequently occurred at the level of 0.5 to 2 % of the gas treating solution and was by far the major unidentified degradation product. The degradation of DEA was summarized as conversion to BHEP and THEED in roughly similar

quantities. Also, it was claimed that no particular problems were expected to be encountered under normal conditions with respect to acid gas removal capacity, regeneration, foaming or corrosion with moderately degraded amine solutions.

Smith and Younger [62,63] reported that degradation depends on temperature, pressure, gas composition, amine concentration, solution pH and the presence of metal ions.

Choy [20], performing several degradation experiments at temperatures and CO_2 partial pressures ranging from 165 to 185 °C and 1.2 to 4.14 MPa, found that DEA degradation was governed by a first order reaction. Also, the rate of degradation was found to be affected by the initial DEA concentration which contradicts the first order reaction concept. Several unidentifiable degradation compounds were detected and their concentration changes with time suggested a series of simultaneous and consecutive degradation reactions.

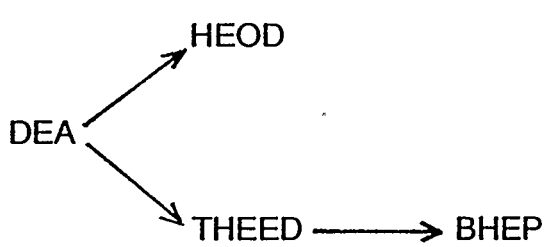
Kennard and Meisen [38,47] reviewed the earlier studies on DEA degradation and included the preliminary results of a comprehensive study of the reaction mechanisms and kinetics of DEA degradation which was published in full later. They interpreted qualitatively the effect of temperature, pressure, initial DEA concentration and degradation products on the degradation of DEA, based on their experimental study in order to develop practical guidelines for plant use.

At the same time, in their study Blanc et al. [7] reacted CO_2 separately with DEA and HEOD solutions in a sealed autoclave, varying the temperature from 90 to 130 °C. They proposed various mechanisms for the formation of

HEOD, THEED, BHEP and other degradation compounds, but they didn't present any quantitative data to support these reaction mechanisms.

In later publications, Kennard [40] and Kennard and Meisen [39] presented a study on the reaction mechanisms and kinetics of DEA degradation. Experiments were conducted to determine the effect of temperature (90 - 250 °C), total pressure (1.5 - 6.9 MPa) and initial DEA concentration (0 - 100 %) on DEA degradation, reacting DEA with CO_2 in a 600 mL, stirred stainless steel autoclave.

As a result of their studies, it was discovered that DEA degradation with CO_2 occurs according to several complex molecular, ionic and thermal routes. Many degradation compounds were detected, but the main ones were found to be HEOD, THEED, and BHEP; HEOD and THEED being produced directly from DEA while BHEP being formed from THEED as follows :



Also, CO_2 was found to act as a catalyst in the degradation of DEA. The range of conditions included in their model is:

Temperature	90 to 175 °C
DEA concentration	0 to 100 wt%
CO_2 loading	> 0.2 g. of CO_2 / g. of DEA

By restricting the CO_2 concentration to be greater than 0.2 g. of CO_2 / g. of DEA, they neglected the effect of CO_2 on the degradation mechanism below this value.

DEA degradation was studied also by Kim and Sartori [41] who found the reaction to be catalyzed by CO_2 and occurring to the following scheme:

$$DEA + CO_2 \rightleftharpoons HEOD + H_2O$$

$$HEOD + DEA \longrightarrow THEED$$

$$THEED \longrightarrow BHEP$$

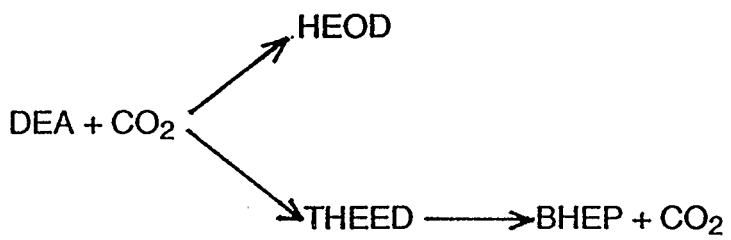
Rate constants for the above model were determined at 120 °C and 100 °C.

In follow-up studies, Chakma [17] and Chakma and Meisen [16] examined the degradation of DEA solutions being passed through a coiled heat transfer tube (2.032 mm. ID, 3.175 mm. OD, 4.8 m. long) immersed in a constant temperature bath. The operating conditions studied were:

DEA flowrate	0.011 to 0.0172 L/s
DEA concentration	20 to 40 wt%
DEA temperature	60 to 200 °C
CO_2 partial pressure	1.38 to 4.18 MPa.

Since the heat transfer tube used in these studies was considered to be too small in diameter compared with industrial heat exchanger tubes, Chakma [18] repeated the experiments with a tube of 4.93 mm. ID, 6.35 mm. OD, 4.8 m. long. The degradation rate was found to increase with temperature, DEA concentration

and CO_2 partial pressure and to decrease slightly with solution flowrate. It was also found that the degradation was accompanied by the formation of a fouling deposit. They modified the Kennard and Meisen's [39] model by introducing a CO_2 term as :



The rate constants for HEOD and THEED production reactions were re-evaluated by dividing them by the total CO_2 loading. Thus, they were able to account for the effects of solution concentration and CO_2 partial pressure for a given temperature and correlate the rate constants as a function of temperature only.

Hsu and Kim [34] in addition to the formation of HEOD, BHEP and THEED, reported significant amounts of triamine derivatives as degradation compounds, identified by mass spectrometric analysis as 3-(2-(bis(2-hydroxyethyl)-amino)ethyl)-2-oxazolidone (HAO), N-(2-(N,N-bis(2-hydroxyethyl) amino)ethyl)-N'-(2-hydroxyethyl)piperazine (HAP), and N,N,N",N"-tetrakis(2-hydroxyethyl)diethylenetriamine (THEDT). A reaction mechanism, which is an extension of the mechanism presented by Kim and Sartori [41], was proposed.

Industrial grade DEA solutions contain small amounts of MEA which also degrades to form oxazolidone (OZD), 1-(2-hydroxyethyl)imidazolidone (HEI),

N,N'-bis(hydroxyethyl)urea (BHEU) and N-(hydroxyethyl)ethylenediamine (HEED) [5,59].

The degradation of di-2-propanolamine (DIPA) was studied by Kim [42] and compared with the DEA degradation mechanism established previously [41]. The rates and products of degradation of DIPA were measured at 100-120 °C in the presence of a controlled amount of CO_2. The main degradation product was found to be 3-(2-hydroxypropyl)-5-methyl-2-oxazolidone (HPMO) and a kinetic model was derived and compared with the model for DEA degradation.

2.1.2 MDEA DEGRADATION WITH CO_2

Aqueous solutions of methyl diethanolamine (MDEA) are gaining industrial acceptance as solvents for the selective removal of hydrogen sulphide from light hydrocarbon gases containing carbon dioxide [45]. MDEA can not form carbamates with carbon dioxide, which provides its selectivity for hydrogen sulphide and also suggests that CO_2 is unlikely to degrade MDEA. It has been stated by Blanc et al. that "No one has been able to show any degradation products in MDEA solutions having been used for several years in industrial units" [6,7]. However, Yu et al. [68] have suggested that MDEA may also form carbamate ions with carbon dioxide and Chakma and Meisen [15] found in preliminary experiments that MDEA degrades at elevated temperatures and high carbon dioxide partial pressures. Later, Chakma [18] examined the degradation of MDEA as a function of temperature, CO_2 partial pressure and initial MDEA concentration. He carried out experiments with CO_2 in a 600 mL stainless steel autoclave with temperatures ranging from 100 to 230 °C; CO_2 partial pressures ranging from 345 to 4654 kPa and initial MDEA concentration ranging from 2.0 to

6.0 mol/L. In these experiments, MDEA was found to degrade fairly rapidly at elevated temperatures and a kinetic model describing MDEA degradation was developed. Also, by using gas chromatography and mass spectrometry, major MDEA degradation compounds were identified to be; methanol, ethylene oxide, trimethylamine, ethylene glycol, 2-(dimethylamino)ethanol, 1,4-dimethylpiperazine, N-(hydroxyethyl)methyl piperazine, triethanolamine and N,N-bis(hydroxyethyl)piperazine [14].

Recently, a paper was presented by Dawodu and Meisen [24] on the degradation of MDEA and MDEA/DEA, MDEA/MEA blends by CO_2. Their experiments consisted of contacting amine blends with CO_2 at a partial pressure of 3.4 MPa and temperatures ranging from 120 to 180 °C. In the case of MDEA/DEA blends, the degradation products were detected to be the same as those found in MDEA solutions. However, for MDEA/MEA solutions, four new degradation products were identified as hydroxyethyl methyl imidazolidone (HEMI), dimethyl bis-hydroxyethyl ethylenediamine (DMBHEED), hydroxyethyl methyl ethyl methyl piperazine (HEMEMP), hydroxyethyl methyl ethyl hydroxyethyl piperazine (HEMEHEP).

2.1.3 DEGRADATION OF ALKANOLAMINES WITH COS AND CS_2

The studies reviewed in the previous sections were all dealing with CO_2-induced degradation of alkanolamines. The acid gases H_2S, CS_2 and COS may also be present in natural, refinery and synthesis gases. Since H_2S is incapable of forming carbamate type compounds, it is generally agreed that it does not cause amine degradation. The results reported by Kim and Sartori [41] and Choy [20] suggest that H_2S in the presence of CO_2 hinders amine degradation.

Little work has been reported on the alkanolamine-COS reactions. Orbach and Selleck [53] contacted pure COS with 20% MEA and 35% DEA solutions in a bench-scale pilot plant simulating a typical, continuous absorption-regeneration process. The absorber and regenerator were operated at 40 °C and 104 °C, respectively. Periodic analysis of the amine solutions using Kjeldahl analysis and acid titration revealed that, while MEA was substantially degraded, no loss of alkalinity occurred in the DEA solution over 8 hours. Although formation of some products, which were too small for isolation and characterization, was examined, it was claimed that these products were formed from small quantities of MEA in the initial DEA solution. Hence, it was concluded that COS did not degrade DEA.

Pearce et al. [55] using a batch reactor, contacted pure COS with 20% MEA solutions at temperatures ranging from 40 to 120 °C. The solutions were analyzed by infrared and mass spectroscopy and were found to contain N(2-hydroxyethyl)imidazolidone, diethanol urea and minor amounts of oxazolidone. COS-DEA systems were also examined under test conditions similar to COS-MEA systems. Minor quantities of ethanol and oxazolidone were detected in comparison to the degradation products observed in similar experiments with MEA. They also contacted COS with DEA continuously using an approach analogous to that of Orbach and Selleck [53]. The concentrations of the DEA solutions at the start and end of the experiments were determined from volumetric analyses and found to be essentially the same. This again led to the conclusion that COS does not degrade DEA.

A study on alkanolamine degradation by CS_2 was conducted by Osenton and Knight [54]. They contacted 40 mL of a 25% aqueous DEA solution with 7

mL of CS_2 for 3 hours in a stirred vessel at 25 °C. Double potentiometric and dithiocarbamate titrations of solution samples revealed the complete conversion of amine to the amine salt of dithiocarbamic acid according to:

$$2\ R_2NH + CS_2 \longrightarrow R_2NC(S)S^-N^+H_2R_2$$

where R denotes $-C_2H_4OH$. When the reaction mixture was boiled for 1 hour and analyzed in the same manner, only 20% of the DEA was recovered from the dithiocarbamate salt. Using MEA instead of DEA, they found that about 40% of the initial MEA was recovered upon boiling. They also detected oxazolidone-2-thione amongst the reaction products.

The degradation of alkanolamines with carbonyl sulphide and carbon disulphide was also studied by Dawodu and Meisen [23]. They performed experiments by contacting well-stirred aqueous DEA solutions (10 to 40%) in a 600 mL stainless steel autoclave with various COS-N_2 and CS_2-N_2 mixtures at temperatures ranging from 120 to 180 °C. Solution samples were analyzed by gas chromatography which revealed a decrease in DEA concentration and the appearance of degradation products over periods of 48 hours. The major reaction products of DEA-CS_2 systems, which were identified by combined GC/MS analysis, were reported to be monoethanolamine (MEA), N,N-bis-hydroxyethyl ethylenediamine (BHEED), N,N'-bis-hydroxyethyl piperazine (BHEP), N-hydroxyethyl oxazolidone (HEOD), N-hydroxyethyl imidazolidone (HEI), N,N,N'-tris-hydroxyethyl ethylenediamine (THEED), and N,N'-bis-hydroxyethyl imidazolidone (BHEI). For the DEA-COS systems, ethyl amino ethanol (EAE), ethyl diethanolamine (EDEA) and N-hydroxyethyl acetamide (HEA) were detected in the degraded solutions in addition to the degradation products of DEA

with CS_2. Other compounds such as acetaldehyde, acetone, butanone, ethanol, diethyl disulphide, 1,2 dithiane and alkyl substituted pyridines were also found. A solid compound which could not be identified was detected in DEA solutions degraded with both COS and CS_2. Reaction mechanisms for degradation were proposed. Also, the effect of operating conditions, such as initial DEA concentration, temperature, COS partial pressure and initial volume of CS_2, on the degradation rates and estimates of the degradation rate constants were discussed. Finally, it was concluded that both COS and CS_2 can cause slow degradation of aqueous DEA solutions but may become significant under typical plant conditions especially over extended periods of time.

2.2 ANALYSIS OF AMINE SOLUTIONS

Availability of an efficient analytical procedure for detecting and measuring the concentrations of degradation compounds is very important in degradation studies.

Brydia and Persinger [9] described a chromatographic technique for the analysis of ethanolamines. As direct gas chromatographic methods led to excessive peak tailing, they investigated derivatization with trifluoroacetic anhydride (TFA) prior to chromatographic separation. However, TFA also reacts with water and the resulting trifluoroacetic acid causes severe tailing in the chromatograms.

Piekos et al. [57] eliminated these problems by converting the alkanolamines into trimethylsilyl derivatives by using N,O-bis(trimethylsilyl) acetamide, which reacts with both the amino and hydroxyl groups of the

alkanolamines. This silylation process yielded fairly stable compounds which are more easily separated and identified by gas chromatography. Although, water concentrations of up to 5% could be tolerated using the silylating agent in excess; the water content of industrial amine solutions ranges from 65 to 90%. So, the method of Piekos et al. [57] is not directly applicable.

Choy and Meisen [19], modified the technique used by Piekos et al. [57], by stripping water from the degraded DEA solutions with air. The removal of water resulted in the precipitation of some of the degradation products. The dried sample was dissolved in dimethylformamide and the resulting mixture silylated with N,O-bis(trimethylsilyl) acetamide. The silylated compounds were then separated using a 1.83 m. x 3.18 mm. OD stainless steel column packed with 8% OV-17 on 80-100 mesh Chromosorb, a flame-ionization detector was used.

Although, the derivative GC methods examined so far are convenient and much shorter as compared to other chemical methods, they are still time consuming for industrial applications because of extensive sample preparation. Also, there is the problem of incomplete formation and instability of the derivatives and the fact that silylation of alkanolamines is difficult [57].

Direct GC, not involving the intermediate step of derivative formation, is a desired analytical method for the alkanolamines which was first studied by Saha et al. [60] in 1977. They used a gas chromatograph, equipped with a 1.22 m. x 6.35 mm. OD stainless steel column containing 60-80 mesh Tenax-GC which is a porous polymer based on 2,6-diphenyl-p-phenylene oxide having a weakly interacting surface, coupled to a flame ionization detector. A 0.30 m. x 3.18 mm. OD pre-column packed with 5% boric acid on Chromosorb-P 80/100 mesh was

used in series with the main Tenax-GC column to subtract the alkanolamines from other compound types. They were able to get good resolution of three ethanolamines (MEA, DEA and TEA) in less than 8 minutes by directly injecting the samples into the chromatograph under programmed temperature conditions.

Based on the work by Saha et al. [60], Kennard and Meisen [37] presented a simple and reliable gas chromatographic technique for the quantitative analysis of partially degraded aqueous diethanolamine solutions. A temperature-programmable gas chromatograph having a 1.83 m. x 3.18 mm. OD stainless steel column packed with Tenax GC and a flame ionization detector was used. The samples were injected, without preparation into the chromatograph, using nitrogen as the carrier gas and temperature programming to achieve good separation of all degradation products. By using this technique, they were able to detect eleven degradation compounds and measure concentrations as low as 0.5 wt% with an accuracy of ± 5%.

Chakma and Meisen [14], modified the GC technique used by Kennard and Meisen [37] for DEA for the analysis of degraded MDEA solutions. They coupled the gas chromatograph to a mass spectrometer operating either in electron impact or chemical ionization mode to identify the degradation products. Fifteen degradation products, nine of them being the major ones, were determined using this method.

2.3 PURIFICATION OF DEGRADED AMINE SOLUTIONS

Degradation represents not only a loss of valuable amine but also the degradation products create operating problems such as foaming, fouling and corrosion.

The corrosivity of degradation products is a matter of considerable practical importance and some studies have been reported on this subject in literature. In 1956 Polderman and Steel [58] reported simple experiments which indicated that the products corroded steel. Moore [49] subsequently published some field data and showed that the corrosion rate increases with the concentration of degradation products. Values as high as 1 mm/year (40 mpy) were found for carbon steel. The corrosivity of degradation products has also been reported by others [51,63]. However, Blanc et al. [7] published data in support of their claim that DEA degradation products are not corrosive under typical industrial conditions. Later, Chakma and Meisen [11] performed weight loss and potentiodynamic tests to determine the corrosivity of carbon steel in aqueous solutions containing DEA and its principal degradation products. The solutions were either free from or saturated with CO_2. The amine solutions were found to be corrosive in the presence of CO_2, and corrosion rates at 100 ^oC and atmospheric pressure ranged from 1.6 to 2.1 mm/year for DEA concentrations of 30 and 60 wt%, respectively. HEOD, a major degradation compound of DEA, was found to be the most corrosive.

In order to deal with this kind of operating problems, degraded amine solutions should be somehow purified. Since the amine solutions thermally

degrade at their boiling point and most of the degradation products are high boiling compounds having vapour pressures similar to that of the amine, distillation was stated to be unsatisfactory for purification [63].

Activated carbon beds are widely used in gas plants and have been claimed to remove all major contaminants including degradation products [56,61,63]. However, laboratory tests as well as analysis of industrial amine samples taken upstream and downstream of activated carbon beds suggest that they do not remove significant quantities of major degradation products [12,47]. Chakma and Meisen [12] conducted batch adsorption experiments to determine the adsorption capacity of diethanolamine, methyl diethanolamine and their major degradation products from partially degraded aqueous solutions onto a lignite based and a bituminous coal based activated carbon. They found the former to be virtually ineffective, whereas the latter was found to adsorb all of the degradation compounds. However, its adsorptive capacity was found to be extremely low, less than 3 mmol / g. of carbon. They provided adsorption isotherms and Freundlich constants for DEA, MDEA and their major degradation products. They also performed laboratory column adsorption experiments and modeled their column using the Ideal Adsorbed Solution theory. Since the characteristics of carbon adsorbers used in gas plants are not known, they are changed arbitrarily by plant operators. Islam and Chakma [35] presented a mathematical model to simulate an activated carbon adsorber used in a diethanolamine based gas plant and predict breakthrough times. Plant data and the model predictions showed that typical carbon adsorbers become saturated in days rather than months and should be regenerated or replaced frequently.

Therefore, activated carbon bed adsorption may not be viable for the removal of degradation compounds.

Several other techniques have been patented for the purification of degraded DEA solutions, mostly dealing with the removal of heat stable salts [1].

Use of a strongly basic anion exchange resin was described by Morgan and Klare [50] to treat DEA solutions contaminated by sodium chloride. Chloride ions are replaced by hydroxyl ions and the sodium hydroxide formed reacts with carbon dioxide to form sodium bicarbonate which precipitates and can be separated by filtration.

Chakma [17] reported another way of purifying degraded amine solutions by reversing the degradation reactions. He performed some preliminary experiments using NaOH to reverse some of the degradation reactions of DEA. It was found that HEOD can be completely converted back to DEA. Some of THEED also disappeared as a result of NaOH addition, but it was not clear whether it was converted back to DEA. This study was further explored later by Chakma and Meisen [13] by conducting systematic tests. They treated 20 mL partially degraded DEA solutions with aqueous NaOH, KOH and NH_4OH solutions ranging from 15 to 20 M in well agitated 100 mL flasks at 25 to 100 ^oC. NaOH and KOH were found to cause rapid and stoichiometric reversion of HEOD and when used in excess of approximately half of THEED to DEA. BHEP was not affected by this treatment and also NH_4OH solutions were ineffective for any of the major degradation products. They also used a strongly acidic cation exchange resin to prevent the build-up of Na^+ and K^+ ions.

This literature review on different aspects of amine degradation shows that a lot of work has been done on this subject but the field is still open for further exploration. For example, there is little work reported in literature on the degradation of MDEA-based mixed solvents which have been replacing the conventional amines in gas treating industry over the recent years. Also, purification of the degraded amine solutions is an industrially important problem that has to be solved. Therefore, the present study aims to investigate the degradation of MDEA-DEA mixtures with CO_2 and the purification of degraded amine solutions as stated earlier in Section 1.4.

CHAPTER 3

EXPERIMENTAL STUDIES ON DEGRADATION AND PURIFICATION

3.1 SOLVENT DEGRADATION

Degradation experiments were initiated by examining the degradation of DEA under realistic conditions, such as low partial pressures of CO_2, by contacting an aqueous DEA solution with mixtures of CO_2-N_2 gases with different compositions. Keeping the gas composition constant during these experiments was the major drawback which prevented a methodical study on DEA degradation under these conditions.

Then, the solvent was changed to MDEA based mixed solvents, since mixed solvents are becoming more widely used in industry, and pure CO_2 gas was used instead of a gas mixture to carry out systematic degradation experiments. The degradation of different concentrations of MDEA-DEA solutions was studied by performing experiments in a high pressure autoclave under different conditions of CO_2 partial pressure, temperature and solution concentration. Samples were taken periodically from the solution in order to follow the progress of the degradation reactions. Analysis of the collected samples was conducted using the gas chromatographic technique proposed by Chakma and Meisen [14] (see Appendix A).

Also, the effect of H_2S gas on the degradation of DEA was investigated by performing similar kind of experiments, contacting aqueous DEA solutions with pure H_2S and mixtures of H_2S-CO_2 gases.

3.1.1 EXPERIMENTAL EQUIPMENT AND PROCEDURE

3.1.1.1 Autoclave

A one liter stainless steel autoclave (Model BC0100SS06AG, Autoclave Engineers, Inc.) was used for the degradation experiments. The autoclave can be operated at a maximum pressure of 40.1 MPa at 343 °C and is equipped with the following standard accessories (see Fig. 3.1) :

- A pressure vessel containing cooling coil, thermowell, sampling tube and safety head rupture disc with a bolted closure (confined gasket).
- Stator and magnetic drive (MagneDrive II unit), magnetically actuated rotary impeller system (0-2500 rpm).
- An electric, external jacket type furnace furnished with a type "K" thermocouple.
- Pressure gauge (0-55.2 MPa), tachometer, vent valves, and gas valve; all front-mounted.
- Stand and belt guard.
- Agitator (AE Dispersimax turbine-type with 1.25 " diameter impeller, 6 blades).

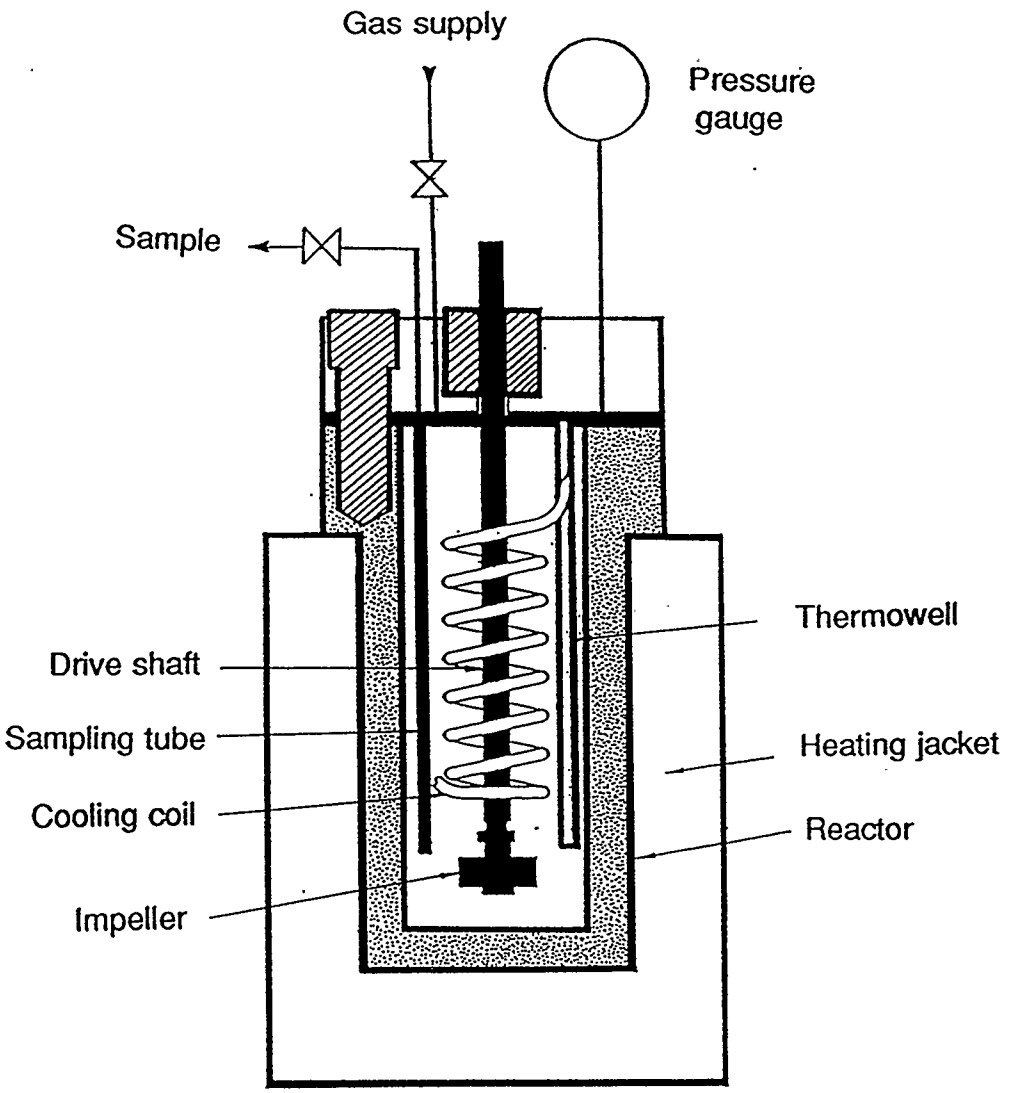


Figure 3.1 Sketch of the autoclave used for degradation experiments

- An automatic autoclave modular furnace and process temperature controller ("MTCP"series, Autoclave Engineers Inc.). The process controller had a temperature range of -250 to +1200 °C with a calibration accuracy of ± 0.15% of reading, and the process temperature and setpoint were digitally displayed. The furnace controller had a temperature range of 0 to 1000 °C and was designed to be used to limit the furnace temperature decreasing the possibility of overshoot and to act as a line of defense against a failure.

3.1.1.2 Sampling

Samples were taken from the reaction mixture periodically by means of a 3 mL sampling coil. The sampling coil was fitted with an inlet and outlet valve. It could be easily connected and removed from the liquid sampling port of the autoclave during a run.

The method used for sampling can be described as follows :

- The sampling coil was connected to the sampling port of the autoclave.
- The autoclave sample valve was opened keeping the inlet and outlet valves of the sampling coil closed.
- The sampling coil inlet valve was then opened and a liquid sample was forced into the coil under the autoclave pressure.
- The outlet valve was opened slightly to bleed a little sample off to wash out any liquid that could be left in the tube from the previous sampling.

- All the valves were closed and the sampling coil was removed from the autoclave.
- The sample was then removed from the sampling coil and stored in screw cap glass vials to be analyzed later.

3.1.1.3 Identification of major degradation products

It was necessary to identify the major degradation products in order to be able to study the degradation reactions. A typical chromatogram of a degraded solution is shown in Figure 3.2.

The first method used for identification was to analyze a degraded sample using gas chromatography. A degraded solution was injected into the gas chromatograph and the retention times of the major peaks were noted from the chromatogram. Then, those retention times were matched with the retention times of the degradation products that were stated in literature [18]. Also, in the case of MDEA, DEA and BHEP which were purchased in pure form, a known amount of the compound was injected into the gas chromatograph and its retention time was compared with that of the degraded sample. However, this method was not sufficient to give a complete identification since there could be various compounds with the same retention times.

Another method used for identification, consisted in a GC/MS analysis for a degraded sample. In the GC/MS (Gas Chromatograph / Mass Spectrometer), the sample is first vaporized and separated into its components and then ions are produced from the neutral molecules that are bombarded with a beam of electrons. This process is called electron impact ionization (EI). In an EI source,

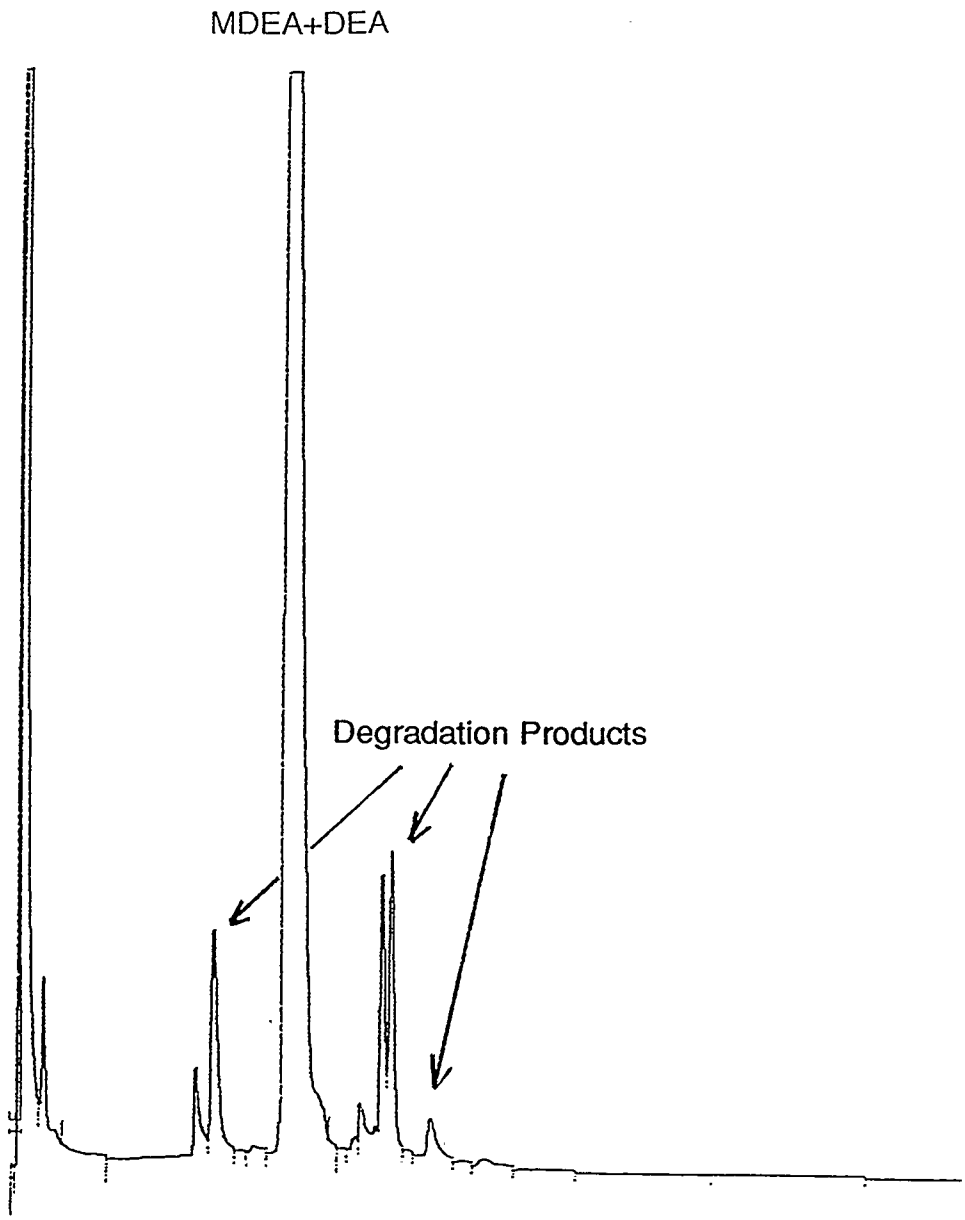


Figure 3.2 Typical chromatogram of a degraded MDEA-DEA mixture

electrons from a heated filament are accelerated across the ionization chamber. The effluent from the gas chromatograph also passes through the ionization chamber. Energy is transferred to the gas molecules as a result of the inelastic collisions with the electrons. The excited molecule releases an electron giving rise to a molecular ion. The bonds of the molecular ion are also broken, producing electrically charged fragments. Various ions generated this way are drawn by the electrical fields in the ion source into the analyzer section where they are separated according to their mass to charge ratios. Each ion normally carries only one electrical charge. The movement of these charges is equivalent to a current flowing that is detected by an electrometer. A mass spectrogram is produced from the output of the electrometer recorded as ion current versus mass number. Each peak represents a different ion and since molecules fragment in the same manner under similar conditions, a compound's mass spectrum is a unique chemical fingerprint.

A compound can be identified by matching its mass spectrum against that of a known compound. The mass spectra of the degradation compounds are not available in the common mass spectral data libraries. Therefore, the degradation compounds were identified by comparing their mass spectra with those available in the study on DEA and MDEA degradation by Chakma [18].

3.1.1.4 Analysis of the samples

The samples taken during the various runs were kept in 3.7 mL screw cap glass vials. The analysis was performed by injecting 0.5 μL samples into the gas chromatograph under the conditions described in Appendix A. Upon completion

of the analysis, the peak areas and the retention times of the major components were recorded in the chromatogram. Calibration curves (see Figures A.1-A.7 in Appendix A) were used to calculate the concentrations of the solvent (MDEA-DEA mixture) and its major degradation products from the recorded peak areas. Curves of concentration versus time were obtained and studied using these data.

3.1.1.5 Experimental procedure

An aqueous MDEA-DEA mixture was reacted with CO_2 at a fixed temperature and pressure for a specific length of time in a typical degradation run. Samples were taken periodically during the run. The subsequent steps were taken throughout each run :

- 600 mL of solution was loaded and the autoclave was sealed.
- The autoclave was tested for any leaks for an hour under 6.9 MPa of N_2 gas.
- After the test, N_2 gas was vented and the stirrer speed was set to 1000 rpm.
- The autoclave was heated to the desired temperature.
- The vapor pressure of the solution in the autoclave was recorded at that temperature.
- CO_2 gas was charged into the autoclave and the pressure was adjusted to the value that was obtained by adding the vapor pressure of the solution and the desired CO_2 partial pressure. Setting the total pressure this way allowed us to have a fixed CO_2 partial pressure at different composition and temperature conditions.

- Initially the CO_2 was absorbed by the solvent, so the autoclave pressure was checked regularly over the first hour to maintain the desired operating pressure.
- Samples were taken at regular intervals during the run using the sampling coil. After the sample had been removed, the sampling coil was cleaned with distilled water and dried with N_2 gas.
- When the run was completed, the heater was turned off and the autoclave and the contents were allowed to cool down to room temperature.
- After reaching room temperature, the pressure was reduced to atmospheric by releasing the CO_2 gas from the autoclave.
- The contents of the autoclave were removed and it was cleaned thoroughly for the next run.

3.1.2 EXPERIMENTAL PROGRAM

3.1.2.1 Experiments on the degradation of DEA with CO_2-N_2 mixture

The aim of these experiments was to examine the degradation of DEA under conditions representative of industrial processes. Because raw natural gas that would be treated contains only 5-15% of CO_2 along with the hydrocarbons and other impurities, it was decided to conduct the degradation experiments with a gas mixture containing CO_2 at these levels. Since the components forming the raw natural gas other than CO_2 do not affect the degradation, N_2 gas which also has no effect on degradation was chosen to replace them.

Numerous experiments were carried out and it was conceived that keeping the composition of the gas mixture constant throughout a run created a problem. The experimental conditions employed in the four runs in which the composition of the gas mixture could be kept almost constant were as follows :

DEA (aq.) concentration	30%
Temperature	150 °C
Pressure	4137 kPa
CO_2 percentage	10, 20, 30, 65 %

Consequently, it was decided to abandon these experiments since it would not be possible to conduct a systematic study under these conditions.

3.1.2.2 Experiments on mixed-solvent degradation

A mixture of MDEA and DEA solvent was contacted with pure CO_2 gas under controlled conditions. The effect of temperature, initial solvent concentration and CO_2 partial pressure was examined. Since each run, depending on the experimental conditions, takes 2-4 weeks, an experimental program which could provide sufficient information to study the operating variables and develop a simple kinetic model with minimum number of experiments was composed. The experimental matrix is given in Table 3.1.

Table 3.1 : Experimental matrix for degradation experiments with mixed solvent at 4137 kPa CO_2 partial pressure

Solvent concentration (wt%)	Temperature (°C) 130	140	150	160
50%MDEA 5% DEA			√	
50%MDEA 10%DEA	√	√	√	√
50%MDEA 20%DEA			√	
50%MDEA			√	
10%DEA			√	

In addition to the experiments summarized in Table 3.1, two more runs were performed using a solvent concentration of 50%MDEA-10%DEA at 150 °C and CO_2 partial pressures of 2068 and 689 kPa.

3.1.2.3 Experiments for determining the effect of H_2S on degradation

Three runs of experiments were carried out in order to determine if H_2S gas, which can be found in raw natural gas in small amounts, causes or has any effect on degradation.

First, a 30% aqueous DEA solution was contacted with 10% H_2S at 150°C and 4137 kPa. In the next two runs, the same concentration of DEA solution was contacted with pure CO_2 gas and a mixture of CO_2-H_2S gases under the same conditions. So, the second run consisted of reacting 30% DEA with CO_2 at 150°C and 4137 kPa. In the last run, the 30% DEA solution was reacted with a CO_2-H_2S mixture containing 10% H_2S at 150 °C and 4137 kPa.

3.2 PURIFICATION STUDIES

Since, degradation represents a loss of amine and the accumulated degradation products create operating problems such as foaming, fouling and corrosion, degraded amine solutions have to be purified somehow. Three different methods, namely chemical purification, vacuum distillation and ion-exchange resins were investigated to purify the degraded amine samples.

3.2.1 CHEMICAL PURIFICATION

Chakma [17] reported a technique of purifying degraded DEA solutions by reversing the degradation reactions. Later, he further explored this method by conducting systematic tests in which degraded DEA solutions were contacted with alkalis to provide hydroxyl ions for the reversal of degradation products to DEA [18]. It was decided to carry out some similar tests with degraded DEA samples in order to be able to make a comparison.

3.2.1.1 Reversal of DEA degradation reactions

The main degradation products of DEA are known to be HEOD, THEED and BHEP [38,47]. The overall DEA degradation with CO_2 can be summarized as:

$$\text{BHEP} + H^+ + HCO_3^-$$

$$\Uparrow\Downarrow$$

$$\text{THEED carbamate} + H^+ + HCO_3^-$$

$$\Uparrow\Downarrow$$

$$\text{DEA carbamate}$$

$$+$$

$$\mathbf{DEA + CO_2} \Leftrightarrow \text{DEA carbamate} \Leftrightarrow \text{HEOD} + H_2O$$

$$+$$

$$\text{DEA}$$

$$\Uparrow\Downarrow$$

$$\text{THEED} + H^+ + HCO_3^-$$

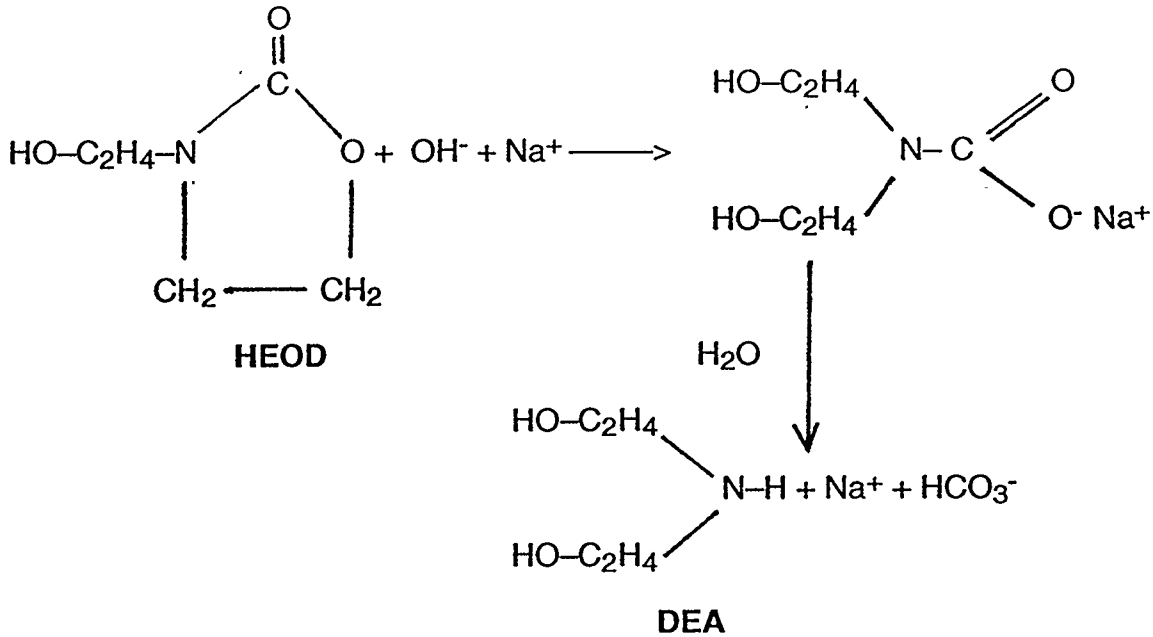
$$\Uparrow\Downarrow$$

$$\text{BHEP} + H_2O$$

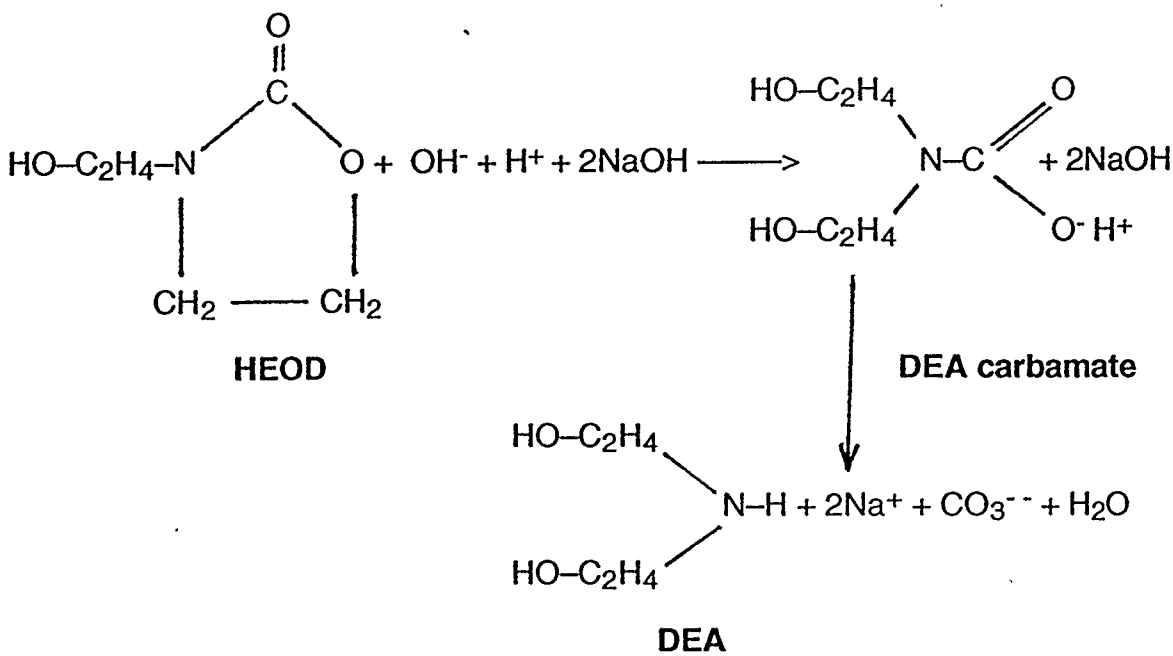
Chakma [17] presented the following chemical reactions that would revert the degradation products to DEA.

HEOD reversal

The HEOD formation is known to be reversible due to the instability of the HEOD ring [39]. It was stated that the addition of a strong alkali, such as NaOH, to a degraded solution causes HEOD to break up by the attack of hydroxyl ions at the electron deficient carbonyl group [17] :

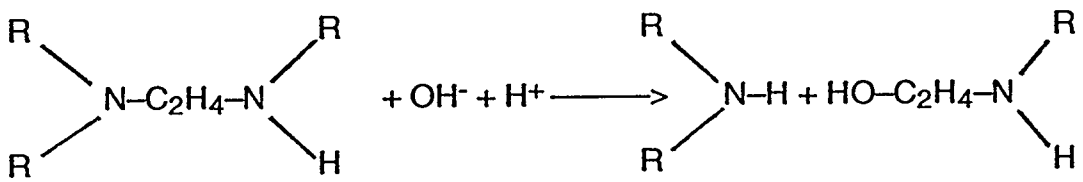

HO–C2H4–N
O + OH- + Na+
HO–C2H4
N– C
O
O- Na+
CH2
CH2
HEOD
H2O
N–H + Na+ + HCO3-
DEA

or,


HO–C2H4–N
O + OH- + H+ + 2NaOH
HO–C2H4
N–C
+ 2NaOH
O- H+
CH2
CH2
HEOD
DEA carbamate
N–H + 2Na+ + CO3- - + H2O
DEA

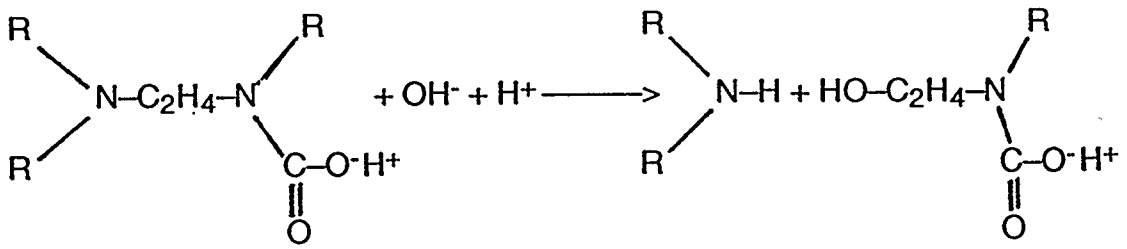
THEED reversal

Different schemes were proposed to explain the THEED reversal reactions [17]. One explanation was that NaOH increased the concentration of HCO_3^- ions in solution by reacting with CO_2 and thus helping to reverse the THEED formation. Also, it was suggested that an increase in the OH^- concentration could cause THEED to break up to form DEA as follows :



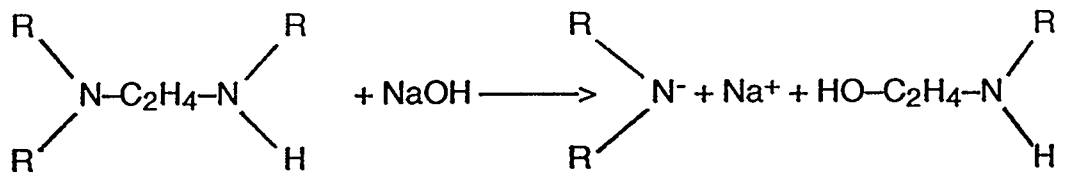
THEED **DEA** **DEA**

THEED carbamate might also be attacked by OH^- ions to form DEA and DEA carbamate:



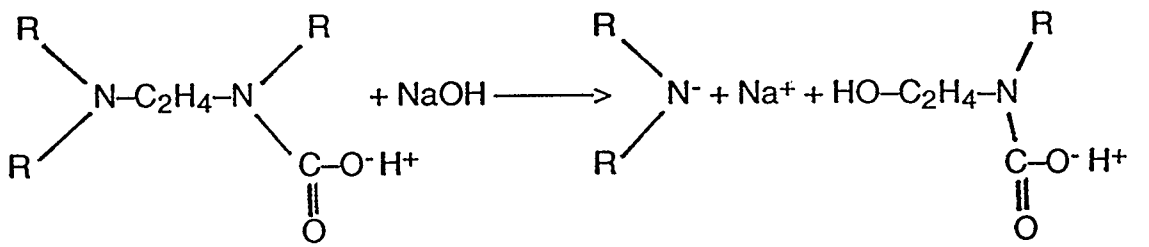
THEED carbamate **DEA** **DEA carbamate**

Alternatively, It was claimed that NaOH could directly react with THEED:



THEED **Na-salt of DEA** **DEA**

It was also stated that THEED carbamate might react with NaOH to form the sodium salt of DEA and DEA carbamate:



THEED carbamate **Na-salt of DEA** **DEA carbamate**

BHEP reversal

Since the BHEP ring is quite stable it was stated to be hard to revert its formation to THEED [17]. But reversal of THEED could prevent formation of BHEP since BHEP is formed from THEED.

3.2.1.2 Experimental materials and method

Different amounts and concentrations of NaOH solutions were used to purify the degraded DEA solutions produced in the laboratory. NaOH solutions were prepared by dissolving NaOH pellets in distilled water. The experiments were performed by the following procedure :

- NaOH solutions of known amounts and concentrations were added to 20 mL stoppered flasks containing 5 mL of degraded DEA solution. One and two milliliters of 10 and 20 M NaOH solutions were added to different samples to see the effect of quantity and concentration.
- Blank samples were prepared by adding distilled water equal to the amount of NaOH solution into 20 mL flasks containing degraded DEA solution. The purpose of adding water was to compensate for the dilution of the samples with the addition of NaOH solution.
- After the addition of the NaOH solution, the flasks were kept in a water bath for 20 minutes for the experiments involving temperature effects.
- The samples were then analyzed by gas chromatography.

3.2.2 VACUUM DISTILLATION

If it is possible to revert some of the major degradation products, namely HEOD and THEED to DEA by chemical treatment, the only remaining product that has to be dealt with is BHEP. Thus, another technique has to be applied to separate BHEP from DEA. Since the amine solutions undergo thermal degradation at their boiling points and most of the degradation products are high boiling compounds with vapour pressures similar to that of the amine, atmospheric distillation is known to be insufficient in purification [63]. Therefore, it was decided to apply vacuum distillation to lower the boiling points and prevent the thermal degradation of DEA solutions.

3.2.2.1 Experimental equipment

The equipment used in the experiments consisted of the following items :

- Vacuum-jacketed Oldershaw distillation column fabricated with 15 sealed-in plates which are perforated with 0.035-inch holes (SGA Scientific Inc.).
- Vacuum/Distillation controller (Model B-168, BÜCHI) with LED display located on the front panel and having a continuously adjustable control and measuring range of 1-1400 mbar.
- 1000 mL electrical heater (Model MS 9505, Electrothermal) with a power supply of 300W.
- Condenser.
- Thermometers.
- Round-bottom flasks used for feed and distillate.

3.2.2.2 Experimental procedure

Experiments were carried out in the following way :

- Aqueous DEA-BHEP solutions were prepared by mixing pure DEA and BHEP and analyzed by gas chromatography prior to distillation.
- A known amount of solution was loaded to the batch still that was heated by an electrical heater.

- The water content of the solution was distilled at atmospheric pressure, then the column was connected to the vacuum controller.
- Top and bottom temperatures were monitored and controlled throughout the distillation.
- Distillation was stopped when a considerable amount of distillate was collected.
- The distillate was analyzed by gas chromatography at the end of the run.

In addition, one distillation was conducted with degraded MDEA-DEA mixture obtained in the laboratory containing all major degradation products.

3.2.3 ION-EXCHANGE RESINS

It is known that hydroxyl ions supplied by adding alkalis into degraded solutions help the reversal of degradation reactions. Hence, basic ion-exchange resins can be used to provide hydroxyl ions. Instead of adding alkalis, continuously passing the degraded solutions through ion-exchange resin beds seems industrially more feasible. Taking this into account, some ion-exchange experiments were performed using industrially degraded solutions.

3.2.3.1 Experimental equipment

Subsequent substances and equipment were used in ion-exchange experiments :

- Polystyrene column (Fisher Scientific, Inc.) with polypropylene fittings having a length of 100 cm and 3.2 cm I.D. Lower fitting holds a 10 μm filter disc.

- Seal-less magnetic drive centrifugal pump (Model AC-2CP-MD, March MGF, Inc.).
- Standard 150 mm, 316 SS flowmeter (Cole Parmer Instrument Company, Inc.) with high-resolution valve.
- Strongly basic, macroreticular Amberlyst A-27 ion-exchange resin (Aldrich Chemical Company, Inc.).
- Strongly basic, gel-type Amberlite IRA-400(OH) ion-exchange resin (Aldrich Chemical Company, Inc.).
- Industrially degraded amine solution.
- 3 M NaOH solution.

3.2.3.2 Experimental procedure

The experiments consisted of passing an industrially degraded amine solution continuously at a constant flowrate through a strongly basic ion-exchange resin bed and taking samples at regular time intervals. Three runs were conducted at different flowrates to see the effect of change in the flowrate. The following procedure was carried out :

- The resin was packed into the column as an aqueous slurry and allowed to settle down until a bed height of 50 cm was obtained.
- The column was back-flushed with an upflow of distilled water to remove air bubbles or channeling.

- The resin was conditioned before the first use and regenerated after each run by passing a 3 M NaOH solution through the column.
- The resin bed was then washed with distilled water to remove any excess of hydroxyl ions until the column effluent was neutral.
- The degraded industrial sample was analyzed using gas chromatography prior to resin treatment.
- The degraded solution was pumped through the column at a constant flowrate and the flowrate was controlled with a flowmeter during the run.
- Samples were taken from the column effluent at regular time intervals and stored in screw cap glass vials.
- The collected samples were later analyzed by gas chromatography.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 DEGRADATION EXPERIMENTS

Experiments were carried out to study the degradation of DEA, mixed-solvent (MDEA-DEA) with CO_2 and the effect of H_2S gas on degradation. Also, the effects of initial solvent concentration, temperature and CO_2 partial pressure on degradation were investigated. The results obtained from degradation experiments will be presented in the following sections.

4.1.1 DEA DEGRADATION

The degradation of DEA was studied by contacting an aqueous DEA solution with a gas mixture of CO_2 and N_2. The aim of the experiments was to investigate the DEA degradation under field conditions, such as using a gas mixture to represent the natural gas instead of pure CO_2. Also, the effect of initial DEA concentration, temperature and gas composition was decided to be studied, but keeping the gas composition constant throughout a run created problems, since CO_2, used in low concentrations, became the limiting reactant and CO_2 concentration in the gas mixture kept decreasing during the run. Hence, the experiments were stopped after a few runs. Therefore a systematic study has not been carried out.

It was observed during the experiments that the colour of the DEA solution became darker, changing from light yellow to brown and the odour of the solution became sharper with degradation. The major degradation products were recorded to be BHEP, HEOD and THEED.

Figure 4.1 shows the concentrations of DEA and its major degradation compounds obtained at 150 °C by contacting 30 wt% DEA with a gas mixture of 20%CO_2-80%N_2. DEA concentration decreases with time as the concentrations of the degradation products increase. DEA degrades at a higher rate initially as can be concluded from the sharp decrease in its concentration within the first 100 hours. HEOD concentration initially increases and then levels off. On the other hand, THEED concentration increases with time, reaching a maximum value and then decreases. BHEP does not appear at the initial stage of the reactions and then its concentration rises steadily with time. All these observations confirm the reaction mechanism presented by Kennard [40] for the degradation of DEA. In his study, HEOD was stated to be produced directly from DEA as a result of a reversible reaction and THEED was stated to be an intermediate that came from DEA and produced BHEP.

The trends of the concentrations of DEA and its degradation products observed in this study are in agreement with the trends obtained in Kennard's work. However, the rate of degradation differs significantly. The degradation experiments that were carried out in his study took less than 10 hours, contrary to the experiments in this study which took approximately 10 days. The reason is that DEA was degraded under a low partial pressure of CO_2 as a result of using a gas mixture instead of pure CO_2 which caused a much slower degradation rate.

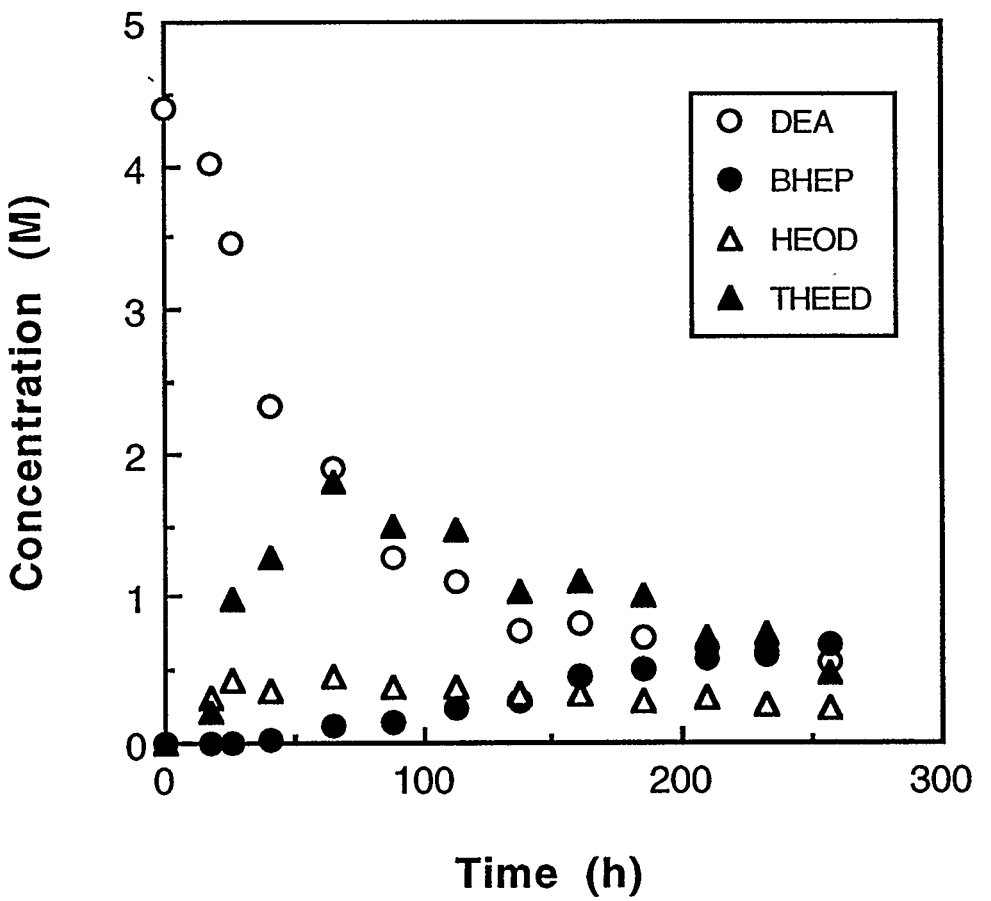


Figure 4.1 Concentrations of DEA and its major degradation products as functions of time (30 wt% DEA, 20% CO_2, 150 °C)

The concentrations of DEA, BHEP, HEOD and THEED were plotted as a function of time and gas composition in Figures 4.2 to 4.5 respectively. In Figure 4.2, it can be seen that although higher CO_2 content in the feed gas causes a more rapid decrease in DEA concentration at the initial stage, as time passes the change in CO_2 concentration does not have a significant effect on DEA degradation. Also, Figures 4.3-4.5 show that the increase in CO_2 content in the gas mixture leads to an increase in the concentrations of the degradation products.

4.1.2 MIXED SOLVENT DEGRADATION

MEA and DEA have been the most widely used alkanolamines for natural gas treatment but they are recently being replaced by MDEA-based solvents. MDEA-based solvents have become prevalent in gas industry since they provide a selective removal of H_2S over CO_2 and reduce the energy costs. Moreover, because of their less corrosive character, they can be used at higher concentrations.

Although mixed solvents have gained an increasing share in industry, no research on mixed solvent degradation was found in literature at the time when this project was started. Thus, the degradation of a mixed solvent consisting of 50%MDEA and 5-20%DEA was investigated in the present study.

Experiments were performed under controlled temperature and pressure conditions and samples were taken periodically from the reaction mixture. The colour of the samples gradually became darker and their odour became more acrid as the degradation proceeded. The major degradation products were

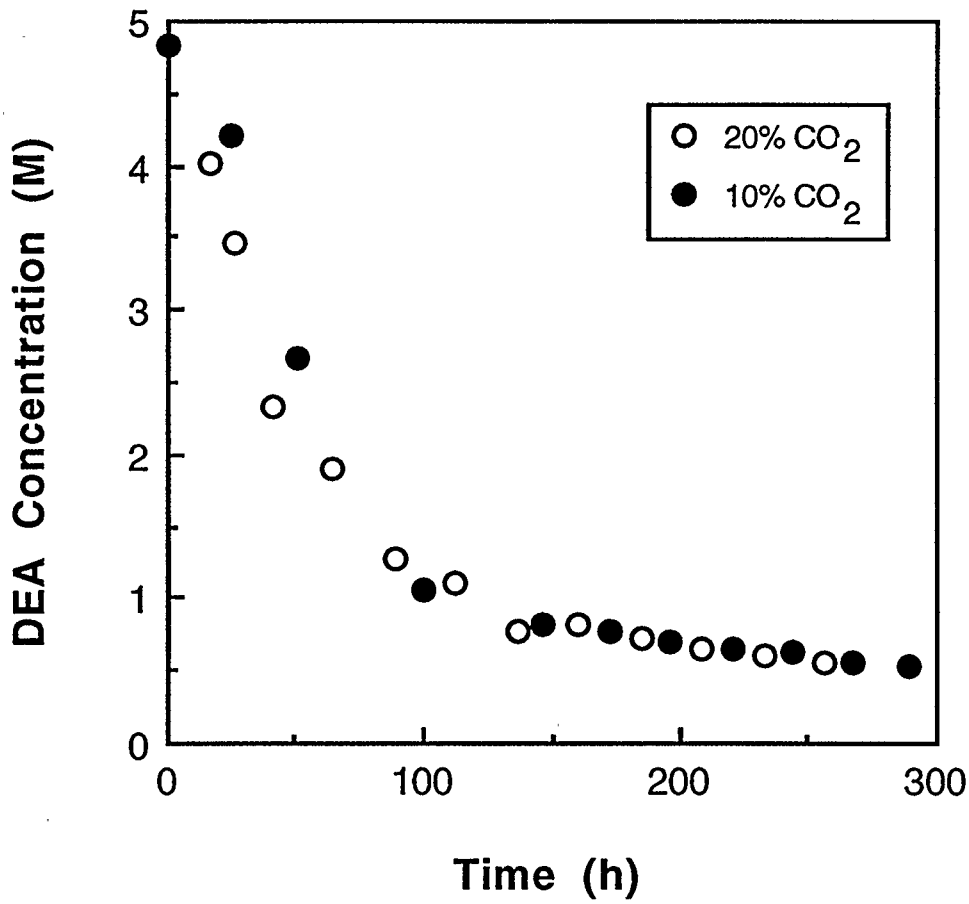


Figure 4.2 DEA concentration as a function of time and %CO_2 (30 wt% DEA, 150 °C)

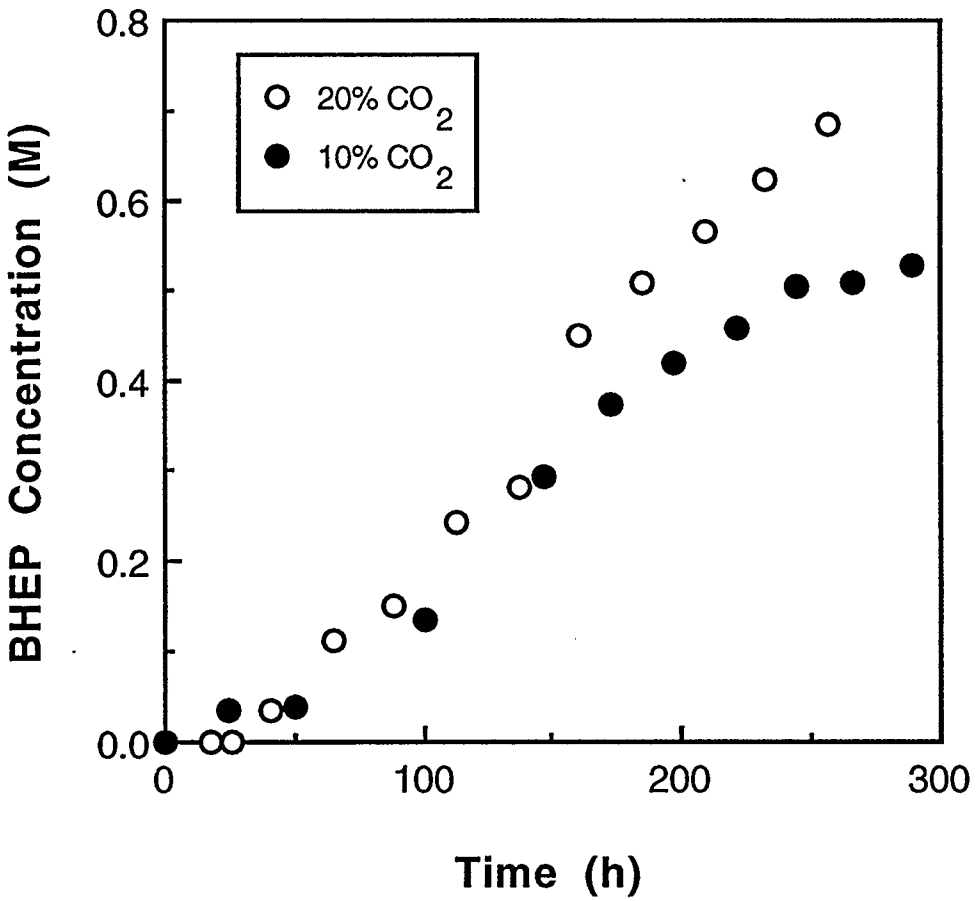


Figure 4.3 BHEP concentration as a function of time and $\%CO_2$ (30 wt% DEA, 150 °C)

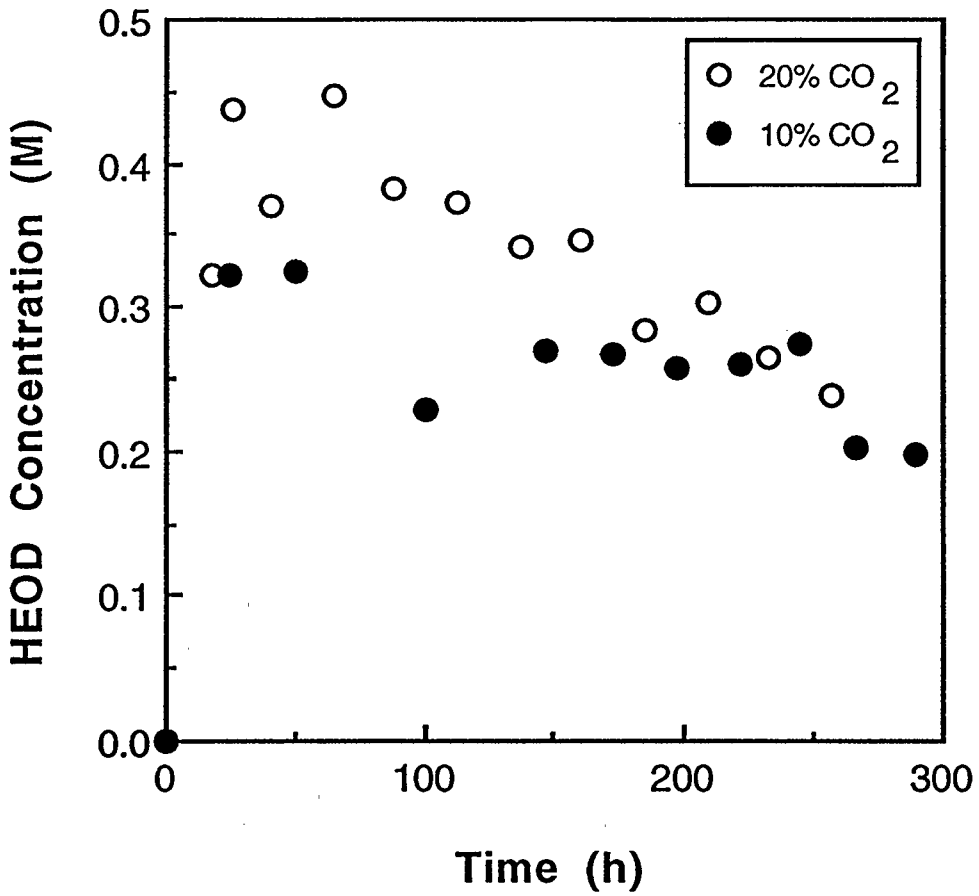


Figure 4.4 HEOD concentration as a function of time and %CO_2 (30 wt% DEA, 150 °C)

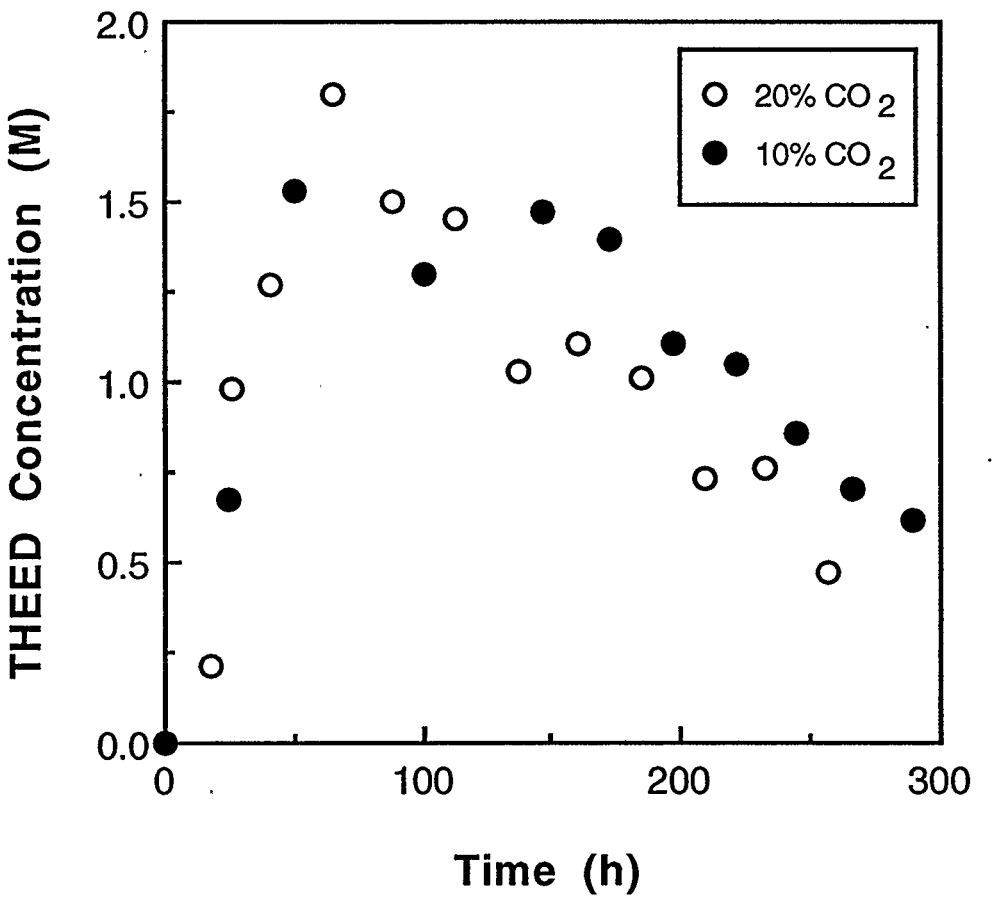


Figure 4.5 THEED concentration as a function of time and %CO_2 (30 wt% DEA, 150 °C)

detected as EG (monoethylene glycol), DMAE (2-dimethylamino ethanol), BHEP, HEOD and THEED. The chemical structures of these compounds are tabulated in Appendix B.

A gas chromatographic technique described in Appendix A was used to analyze the samples. This technique was stated to be effective for the analysis of degraded DEA and MDEA solutions in the literature [18,40]. Although it was sufficient in detecting the degradation products, MDEA and DEA could not been detected separately, since the amount of DEA in the solution was too little compared to MDEA. Figure 4.6 shows a typical chromatogram of a degraded solution. As can be seen, MDEA and DEA appear as one peak in the chromatogram. Efforts to improve the analytical technique were made by using various kinds of GC columns and different conditions, but it was not possible to separate MDEA and DEA, unless both of them existed in the solution in sufficient quantities. Therefore, the degradation of each could not been examined separately, but the overall degradation of the mixed solvent was observed.

In addition to mixed solvent experiments, two runs were carried out with aqueous solutions of 50%MDEA and 10%DEA in order to follow the progress of the degradation of each, separately. Figures 4.7-4.9 show plots of the concentrations of degradation products versus time for the runs conducted with 10%DEA, 50%MDEA and a mixture of 50%MDEA-10%DEA, respectively at 150°C and 4137 kPa CO_2 partial pressure. If these three figures are compared with each other, it can be seen that BHEP, HEOD and THEED are the common degradation products of both MDEA and DEA. On the other hand, EG and DMAE are produced only by MDEA.

Figure 4.6 Typical chromatogram of a degraded MDEA-DEA mixture

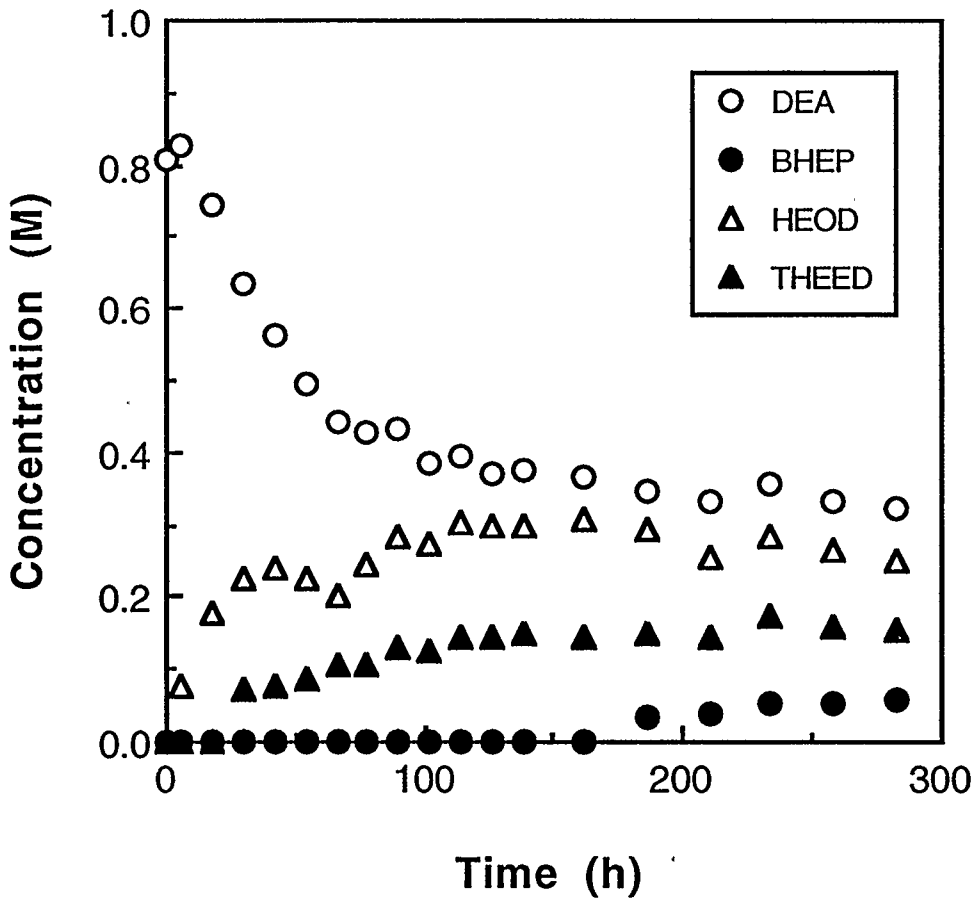


Figure 4.7 Concentrations of DEA and its major degradation products as functions of time (10 wt%DEA, 4137 kPa CO_2, 150 °C)

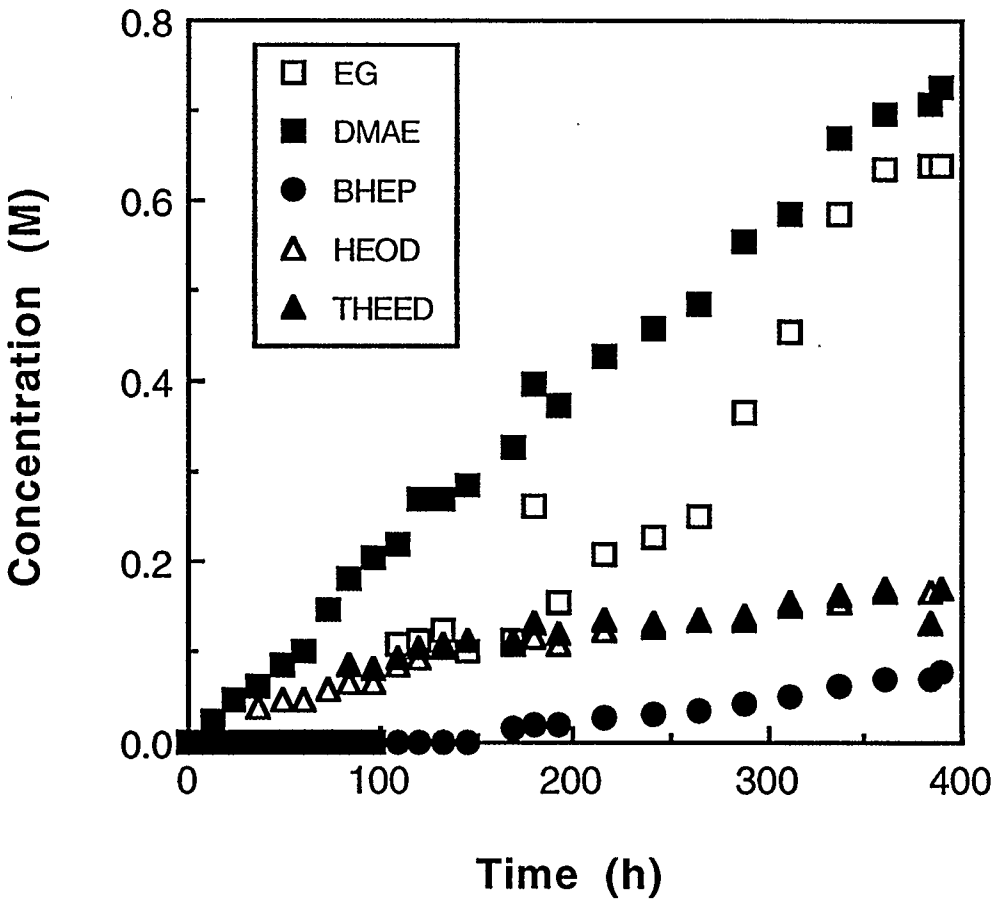


Figure 4.8 Concentrations of the degradation products of MDEA as functions of time (50 wt% MDEA, 4137 kPa CO_2, 150 °C)

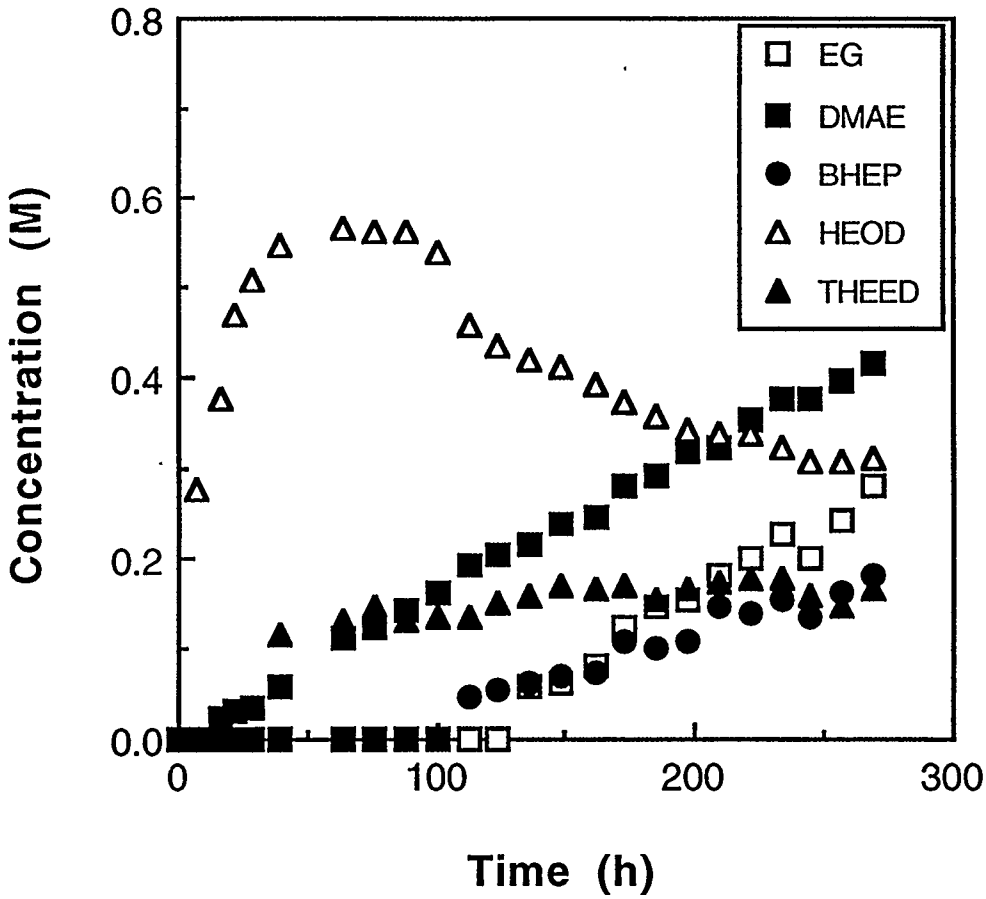


Figure 4.9 Concentrations of the degradation products of MDEA-DEA mixture as functions of time (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2, 150 °C)

In Figure 4.9, it can be observed that concentrations of the degradation products of the MDEA-DEA mixture as a function of time show different trends than those observed with the separate solvents. HEOD concentration first increases and decreases after reaching a maximum. DMAE concentration keeps increasing steadily, while THEED concentration increases and levels off with time. On the other hand, EG and BHEP do not appear initially but they appear and their concentrations keep increasing after a certain time, which suggests that they are the end products coming from some intermediates.

4.1.2.1 Effect of temperature

Figure 4.10 shows the change of solvent (50%MDEA-10%DEA) concentration with time at different temperatures. It is apparent that degradation has a strong dependence on temperature. The data plotted in Figure 4.10 fall on a straight line at high temperatures, whereas the degradation rate slows down after a certain time at lower temperatures.

The concentration of EG is plotted against time as a function of temperature in Figure 4.11. It can be seen that production rate of EG increases with increasing temperature. Moreover, at low temperatures, a longer time gap is observed before EG production starts. BHEP concentration shows the same trend as EG when plotted against time at different temperatures (Figure 4.12).

Figures 4.13 and 4.14 show DMAE and THEED concentrations as functions of time and temperature. DMAE concentration rises sharply with time, especially at higher temperatures. Similarly, THEED concentration initially increases at a higher rate at high temperatures and then becomes almost

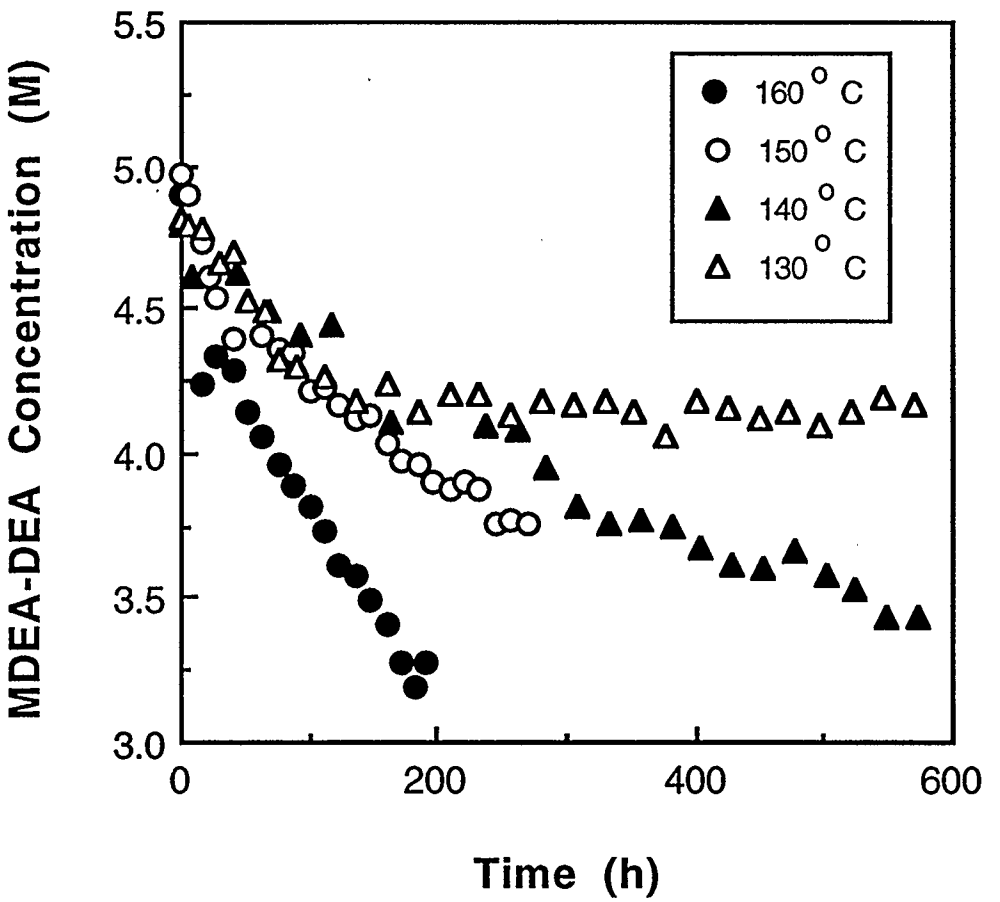


Figure 4.10 Concentration of MDEA-DEA mixture as a function of time and temperature (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2)

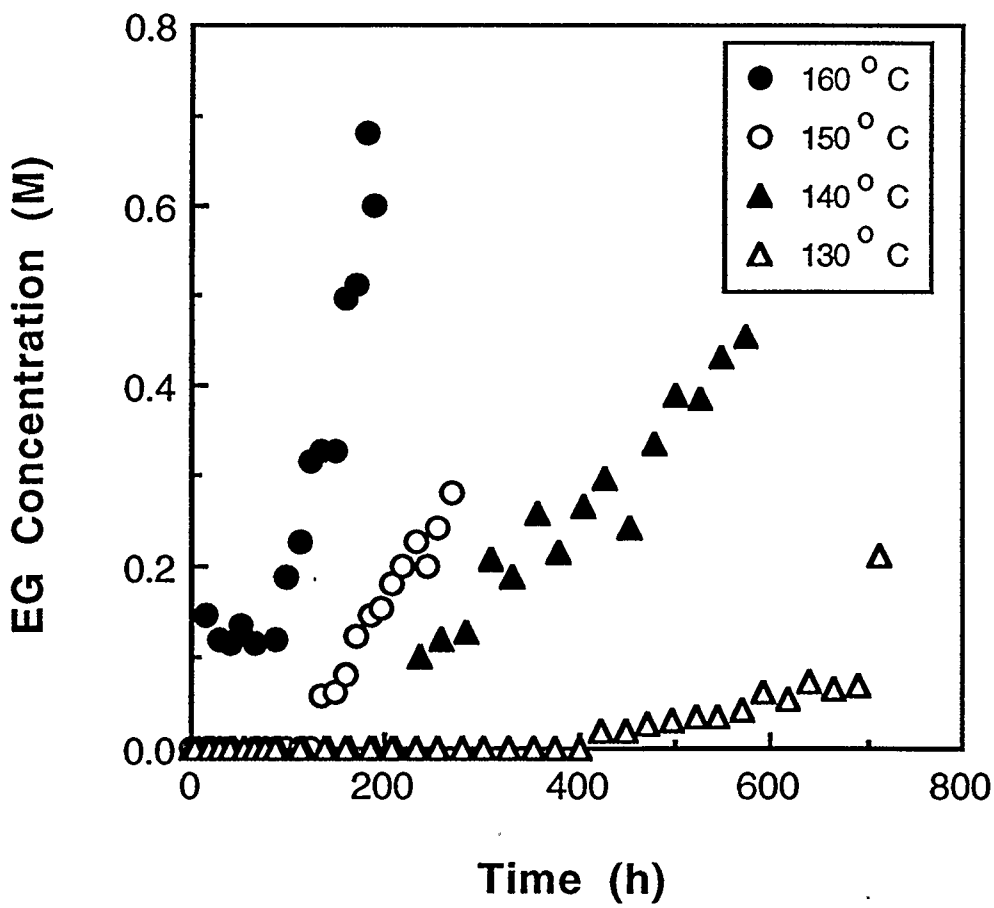


Figure 4.11 EG concentration as a function of time and temperature (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2)

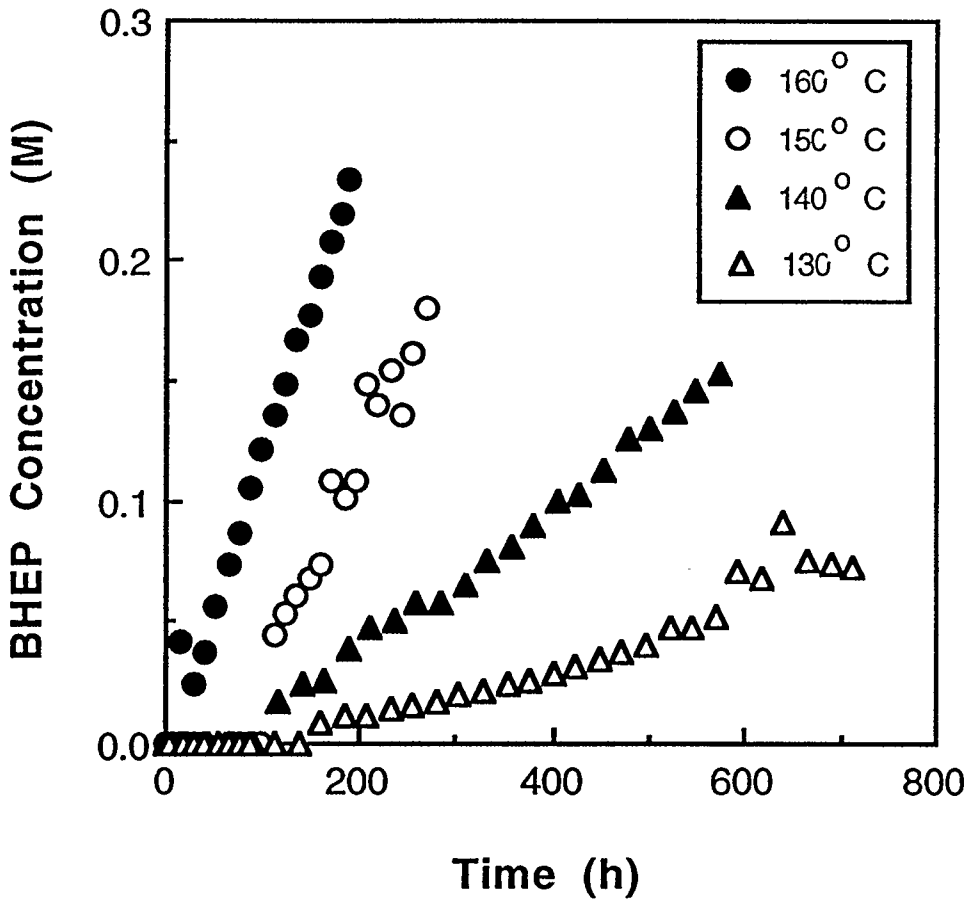


Figure 4.12 BHEP concentration as a function of time and temperature (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2)

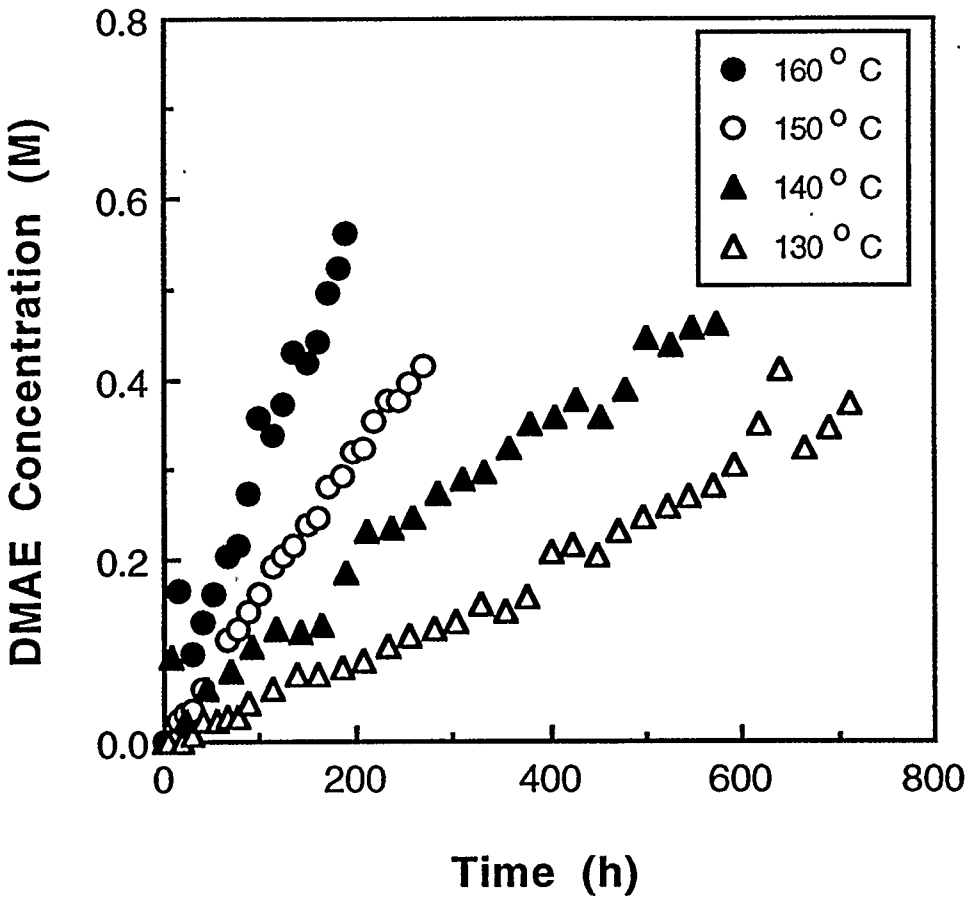


Figure 4.13 DMAE concentration as a function of time and temperature (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2)

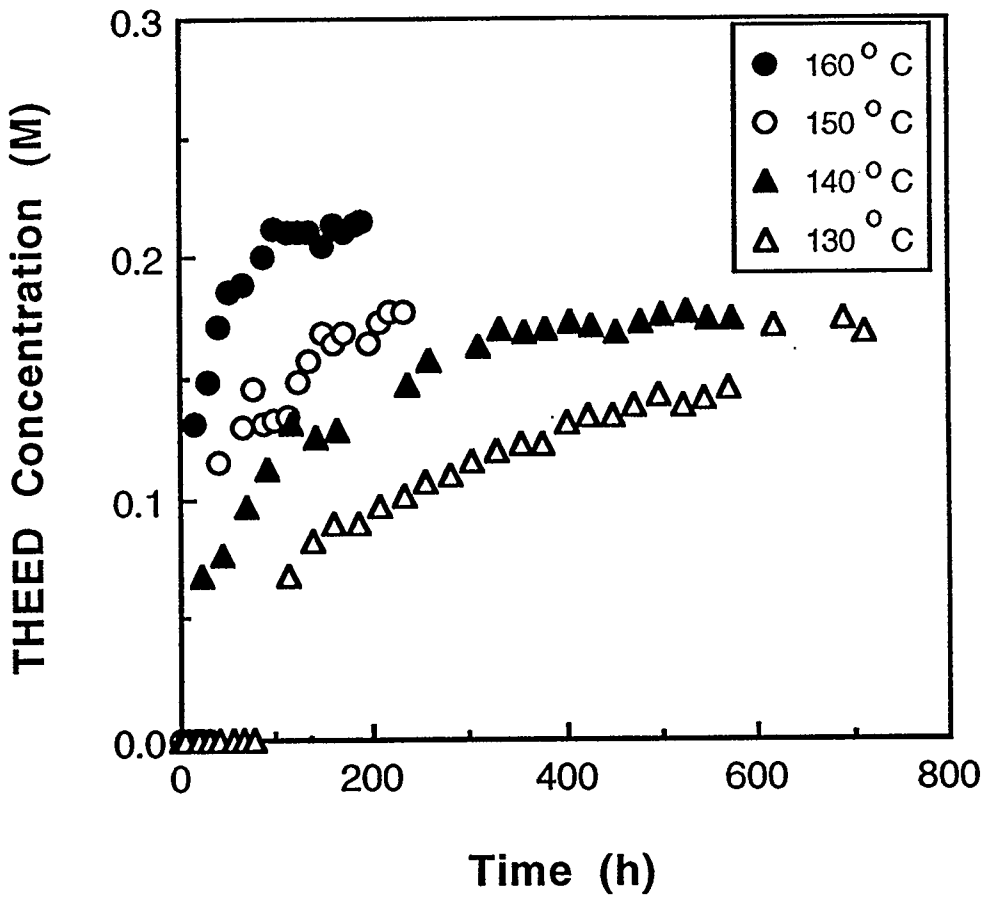


Figure 4.14 THEED concentration as a function of time and temperature (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2)

constant. However, at 130 °C which is the lowest temperature, THEED concentration keeps increasing slowly instead of leveling off. This may be due to the decreased production rate of BHEP, which comes from THEED, at this temperature.

HEOD concentration, on the other hand, shows a different trend when plotted versus time at different temperatures. It can be seen in Figure 4.15 that initial production rate of HEOD increases, but the maximum concentration of HEOD falls with increasing reaction temperature. Therefore, the overall amount of HEOD produced decreases at high temperatures unlike the other degradation products. This may be explained by HEOD being thermally unstable or other degradation reactions may be more temperature sensitive and favoured at high temperatures. Also, the mechanism of HEOD formation might be changing with temperature since its production rate does not show the common dependency on temperature.

4.1.2.2 Effect of CO_2 partial pressure

The solvent concentration is plotted against time at three different CO_2 partial pressures in Figure 4.16. As this figure implies, degradation rate is affected by CO_2 partial pressure. The rate of degradation increases significantly with CO_2 partial pressure increasing from 689 to 2068 kPa, but there is a slight increase in degradation between 2068 and 4137 kPa. The higher degradation rate with higher CO_2 partial pressure can be explained by increasing CO_2 solubility at high pressures and also CO_2 being the limiting reactant at low pressures.

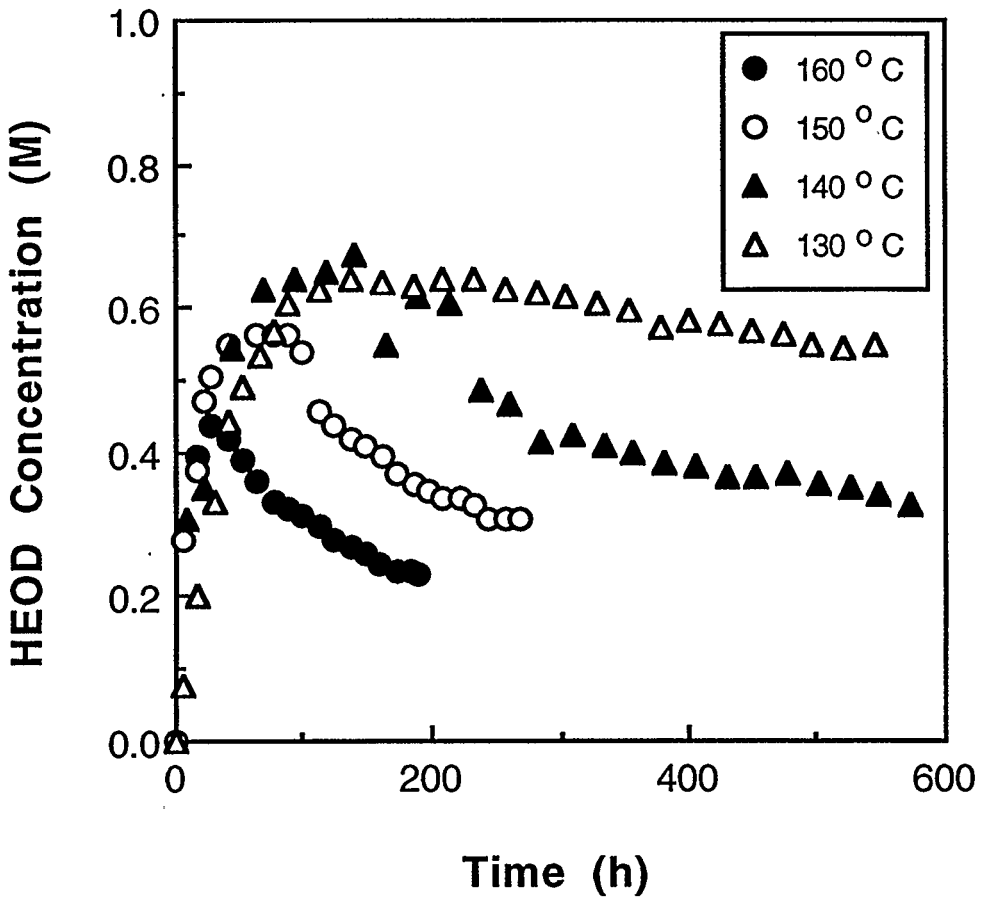


Figure 4.15 HEOD concentration as a function of time and temperature (50 wt% MDEA - 10 wt% DEA, 4137 kPa CO_2)

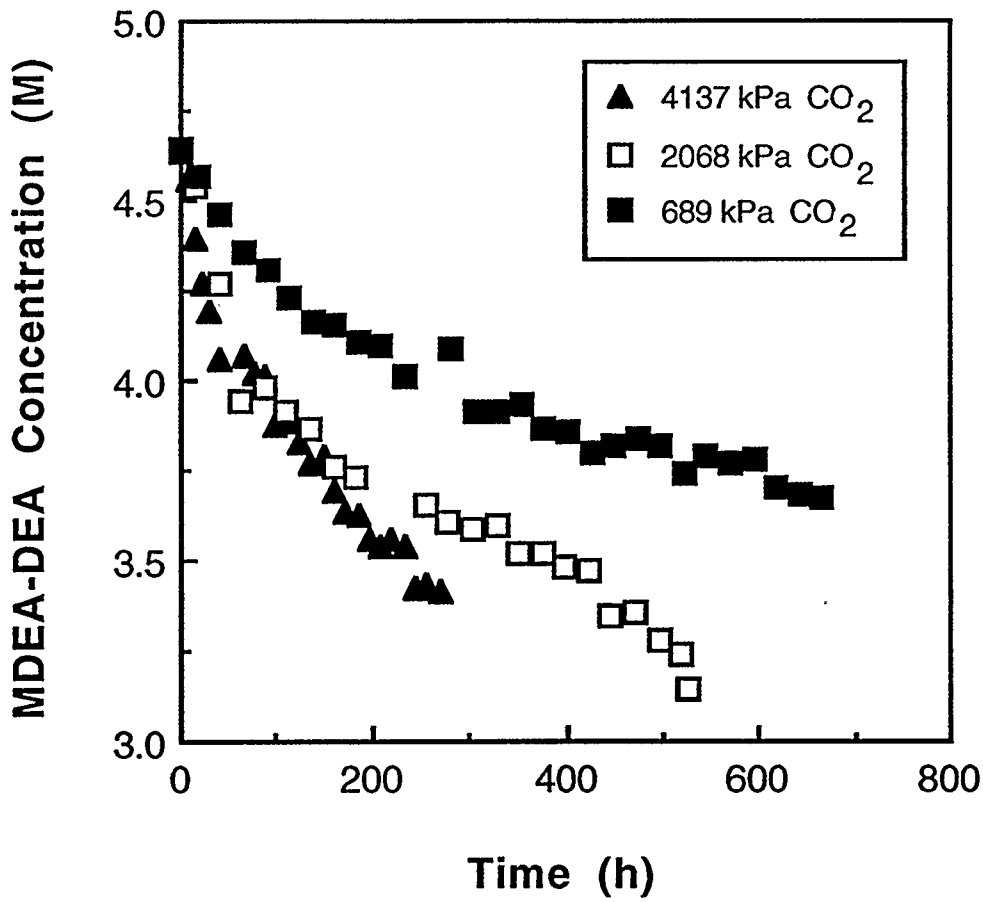


Figure 4.16 Concentration of MDEA-DEA mixture as a function of time and CO_2 partial pressure (50 wt% MDEA - 10 wt% DEA, 150 °C)

Figures 4.17 to 4.21 show plots of EG, DMAE, BHEP, HEOD and THEED concentrations as functions of time and CO_2 partial pressure. The production rates of all the degradation products increase with increasing CO_2 partial pressure as can be seen in these figures.

4.1.2.3 Effect of initial solvent concentration

The DEA concentration in the initial solvent mixture was varied while keeping MDEA concentration constant at 50 wt% in order to see the effect on the degradation products. Changing DEA concentration had different consequences on different degradation products.

As can be seen in Figure 4.22, the EG production is not affected significantly by the change of DEA concentration. This confirms that EG is a degradation product produced only by MDEA.

DMAE concentration decreases with increasing DEA percentage in the solvent (Figure 4.23). The production rate of DMAE is the highest when DEA is not present in the initial solution, which implies that DMAE is not produced by DEA. Moreover the presence of DEA hinders DMAE production since some of the CO_2 dissolved in the solution is used up by DEA. Therefore, less CO_2 is available for MDEA to produce DMAE.

The production rate of HEOD, which is a common product of MDEA and DEA, increases with increasing DEA concentration as can be seen in Figure 4.24. It also can be observed that the plot of HEOD concentration versus time shows a different trend in the absence of DEA in the solvent. The concentration

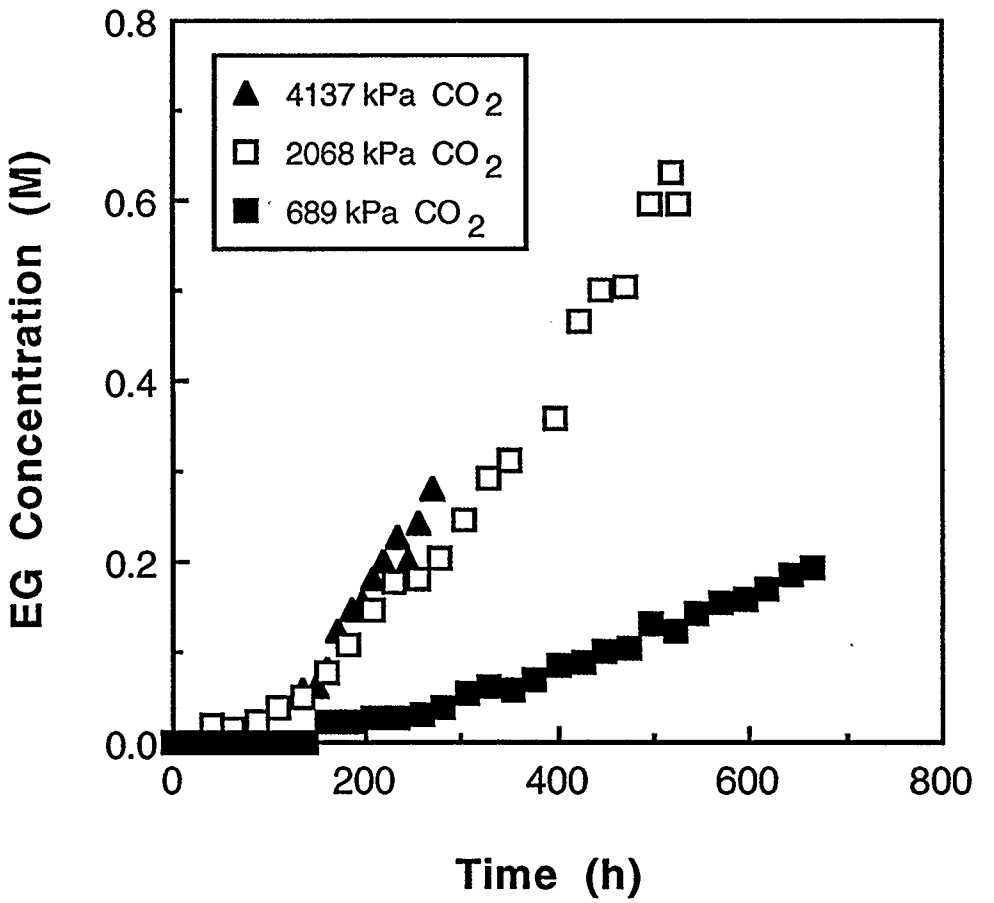


Figure 4.17 EG concentration as a function of time and CO_2 partial pressure (50 wt% MDEA - 10 wt% DEA, 150 °C)

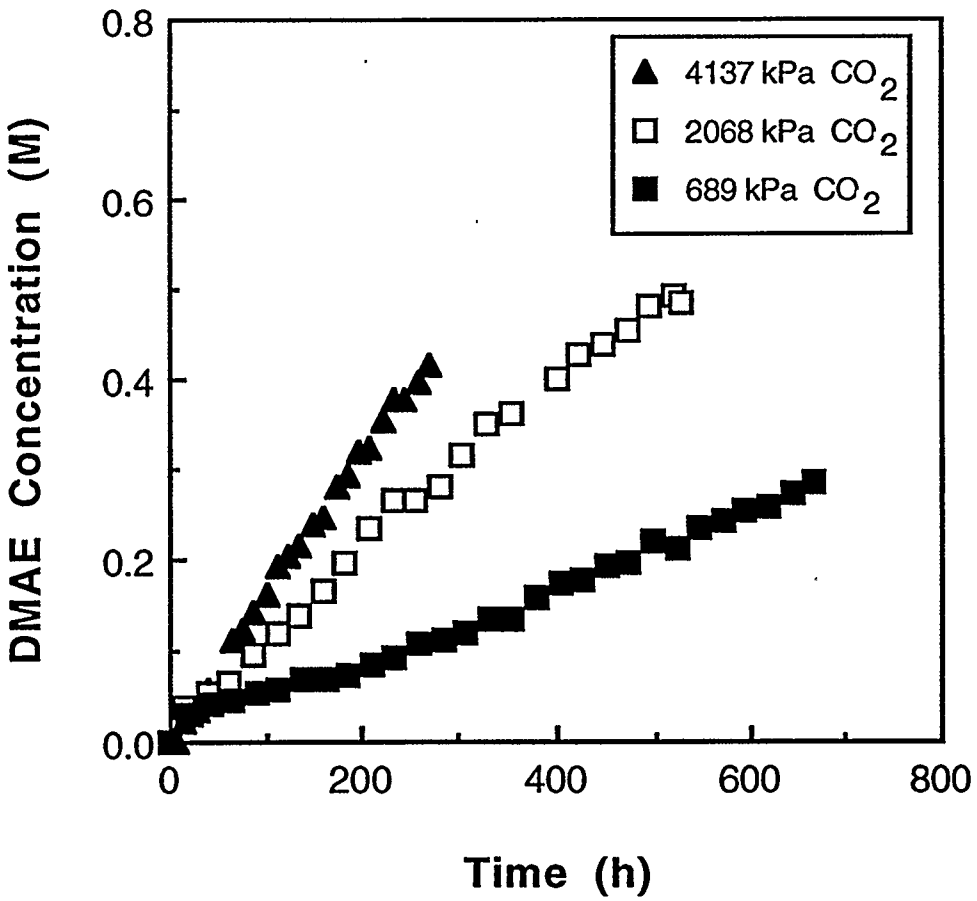


Figure 4.18 DMAE concentration as a function of time and CO_2 partial pressure (50 wt% MDEA - 10 wt% DEA, 150 °C)

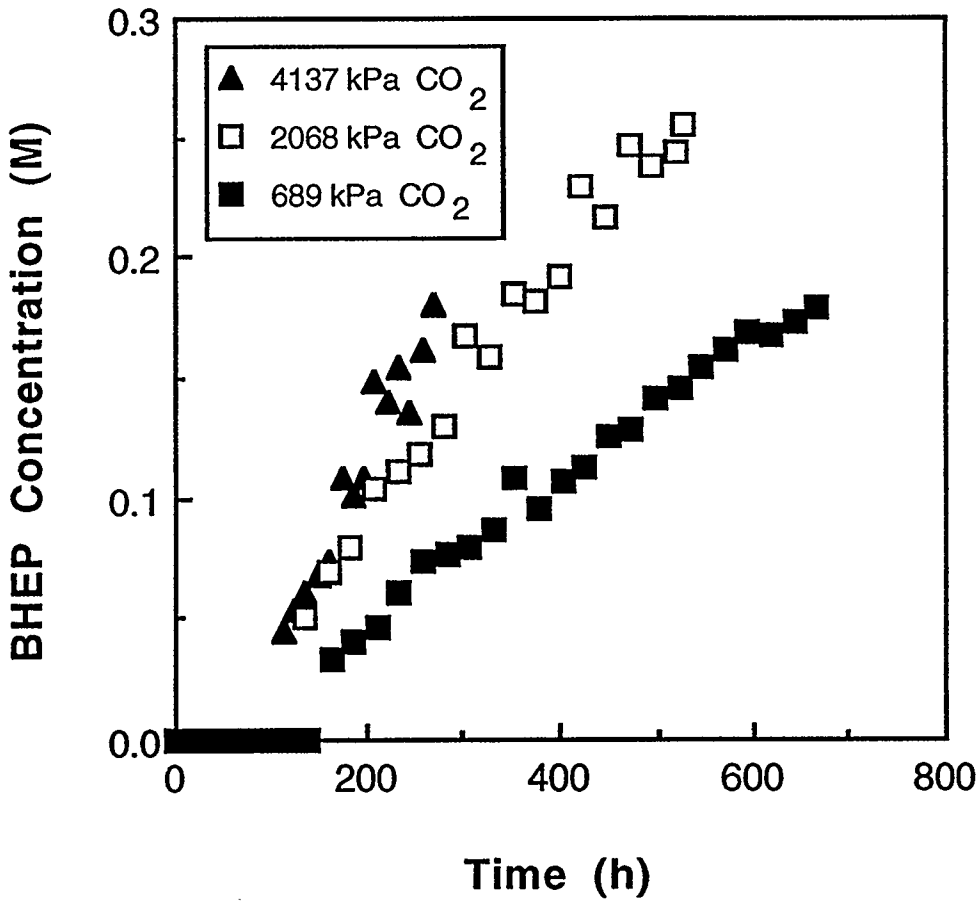


Figure 4.19 BHEP concentration as a function of time and CO_2 partial pressure (50 wt% MDEA - 10 wt% DEA, 150 °C)

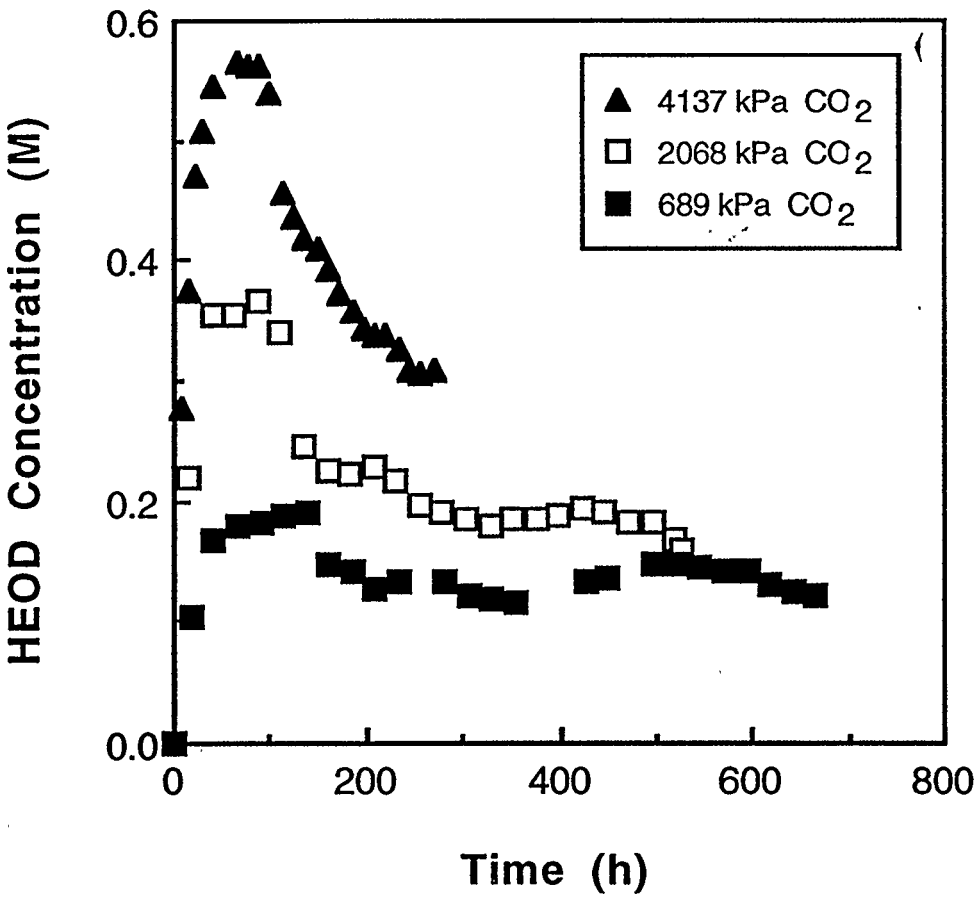


Figure 4.20 HEOD concentration as a function of time and CO_2 partial pressure (50 wt% MDEA - 10 wt% DEA, 150 °C)

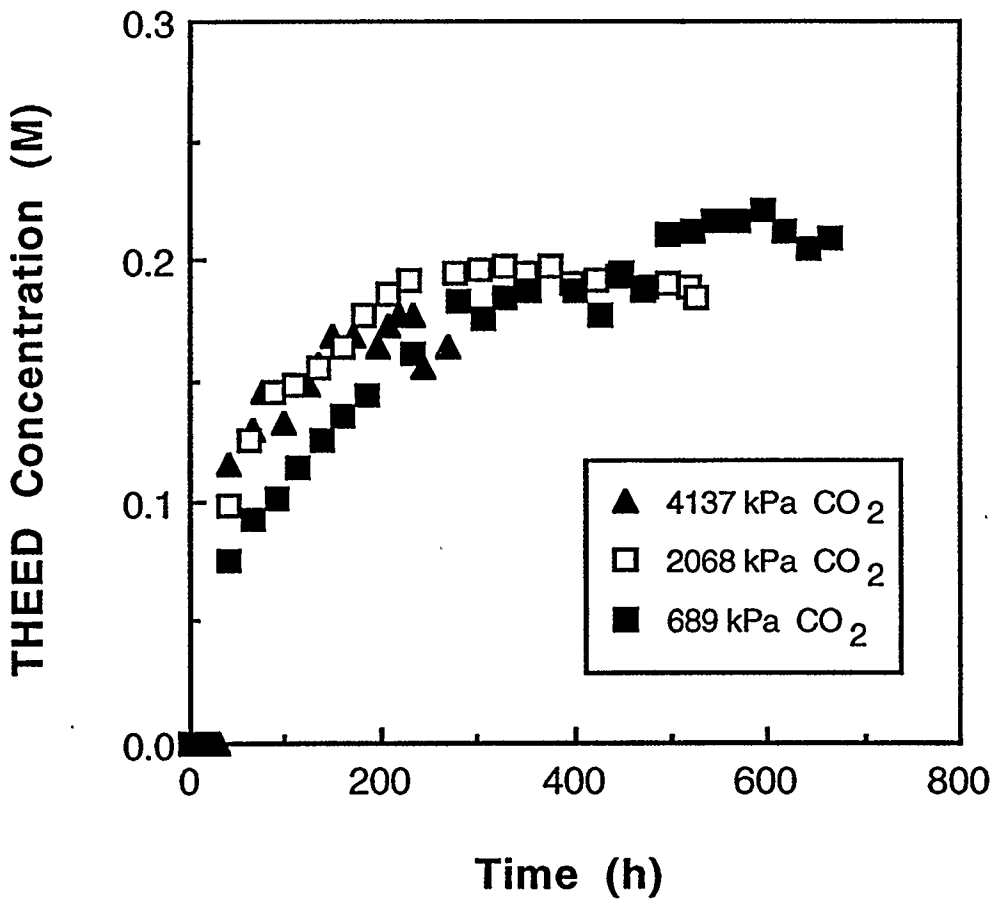


Figure 4.21 THEED concentration as a function of time and CO_2 partial pressure (50 wt% MDEA - 10 wt% DEA, 150 °C)

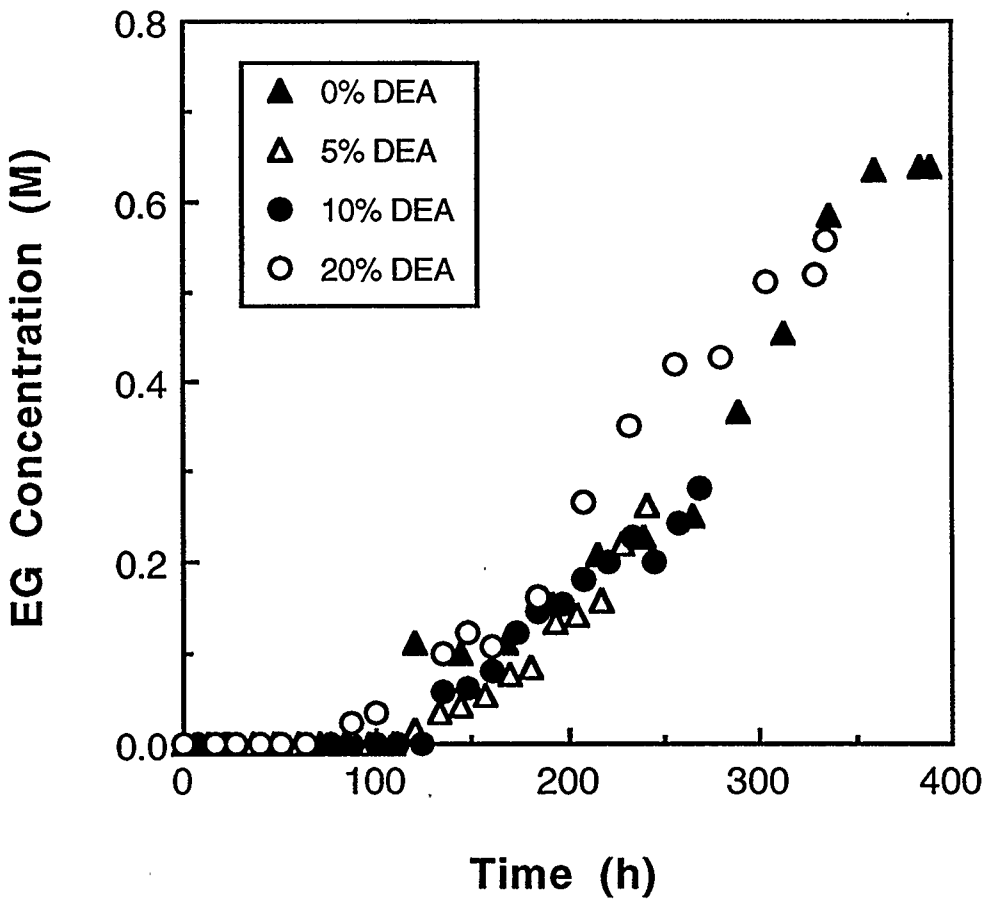


Figure 4.22 EG concentration as a function of time and initial DEA concentration in the mixed-solvent (4137 kPa CO_2, 150 °C)

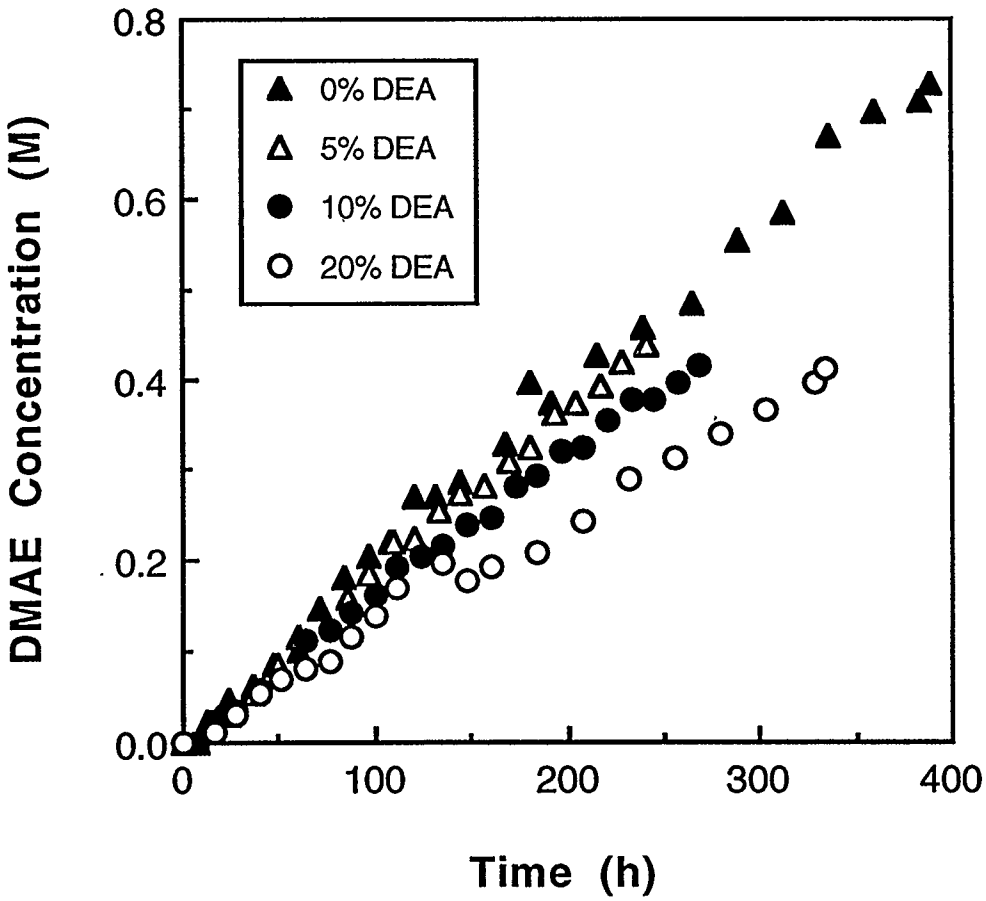


Figure 4.23 DMAE concentration as a function of time and initial DEA concentration in the mixed-solvent (4137 kPa CO_2, 150 °C)

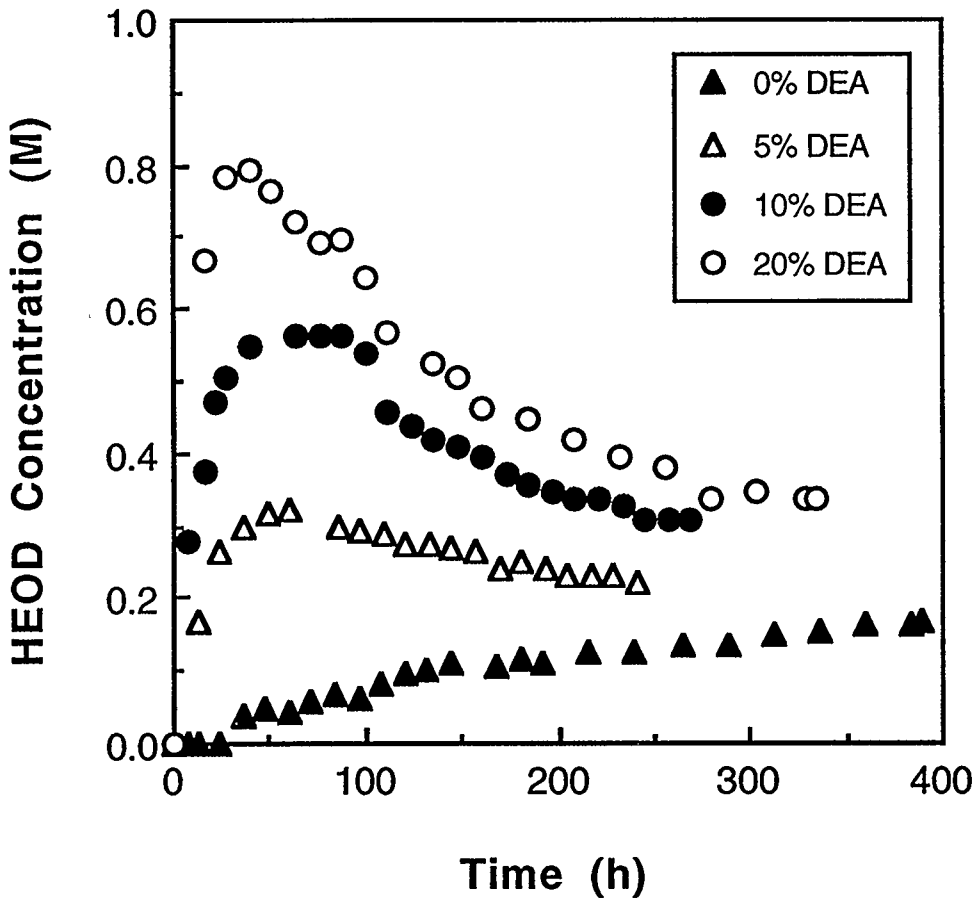


Figure 4.24 HEOD concentration as a function of time and initial DEA concentration in the mixed-solvent (4137 kPa CO_2, 150 °C)

of HEOD increases, reaches a maximum and then decreases when there is 5 to 20% DEA in the solvent. However, it first increases and then levels off in the absence of DEA. This suggests that different reaction mechanisms take place for the production of HEOD from MDEA and DEA.

THEED and BHEP are also produced by both MDEA and DEA. Figures 4.25 and 4.26 show the concentrations of THEED and BHEP plotted against time at different DEA percentages. The production rates of both of them increase with increasing DEA concentration.

4.1.3 EFFECT OF H_2S ON DEGRADATION

In literature, it has been generally accepted that H_2S does not undergo irreversible reactions with amines, so it does not cause degradation. Furthermore, it was reported that H_2S, in the presence of CO_2, hindered the amine degradation [20,41].

Experiments have been carried out by contacting 30% DEA solution with H_2S, CO_2 and a mixture of CO_2 and H_2S at 150 °C , in order to investigate if H_2S has any effect on amine degradation. Figure 4.27 shows the chromatograms of the DEA solution before and after contact with H_2S for 9 hours. It can be seen that no degradation products were detected. Hence, H_2S gas does not cause amine degradation.

The concentrations of the degradation products are plotted against time for the runs carried out with and without H_2S, in the presence of CO_2, in Figures 4.28 and 4.29. When these two figures are compared with each other, it is seen

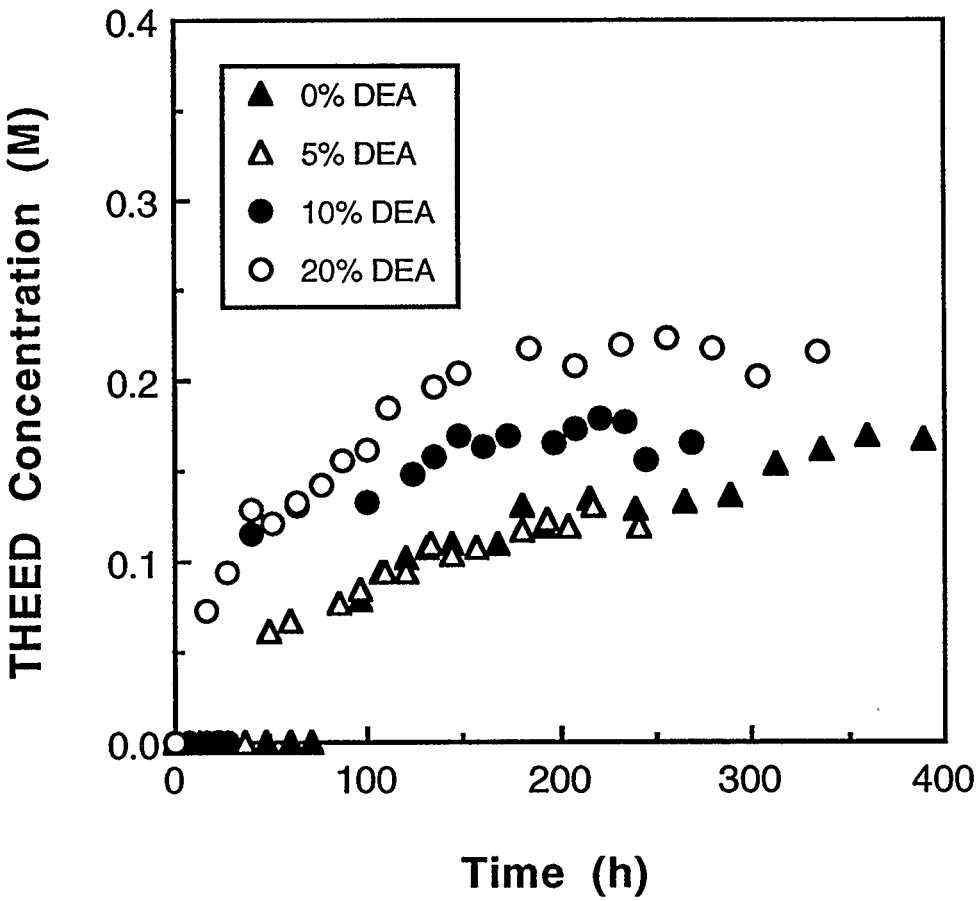


Figure 4.25 THEED concentration as a function of time and initial DEA concentration in the mixed-solvent (4137 kPa CO_2, 150 °C)

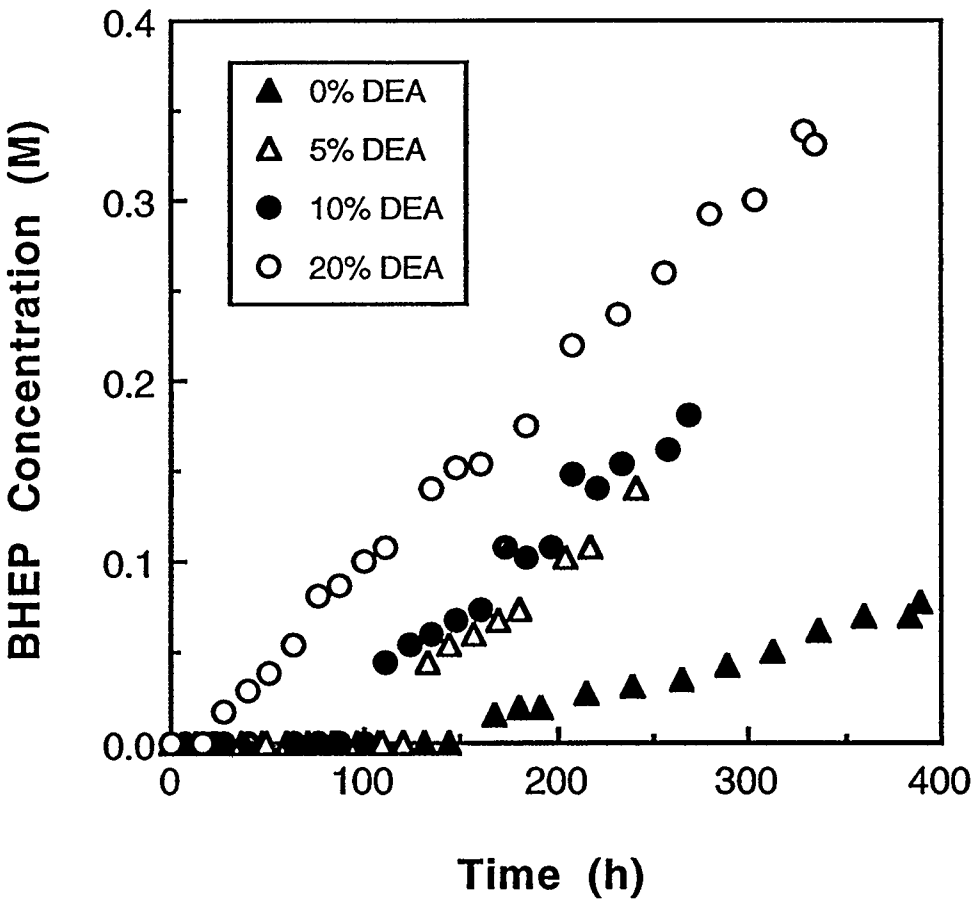


Figure 4.26 BHEP concentration as a function of time and initial DEA concentration in the mixed-solvent (4137 kPa CO_2, 150 °C)

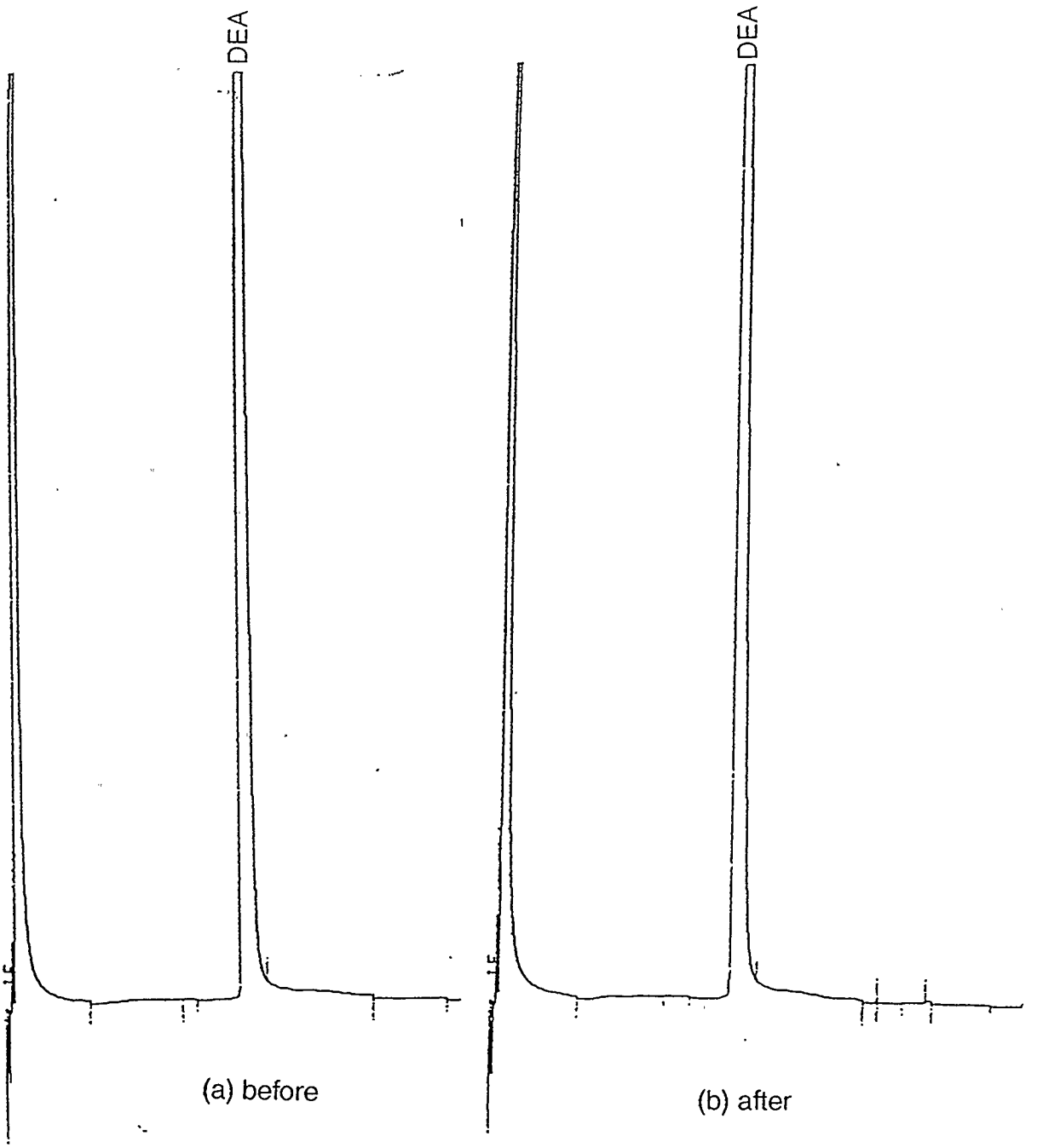


Figure 4.27 Chromatograms of 30 wt% DEA solution (a) before and (b) after being contacted with H_2S at 150 °C

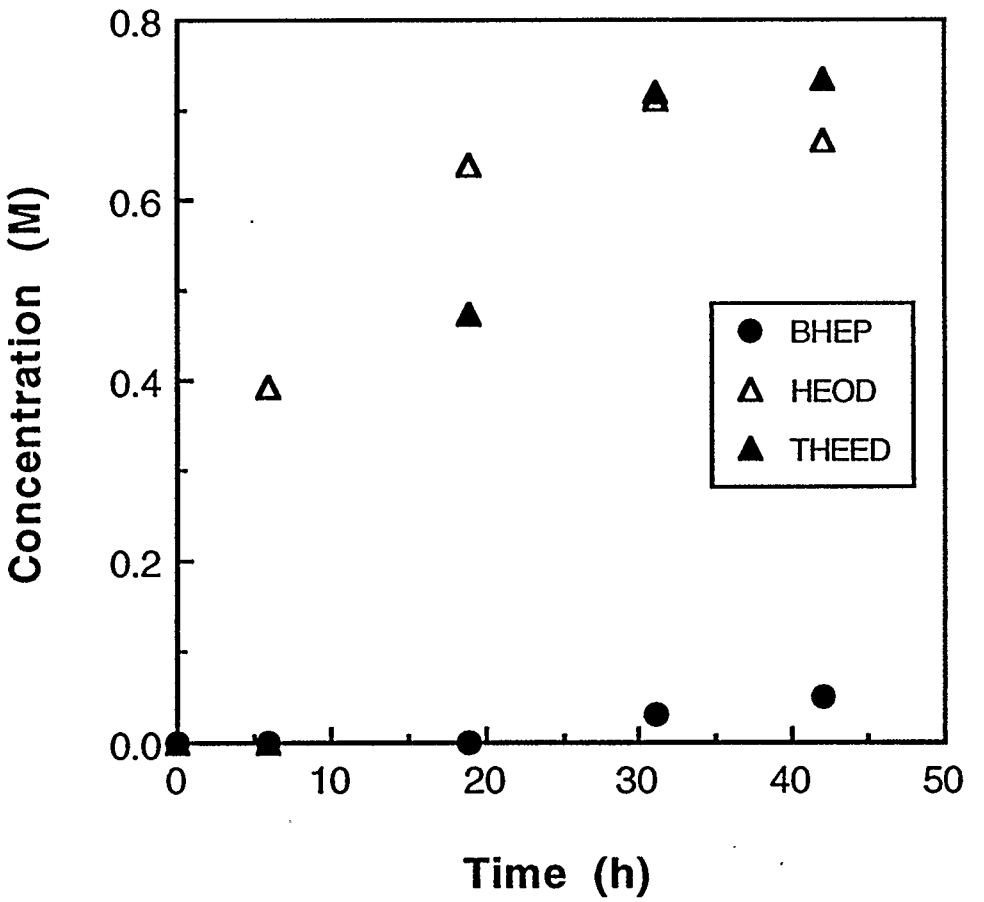


Figure 4.28 Concentrations of the degradation products of DEA as functions of time (30 wt% DEA degraded with 10%H_2S - 90%CO_2, 150 °C, 4137 kPa)

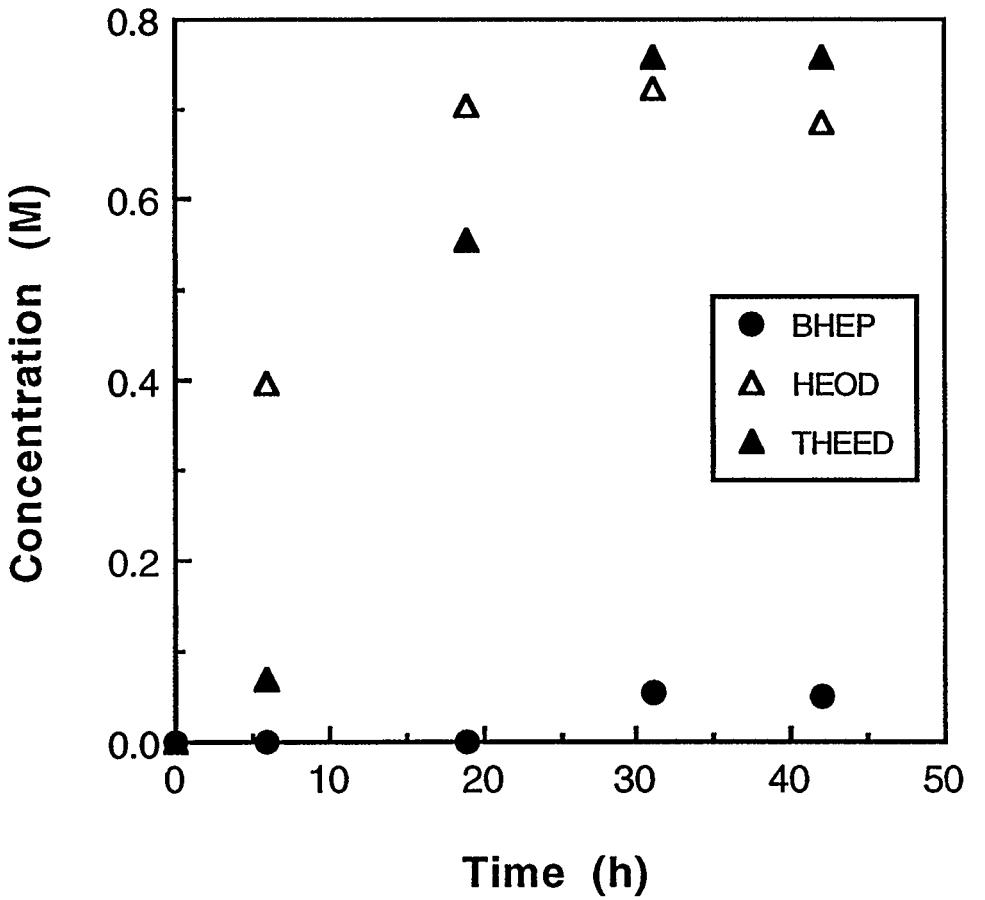


Figure 4.29 Concentrations of the degradation products of DEA as functions of time (30 wt% DEA degraded with CO_2, 150 °C, 4137 kPa)

that HEOD, THEED and BHEP concentrations have the same trends with time for both cases. Likewise, no notable difference can be observed between the concentrations of the DEA solutions, degraded with CO_2 and a CO_2-H_2S mixture, plotted versus time (Figure 4.30). Therefore, it can be concluded that H_2S gas neither causes nor has a significant effect on degradation.

4.2 PURIFICATION EXPERIMENTS

The degraded amine solutions have to be purified in order to reduce the operating problems created by degradation products and described in Chapter 2, Section 2.3. However, purification of degraded amine solutions is known to be difficult. Activated carbon beds are being used in industry for the removal of major contaminants even if laboratory tests and analysis of industrial samples taken upstream and downstream of activated carbon beds indicate that they do not remove significant quantities of major degradation products [12,47].

In this study, purification of degraded solutions was attempted using chemical methods, vacuum distillation and ion-exchange resins. The results of purification experiments are reported in the following sections.

4.2.1 CHEMICAL PURIFICATION

The technique of chemical purification basically consists of contacting a degraded solution with alkali which provides hydroxyl ions for the reversal of degradation reactions (see Section 3.2.1).

A few tests were carried out with degraded DEA solutions, using NaOH as the alkali. Figure 4.31 shows the chromatograms, before and after the addition of

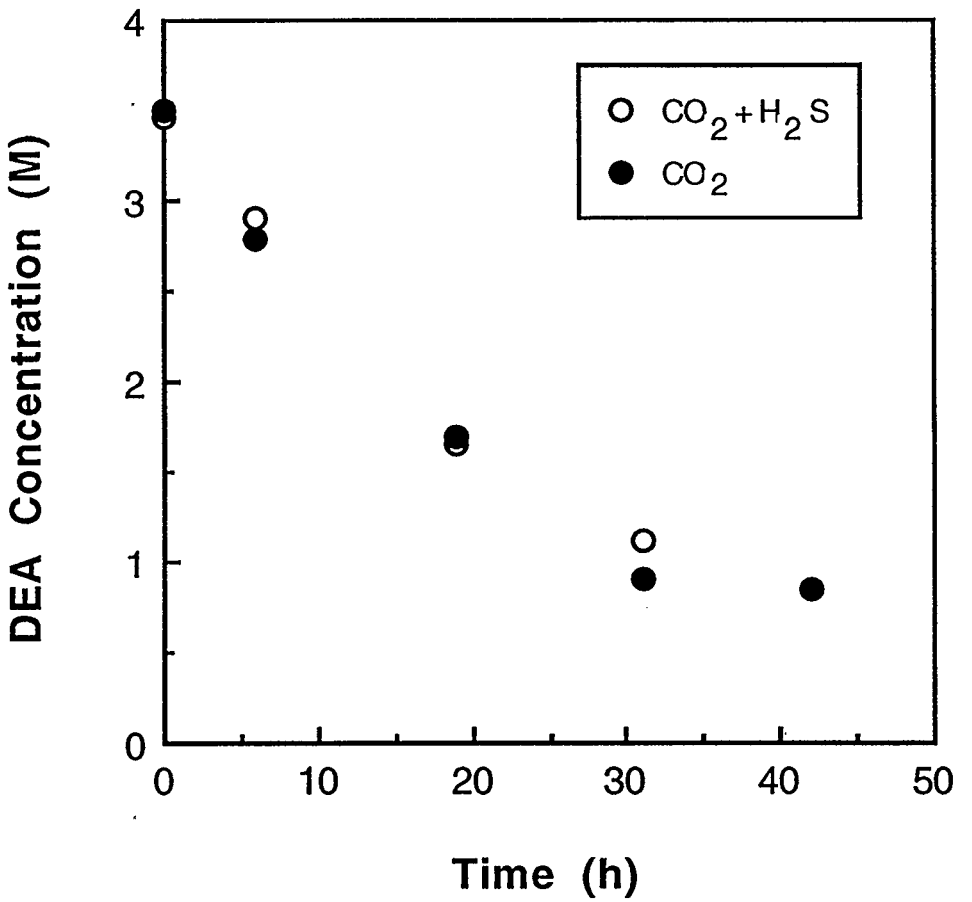


Figure 4.30 DEA concentrations, degraded with and without H_2S, as functions of time (30 wt% DEA, 150 °C; 4137 kPa)

1 mL of 10 M NaOH solution to 5 mL degraded DEA sample. No significant change was observed in the solution concentration of 0.48 M DEA, 0.40 M BHEP, 0.34 M HEOD and 0.27 M THEED after the addition of NaOH, as also can be seen in the figure. On the other hand, adding 1 mL of 20 M NaOH solution to the same sample caused the DEA concentration to increase to 0.56 M, HEOD concentration decrease to 0.16 M but had no effect on BHEP and THEED concentrations (Figure 4.32). Likewise, 2 mL of 10 M NaOH solution was added to a degraded DEA sample containing 0.42 M DEA, 0.34M BHEP, 0.28 M HEOD and 0.22 M THEED. As can be observed from the chromatograms in Figure 4.33, DEA concentration increased to 0.58 M, HEOD concentration decreased to 0.07 M, THEED almost disappeared and BHEP concentration did not change.

In order to examine the effect of temperature on the reversal reactions, a degraded sample consisting of 0.47 M DEA, 0.38 M BHEP, 0.33 M HEOD and 0.32 M THEED after addition of 1 mL of 10 M NaOH solution was kept at 70 °C for 20 minutes. The chromatograms of the solution before and after heating are shown in Figure 4.34. No notable change was observed in the solution concentration after heating.

Since a systematic study has not been conducted, it is not possible to give quantitative information depending on the few tests that have been carried out. However, it can be stated that addition of NaOH solution to degraded DEA samples changes the solution concentration by creating an increase in DEA and a decrease in HEOD and THEED quantities, yet it has no effect on BHEP. These observations are in agreement with the results of Chakma's investigation on the same subject [17,18].

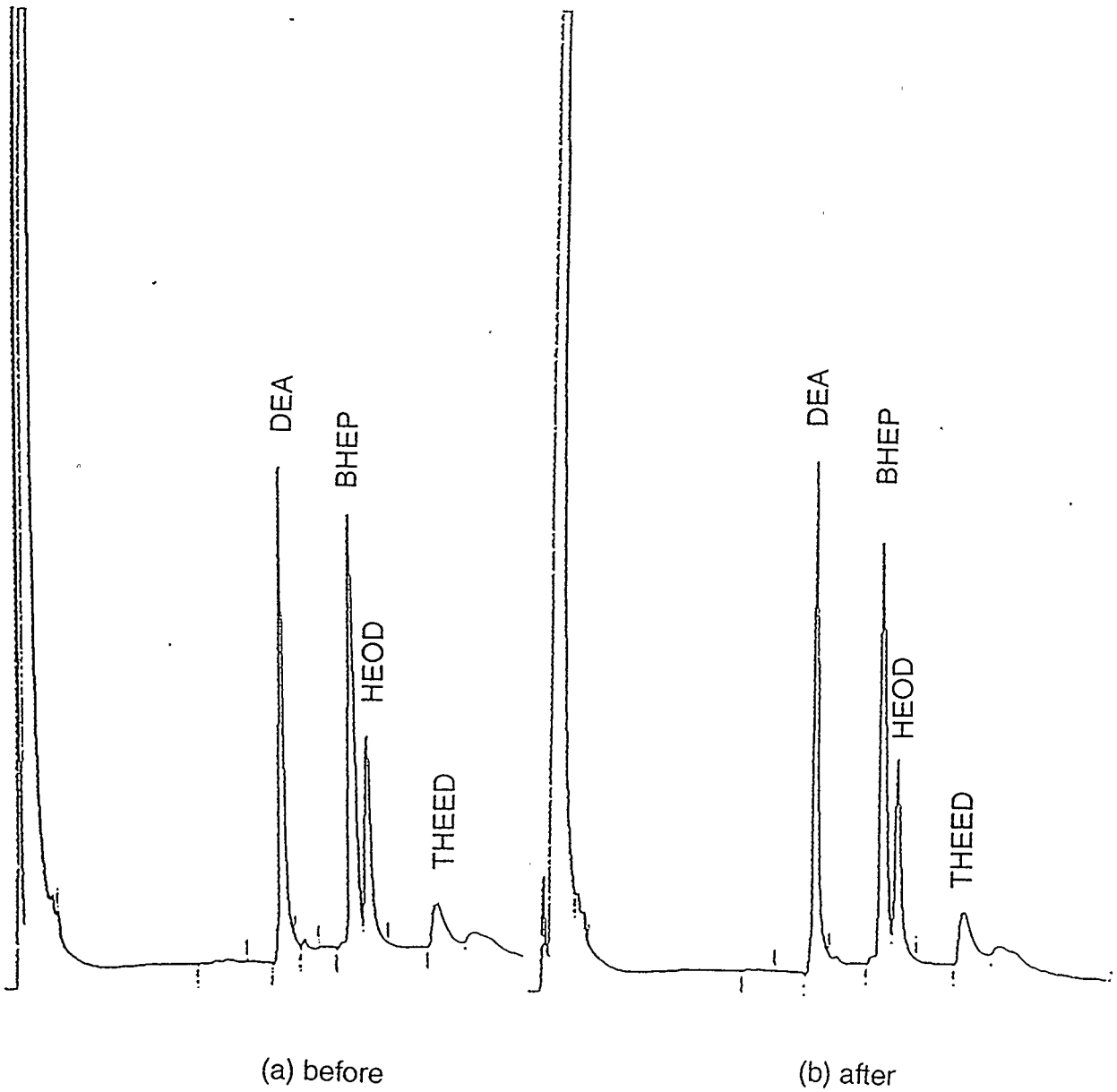


Figure 4.31 Chromatograms of 5 mL degraded DEA samples (a) before and (b) after addition of 1 mL of 10 M NaOH solution

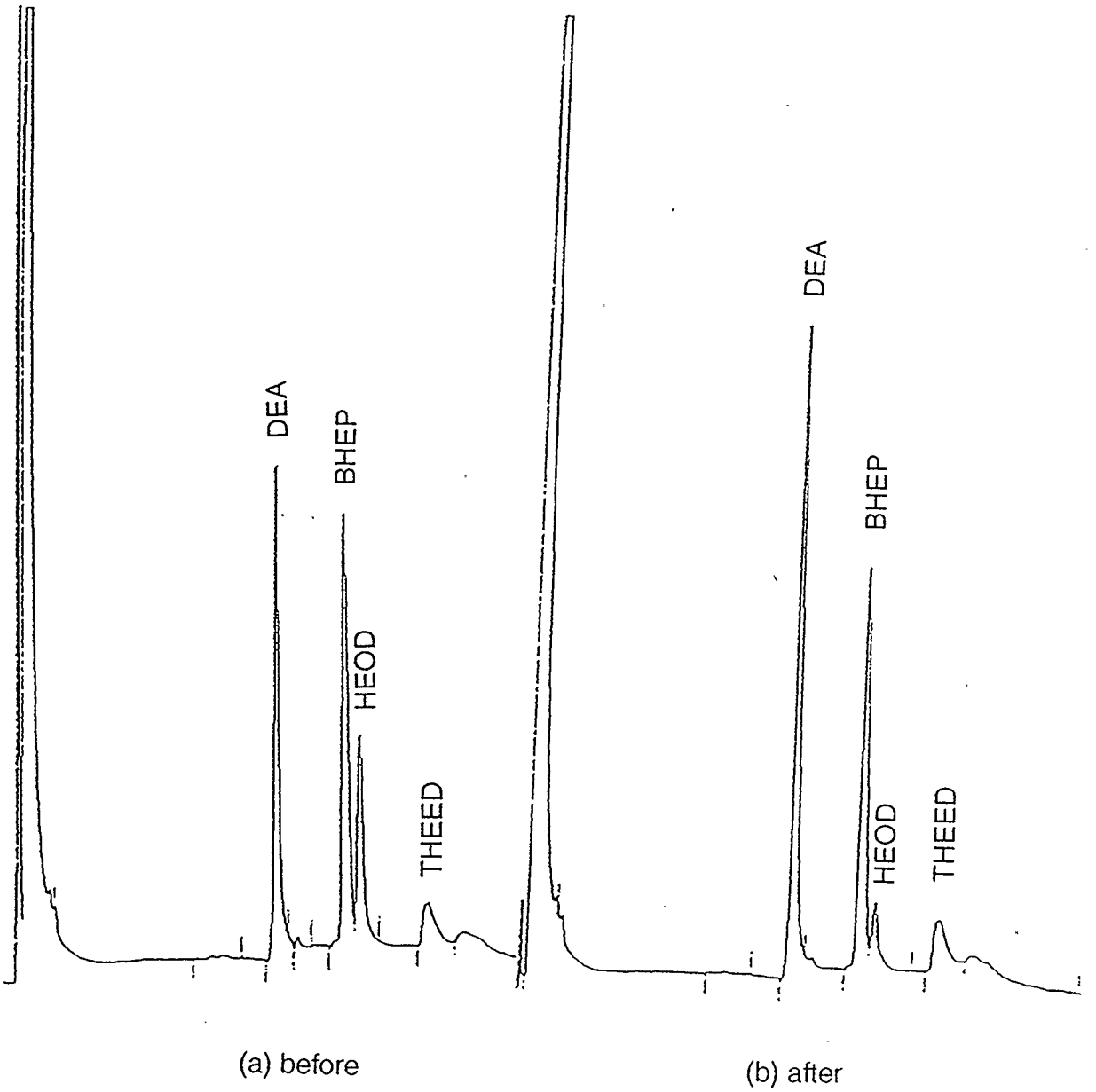


Figure 4.32 Chromatograms of 5 mL degraded DEA samples (a) before and (b) after addition of 1 mL of 20 M NaOH solution

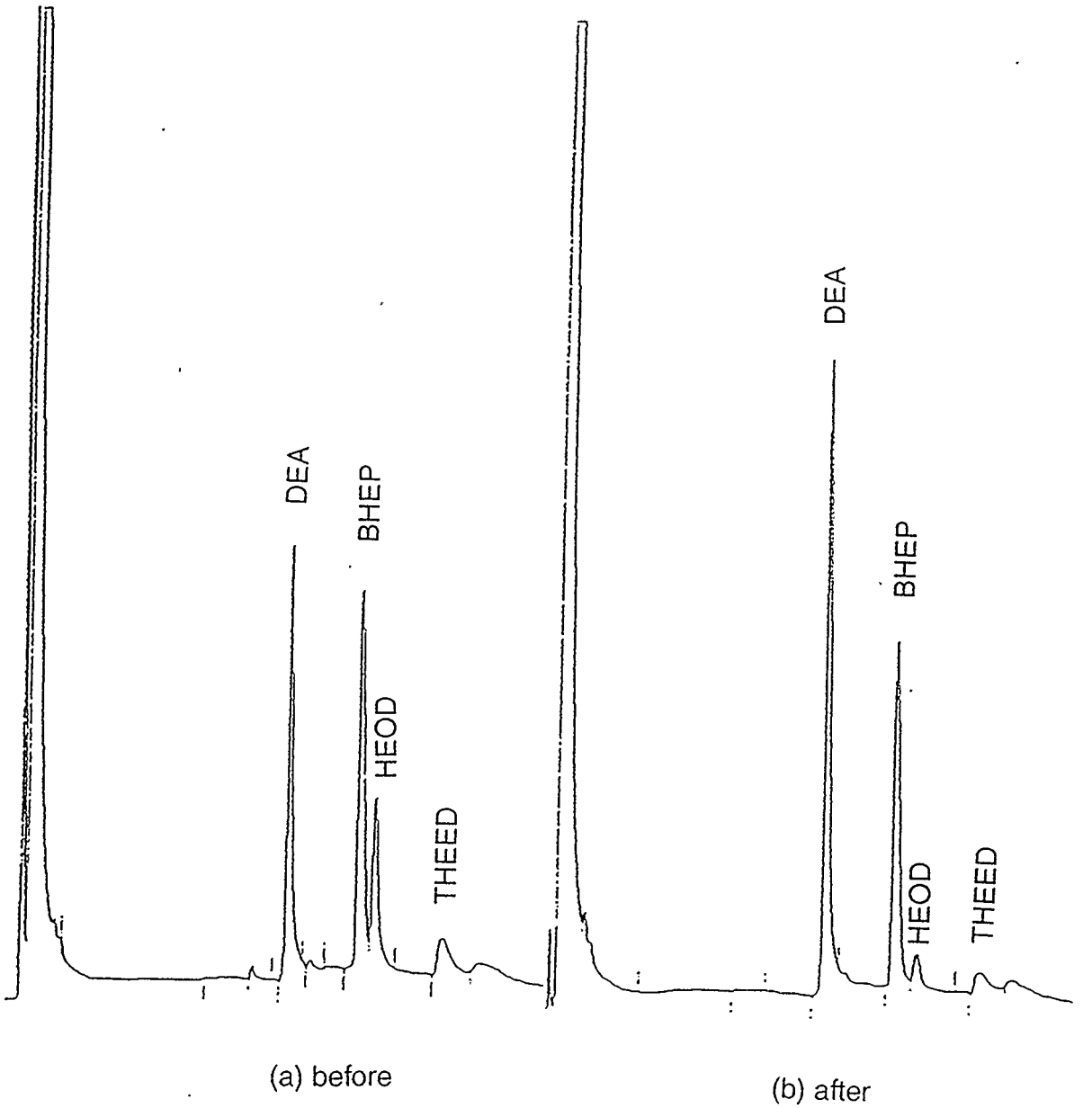


Figure 4.33 Chromatograms of 5 mL degraded DEA samples (a) before and (b) after addition of 2 mL of 10 M NaOH solution

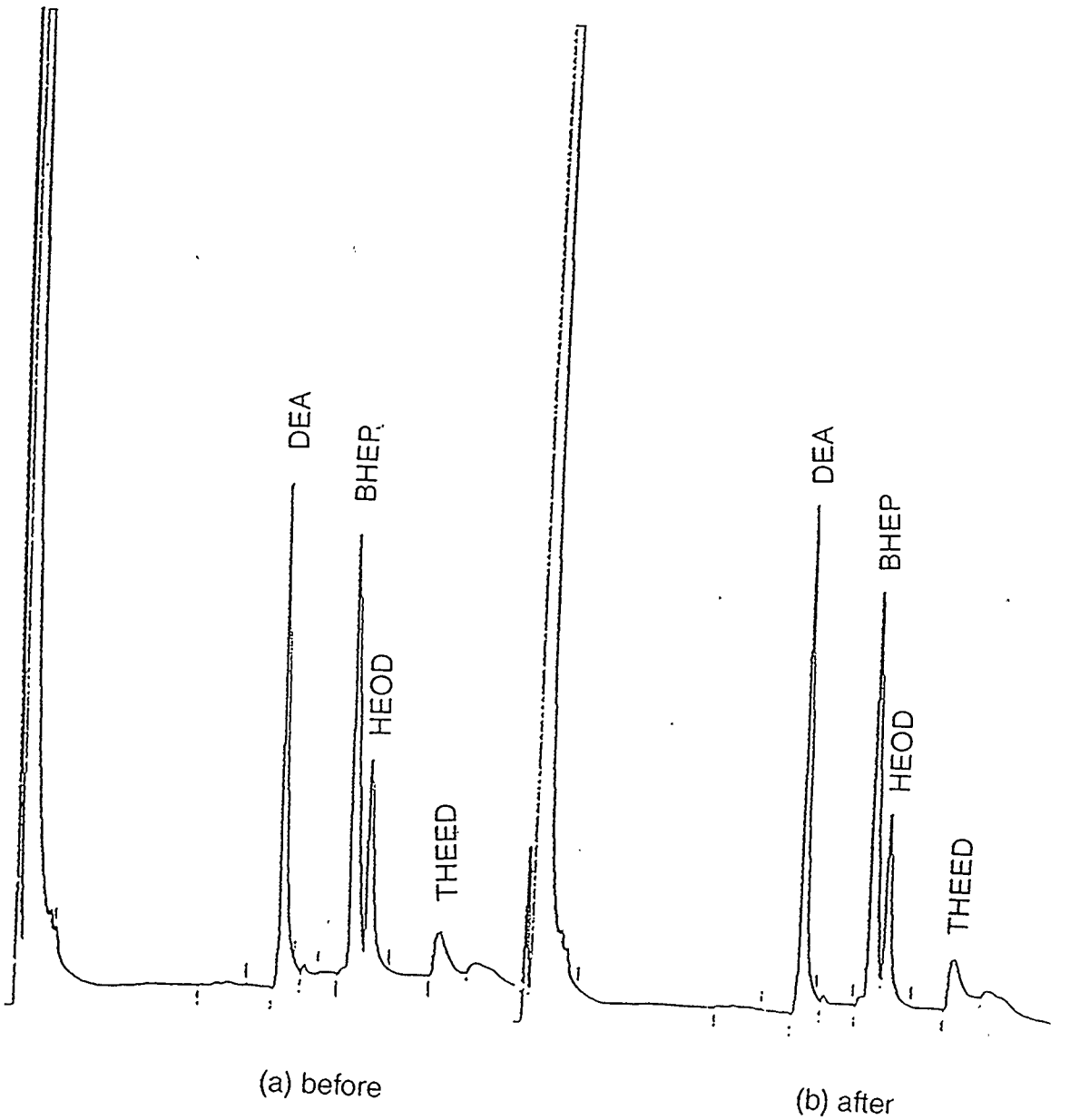


Figure 4.34 Chromatograms of 5 mL degraded DEA samples (a) before and (b) after treatment with 1 mL of 10 M NaOH solution at 70 °C for 20 minutes

4.2.2 VACUUM DISTILLATION

As concluded in the previous section and also stated in the literature, chemical treatment of degraded DEA samples leads to the reduction of HEOD and THEED amounts in the solution to a certain extent. However, chemical treatment did not cause any change in BHEP concentration. Therefore, it was decided to apply distillation to separate BHEP from DEA, assuming that HEOD and THEED had been eliminated before.

Atmospheric distillation is known to be ineffective since DEA and the degradation products have high boiling points and DEA undergoes thermal degradation at such high temperatures. Hence, vacuum distillation was decided to be used for DEA-BHEP separation, in order to lower the boiling points and prevent thermal degradation.

Seven vacuum distillation experiments have been carried out with aqueous DEA-BHEP mixtures prepared in the laboratory. A distillate other than water could be obtained only in three of them. Main problems encountered during the experiments were flooding and the difficulty of controlling the bottom temperature in a narrow range. Some runs had to be stopped because of flooding which may be due to high vacuum or the way the vacuum was applied. Vacuum was not continuous but pulsating, so the pulsations might have caused flooding.

It was necessary to find an optimum temperature range in order not to cause thermal degradation and to have a considerable amount of distillate. Thermal degradation is known to occur above 200 ^{o}C, so the temperature has

been kept lower than that. First, a temperature range of 180-185 °C (temperature could be controlled within a 5 °C range) was tried at 30 mbar vacuum and no DEA or BHEP was detected in the distillate. Then, the temperature was raised to 185-190 °C at 30 mbar and the distillate was again water. When a DEA-BHEP mixture containing 3.9 M DEA and 0.7 M BHEP was distilled at 190-195 °C and 30 mbar for 3 hours, small amounts of DEA and BHEP were detected in the distillate. Figure 4.35 shows the chromatograms of the feed and distillate samples. The BHEP/DEA ratio which was 0.17 in the feed decreased to 0.06 in the distillate. However, the distillation rate was so low that the quantity of the distillate obtained was very small. Therefore, it was decided to carry out another run at the same conditions for a longer time. This time, the experiment lasted 6 hours and the concentration ratio of BHEP to DEA dropped to 0.03 from 0.17, but the EG peak was observed in the distillate which was formed as a result of thermal degradation (Figure 4.36). At the same time, THEED was detected in the bottoms which was also due to thermal degradation. Hence, it can be stated that exposing a DEA solution to temperatures in the range of 190-195 °C for a long time period causes thermal degradation.

Since flooding created problems during the experiments performed at 30 mbar, it was decided to decrease the vacuum to 50 mbar to see if the flooding could be avoided. A mixture containing 3.7 M DEA and 0.6 M BHEP was distilled at 190-195 °C and 50 mbar for 3 hours. No BHEP and DEA was obtained in the distillate. Then, a mixture with the same concentration was distilled at 195-200 °C and 50 mbar and very little DEA and BHEP was detected in the distillate (Figure 4.37). BHEP/DEA ratio decreased to 0.06 from 0.18 in the feed.

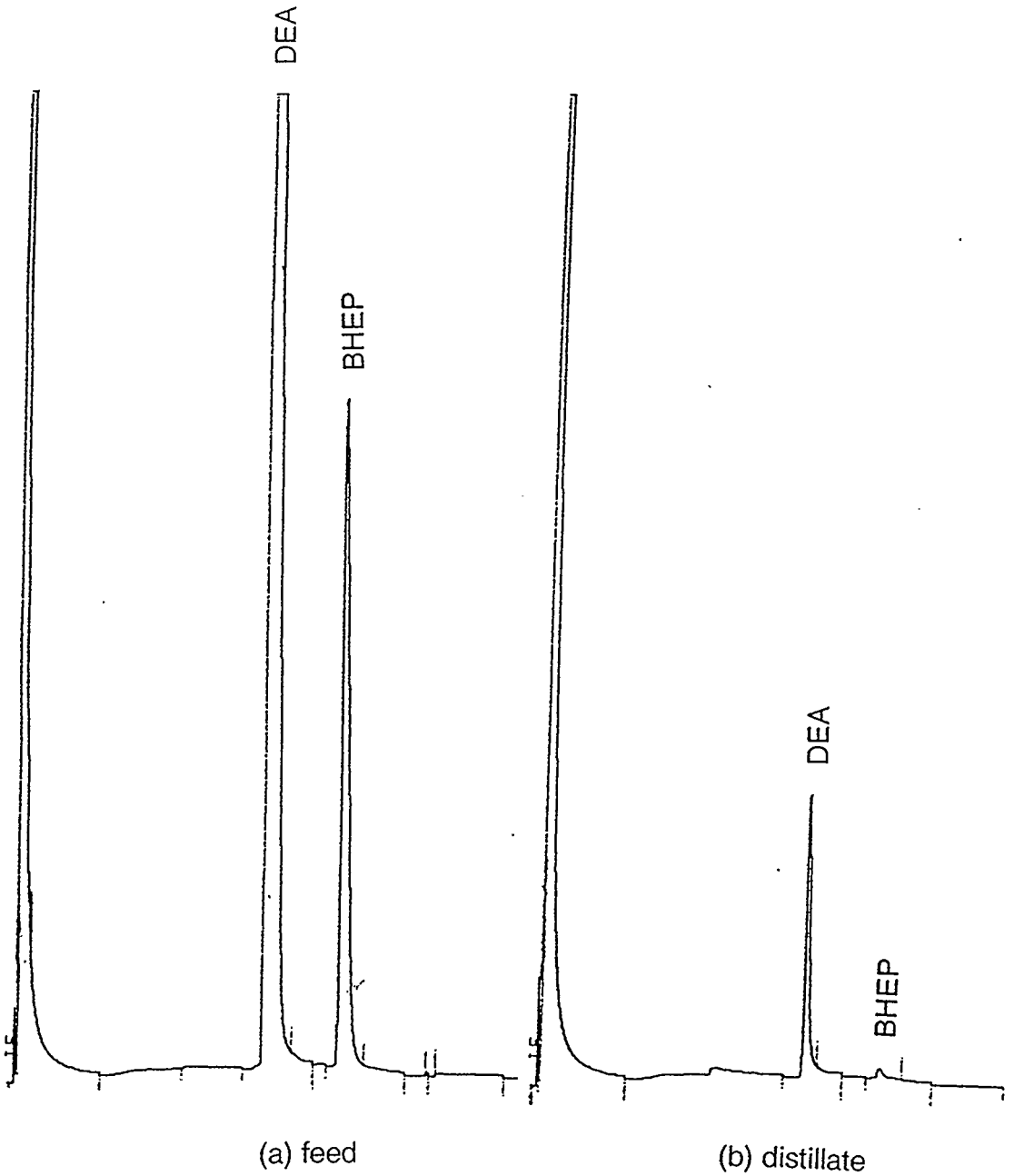


Figure 4.35 Chromatograms of (a) feed and (b) distillate samples of a DEA-BHEP mixture distilled at 190-195 °C and 30 mbar vacuum for 3 hours

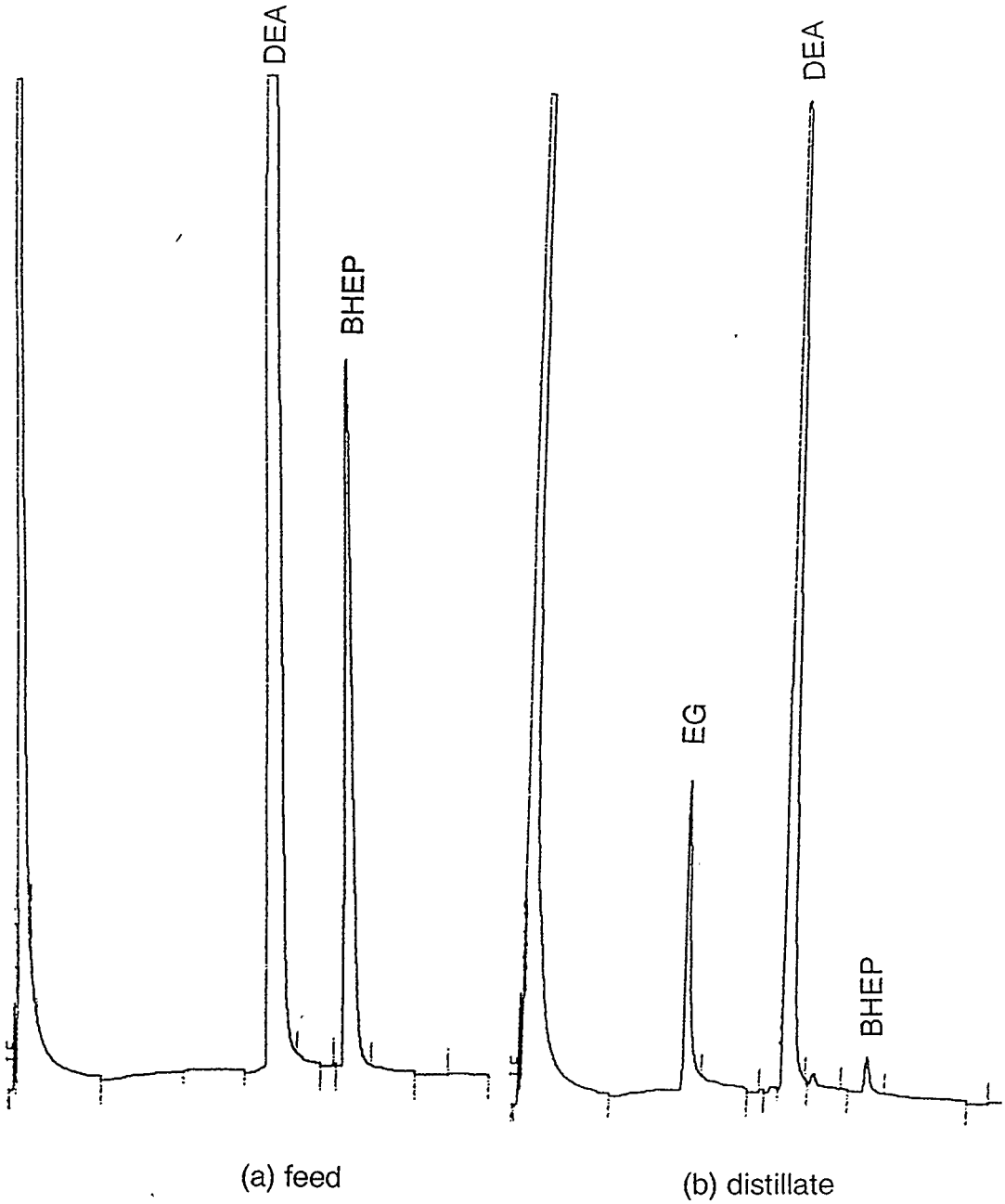


Figure 4.36 Chromatograms of (a) feed and (b) distillate samples of a DEA-BHEP mixture distilled at 190-195 °C and 30 mbar vacuum for 6 hours

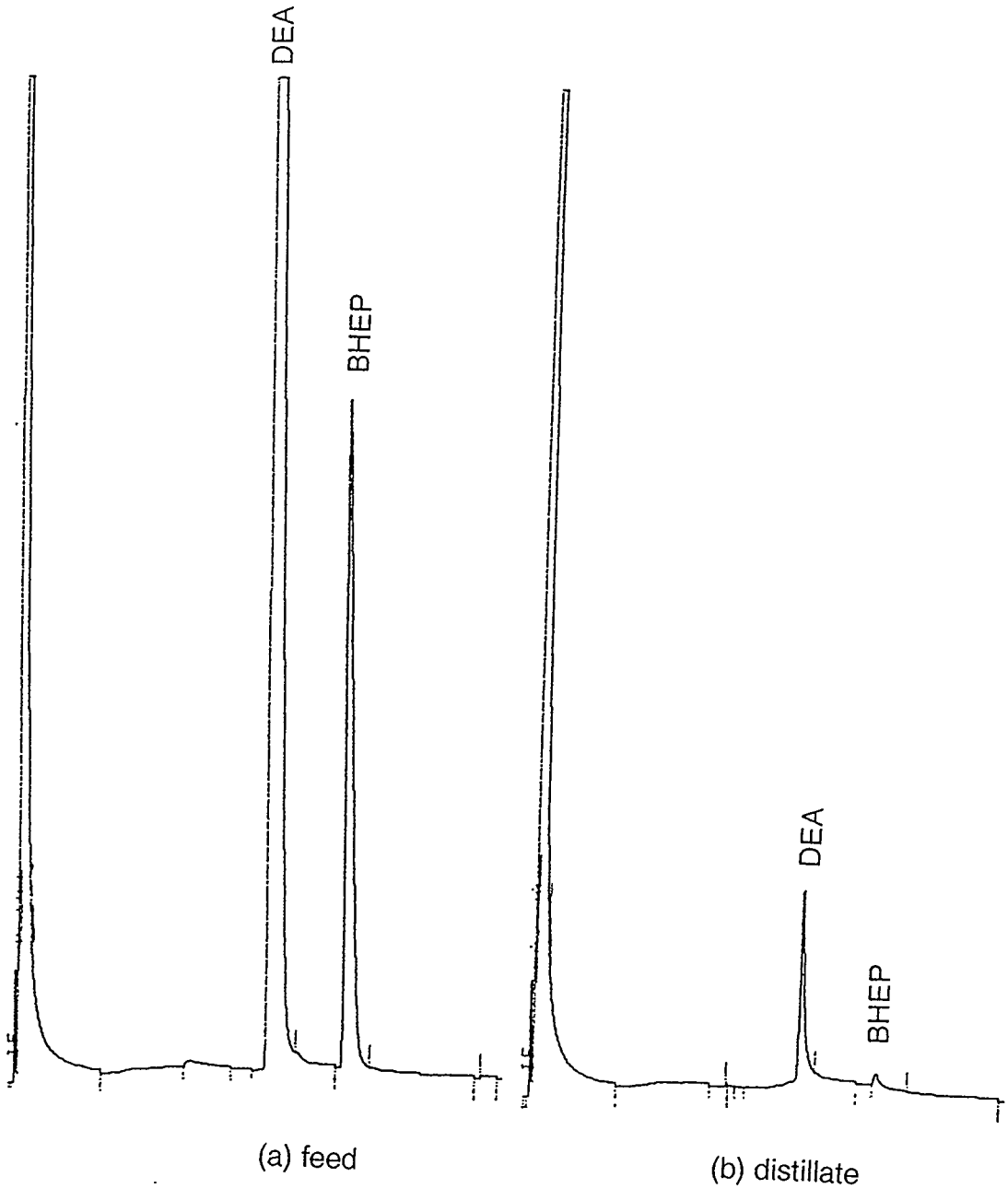


Figure 4.37 Chromatograms of (a) feed and (b) distillate samples of a DEA-BHEP mixture distilled at 195-200 °C and 50 mbar vacuum for 3 hours

One vacuum distillation was carried out with a degraded solution produced in the laboratory during mixed-solvent degradation experiments. The solution consisting of 0.1 M EG, 0.5 M DMAE, 0.2 M BHEP, 0.3 M HEOD, 0.1 M THEED and 3.6 M solvent (MDEA-DEA) was distilled at 185-190 °C and 30 mbar. The distillate mostly contained EG and DMAE which have lower boiling points than DEA and MDEA (Figure 4.38). The EG/SOLVENT and DMAE/SOLVENT ratios in the feed were 0.03 and 0.14 respectively. These ratios increased to 4.8 and 16.0 in the distillate.

As a result, it can be concluded that at temperatures below 190 °C at 30 mbar of vacuum, DEA and BHEP can not be distilled. Whereas, between 190 and 195 °C, if the distillation is carried out for a short time, no significant quantities of DEA and BHEP can be detected in the distillate. On the other hand, if the heating period lasts long, thermal degradation occurs. Moreover, flooding creates problems in the separation of DEA and BHEP by vacuum distillation. Therefore, vacuum distillation is not feasible in purification of degraded samples.

4.2.3 ION-EXCHANGE RESINS

Three ion-exchange column experiments were performed by passing industrially degraded amine solutions through a bed of strongly basic Amberlyst A-27 ion-exchange resin at three different flowrates of 1.1, 7.7 and 14.9 mL/min., as described in Section 3.2.3.

The degraded DEA solutions, provided by gas processing plants contained EG, BHEP, HEOD and THEED as the major degradation products. Samples taken from the column effluent throughout the experiments were

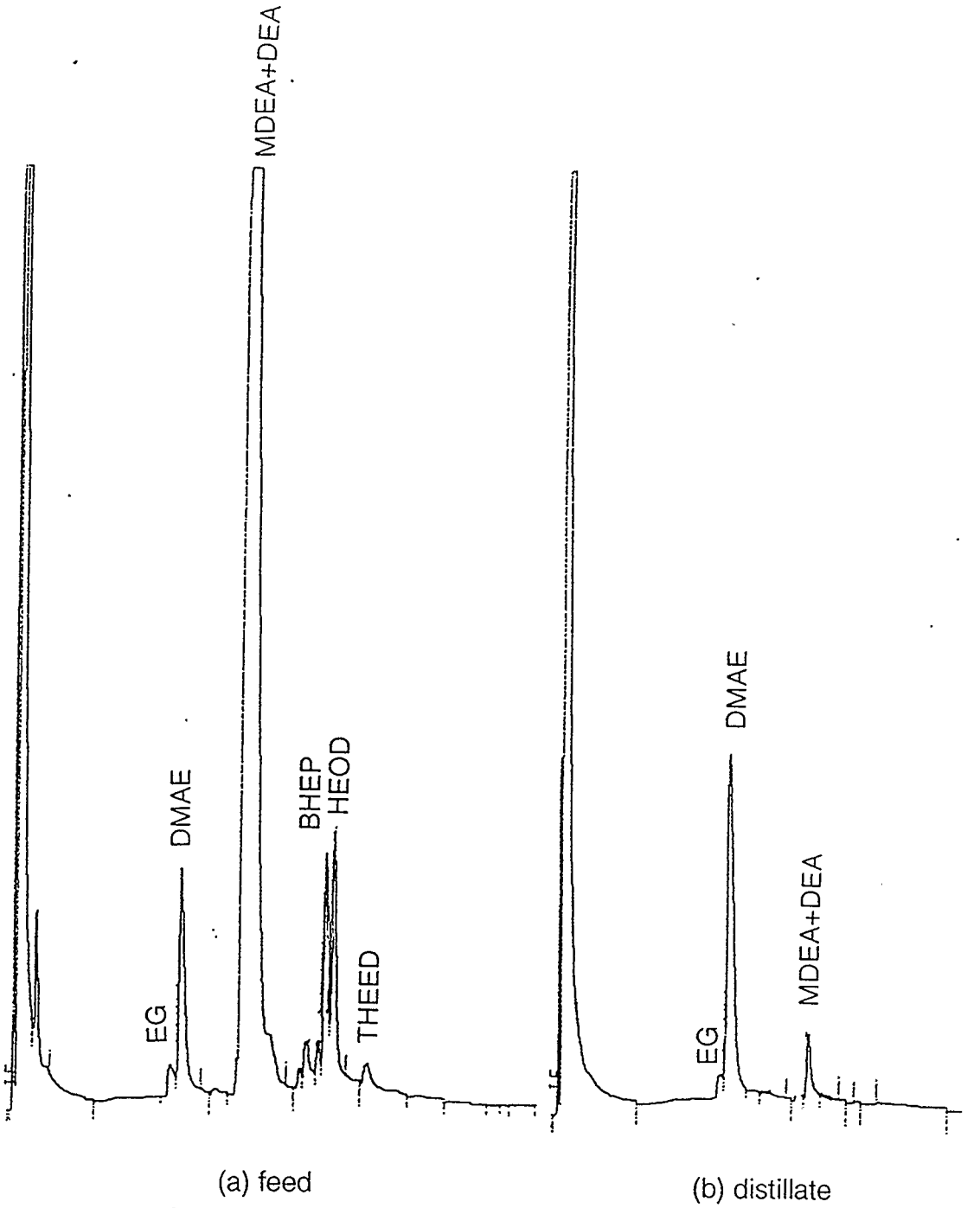


Figure 4.38 Chromatograms of (a) feed and (b) distillate samples of a degraded MDEA-DEA mixture distilled at 185-190 °C and 30 mbar vacuum

analyzed by gas chromatography. It was observed that HEOD peak disappeared from the solutions as a result of the contact with the resin, but a new minor peak appeared with a retention time close to HEOD. This is in agreement with Chakma's observation of a new unidentified peak along with the disappearance of HEOD during alkali treatment of industrial samples [18]. It was also detected that the concentrations of EG, BHEP, THEED and also DEA decreased. This concentration drop in all the compounds that exist in ionic forms in the solution can be explained by their reacting and being hold by the resin [18]. Figures 4.39-4.41 show the concentrations, made dimensionless by dividing by the initial concentrations prior to resin treatment, of EG, BHEP, THEED and DEA plotted against time for the experiments at different flowrates of 1.1, 7.7 and 14.9 mL/min., respectively.

The dimensionless concentrations of EG, BHEP, THEED and DEA are plotted as functions of time and flowrate in Figures 4.42-4.45, respectively. It can be seen that all the compounds experience higher concentration decreases at lower flowrates and it takes more time to reach the saturation of the resin as the flowrate decreases.

The collected samples which were analyzed right after the experiments were analyzed for the second time after 6 weeks. It was found that the concentrations of the samples changed with time. The concentrations of THEED, BHEP and EG in the samples decreased as time passed. It can be seen in Figures 4.46-4.48 that THEED concentration encounters the highest decrease with time, followed by BHEP and EG. On the other hand, a significant change was not observed in DEA concentration with time (Figure 4.49). The changes of

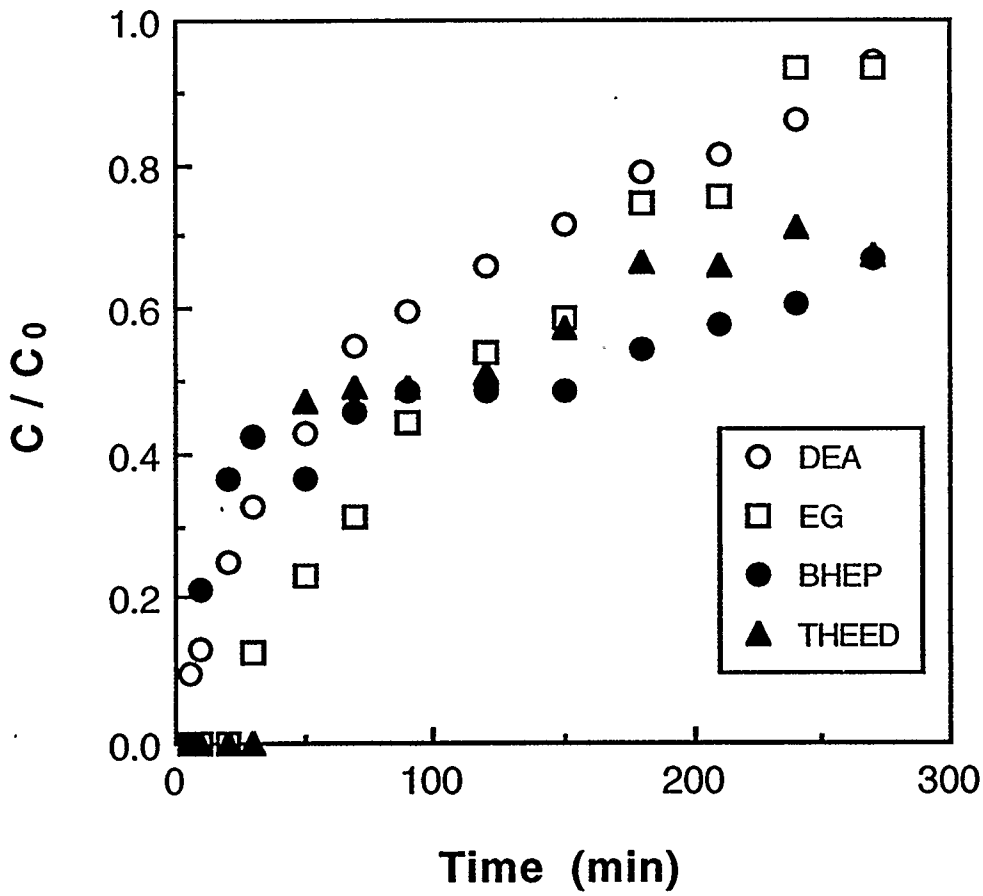


Figure 4.39 Dimensionless concentrations of DEA and its degradation products as functions of time (Resin : Amberlyst A-27, Flowrate : 1.1 mL/min.)

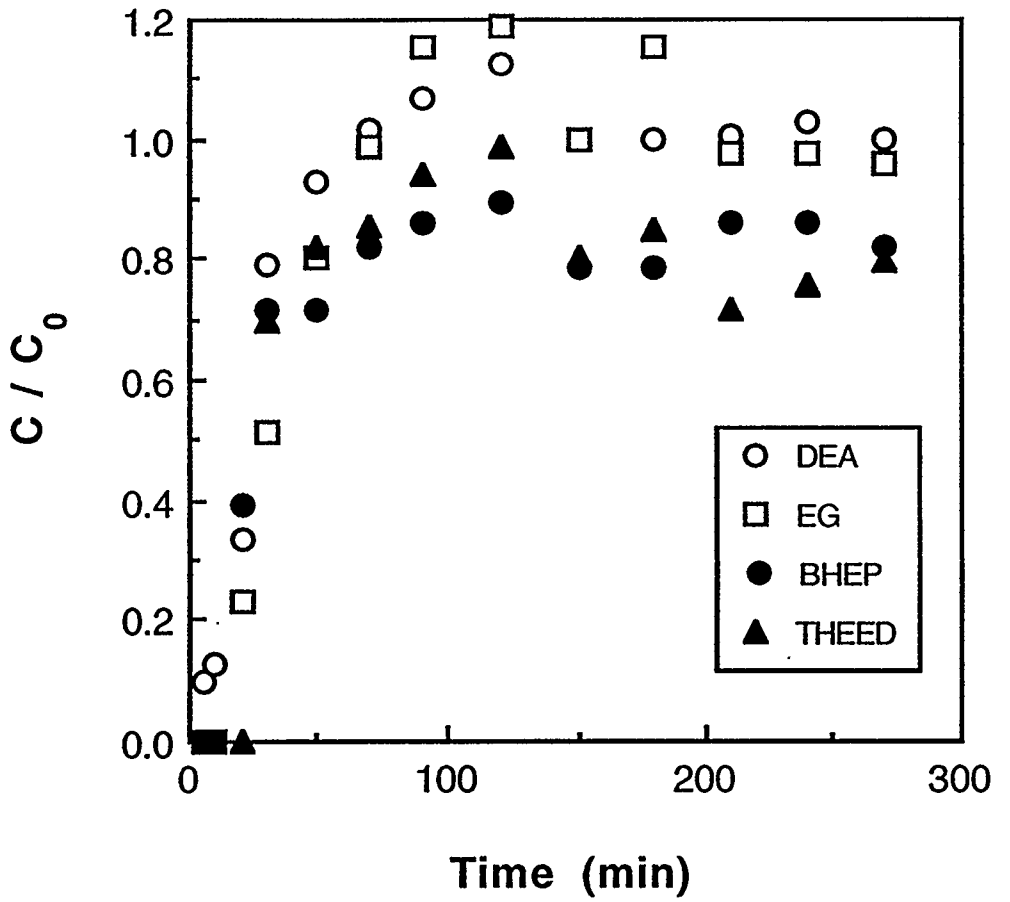


Figure 4.40 Dimensionless concentrations of DEA and its degradation products as functions of time (Resin : Amberlyst A-27, Flowrate : 7.7 mL/min.)

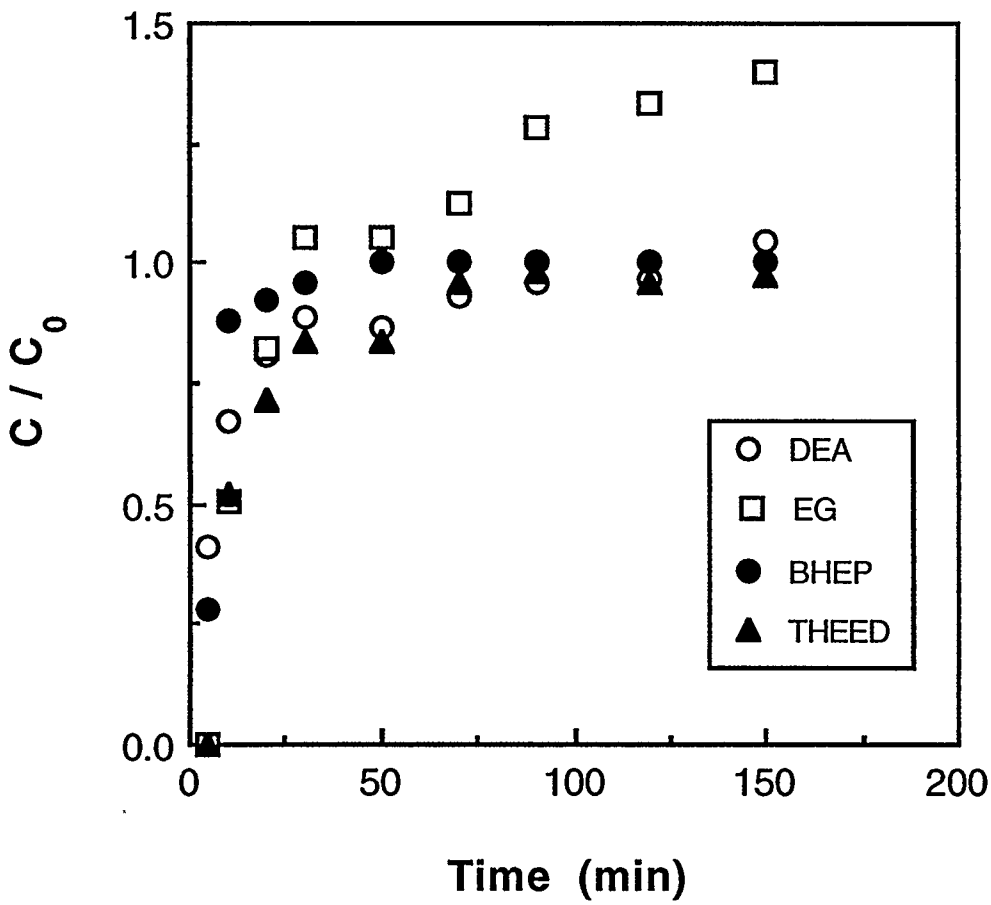


Figure 4.41 Dimensionless concentrations of DEA and its degradation products as functions of time (Resin : Amberlyst A-27, Flowrate : 14.9 mL/min.)

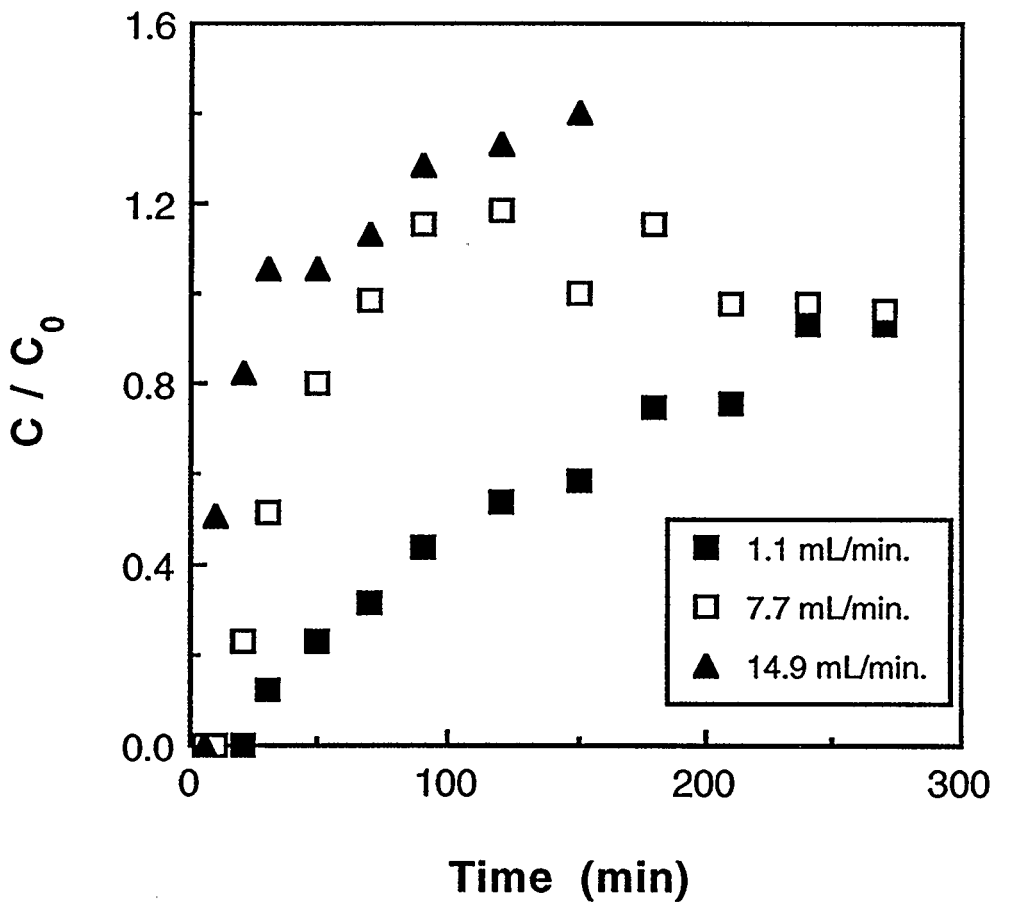


Figure 4.42 Dimensionless EG concentration as a function of time and flowrate (Resin : Amberlyst A-27)

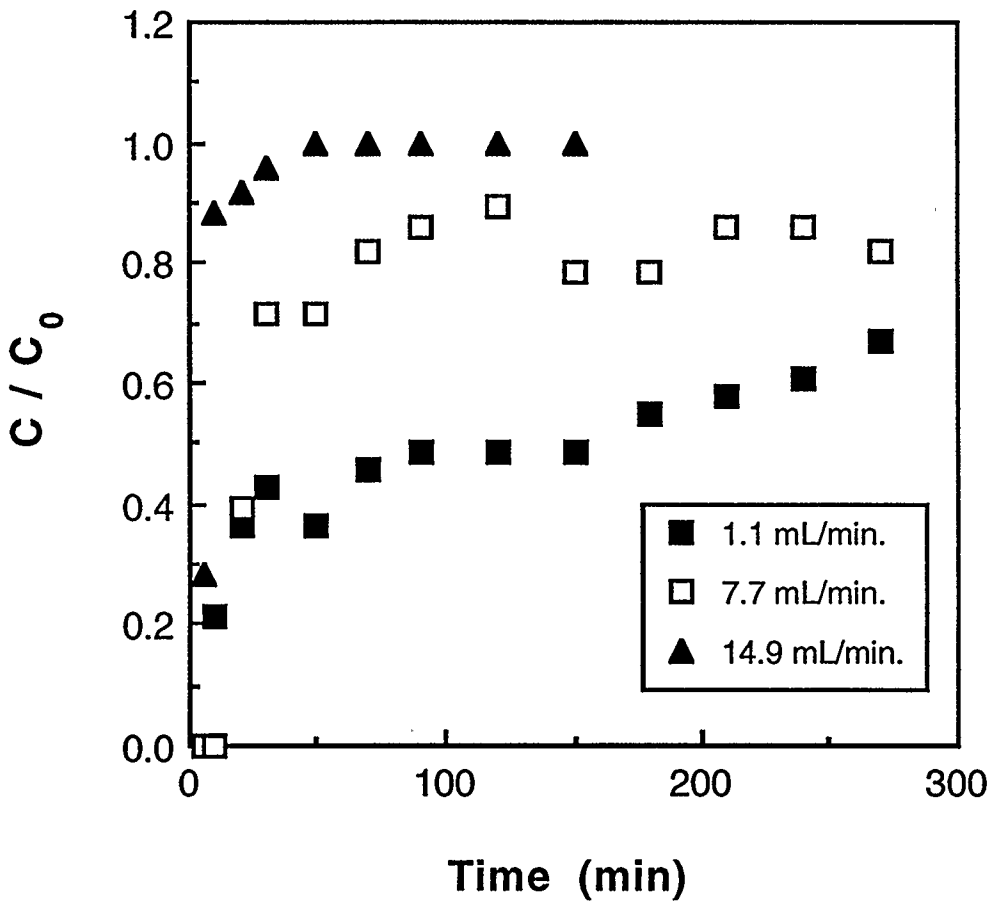


Figure 4.43 Dimensionless BHEP concentration as a function of time and flowrate (Resin : Amberlyst A-27)

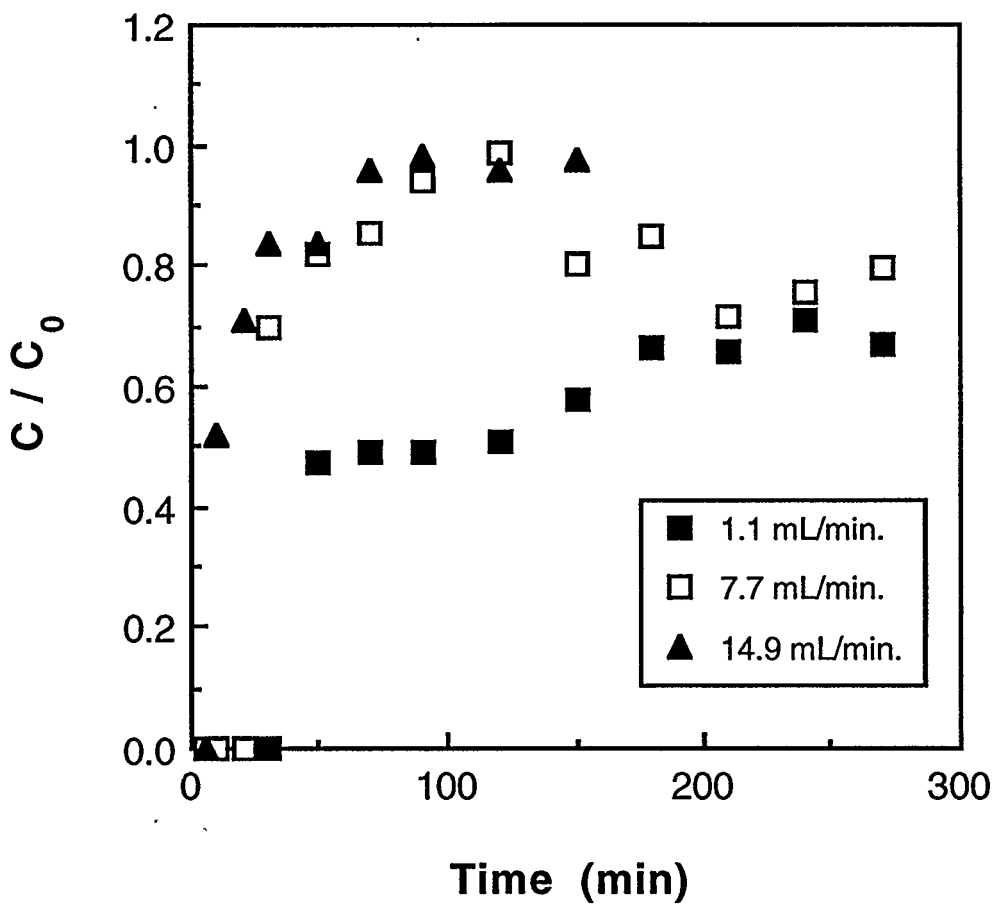


Figure 4.44 Dimensionless THEED concentration as a function of time and flowrate (Resin : Amberlyst A-27)

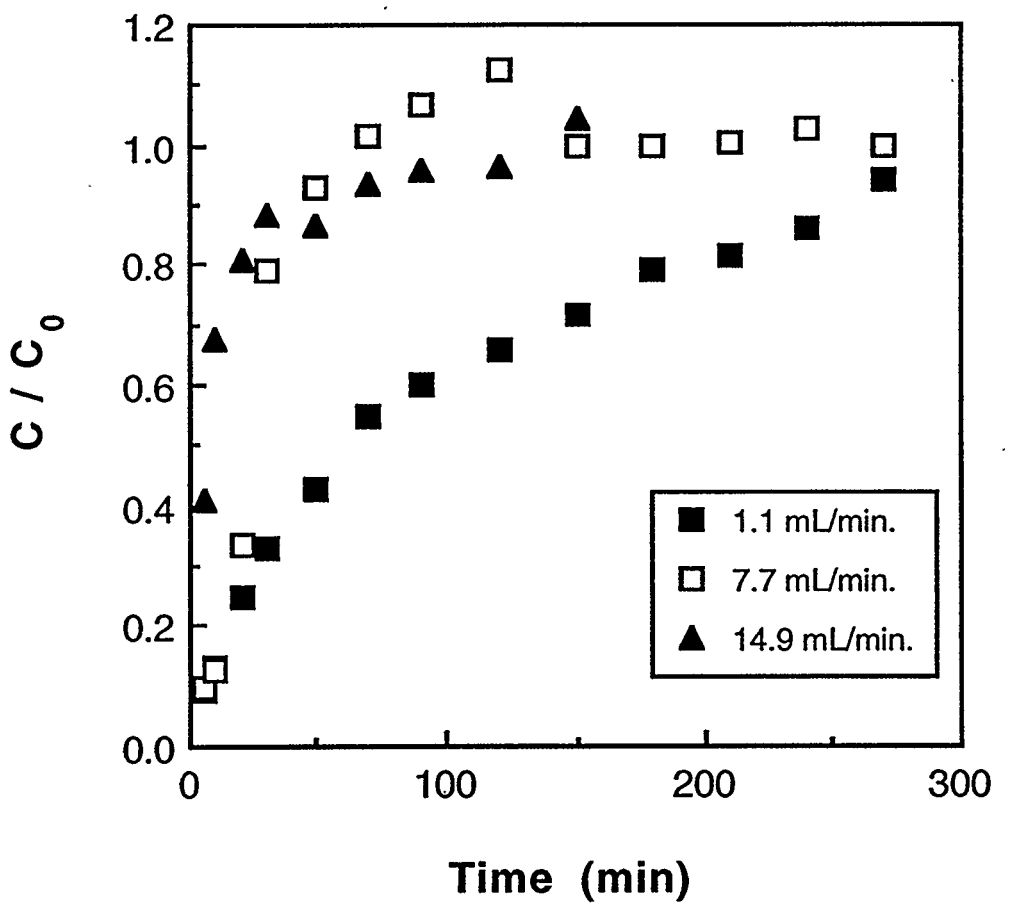


Figure 4.45 Dimensionless DEA concentration as a function of time and flowrate (Resin : Amberlyst A-27)

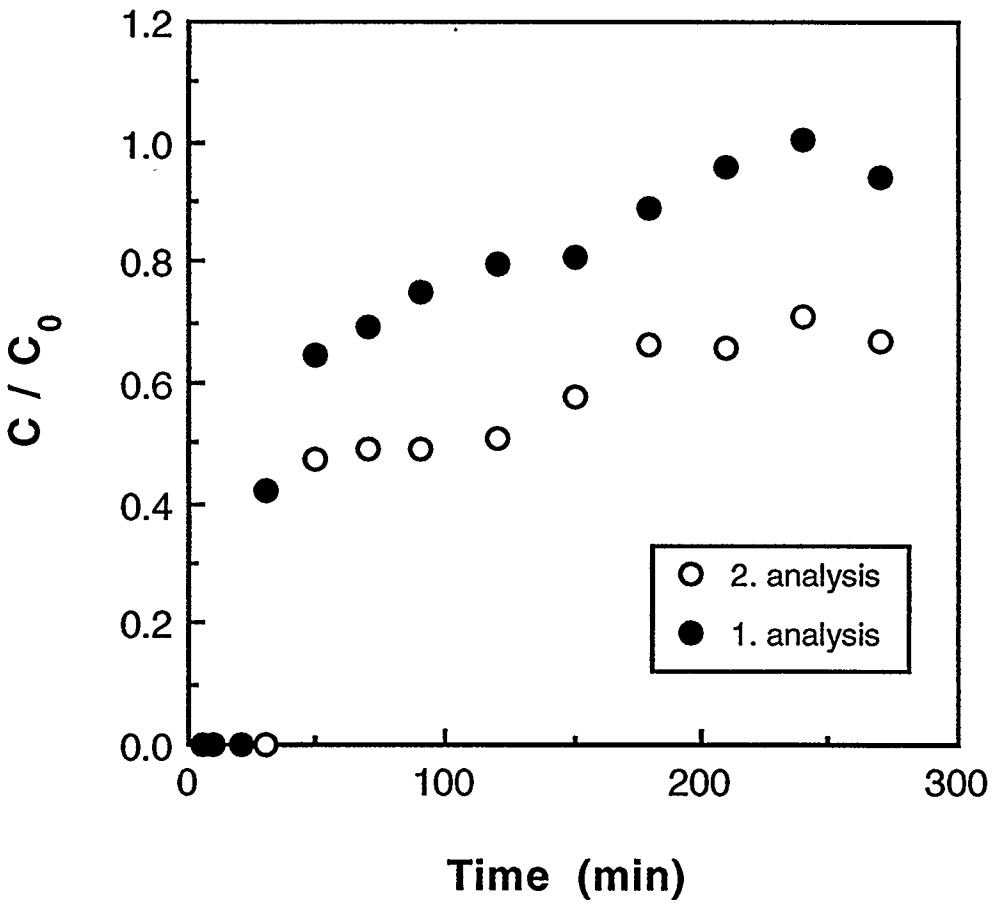


Figure 4.46 Comparison of the dimensionless THEED concentration curves resulted from analyses at two different times (Resin : Amberlyst A-27, Flowrate : 1.1 mL/min.)

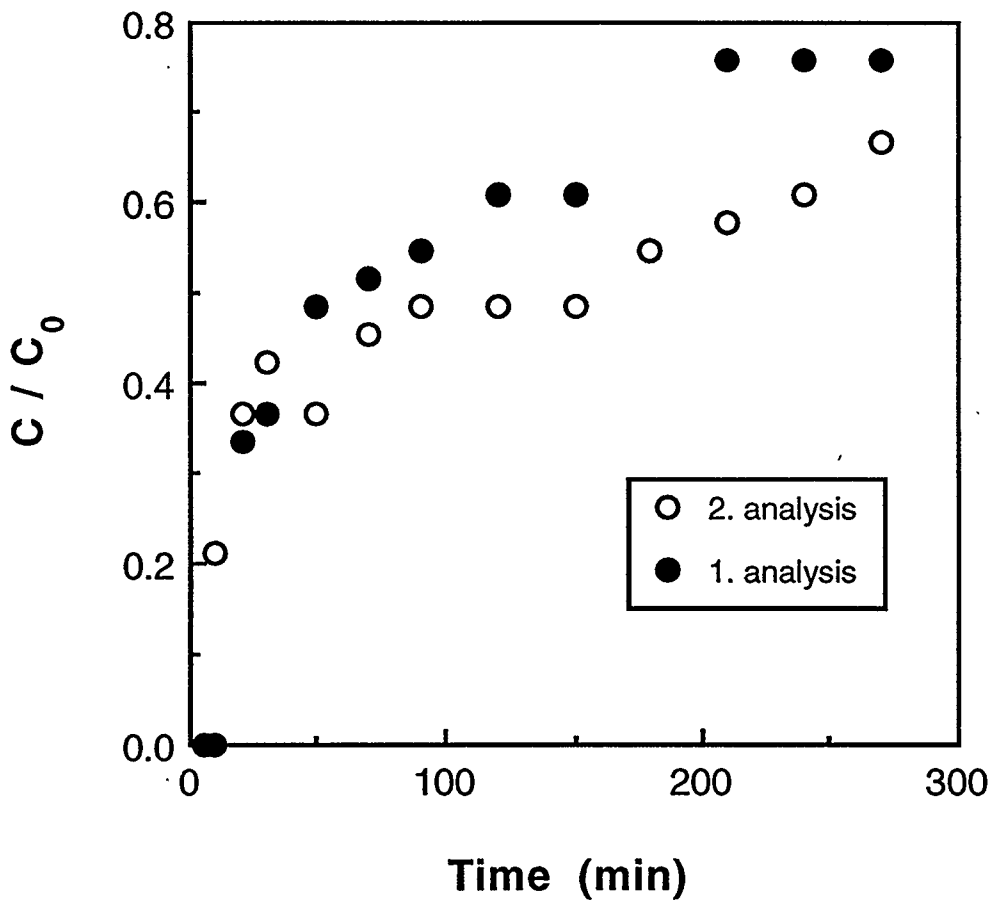


Figure 4.47 Comparison of the dimensionless BHEP concentration curves resulted from analyses at two different times (Resin : Amberlyst A-27, Flowrate : 1.1 mL/min.)

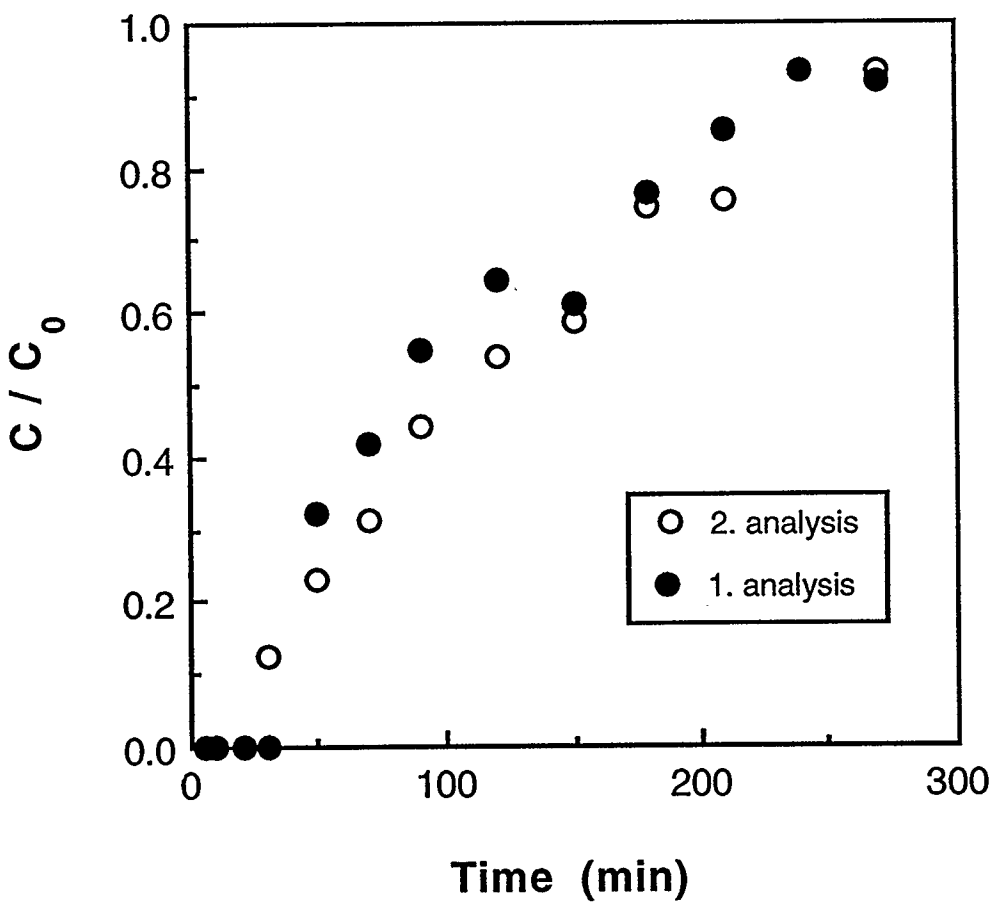


Figure 4.48 Comparison of the dimensionless EG concentration curves resulted from analyses at two different times (Resin : Amberlyst A-27, Flowrate : 1.1 mL/min.)

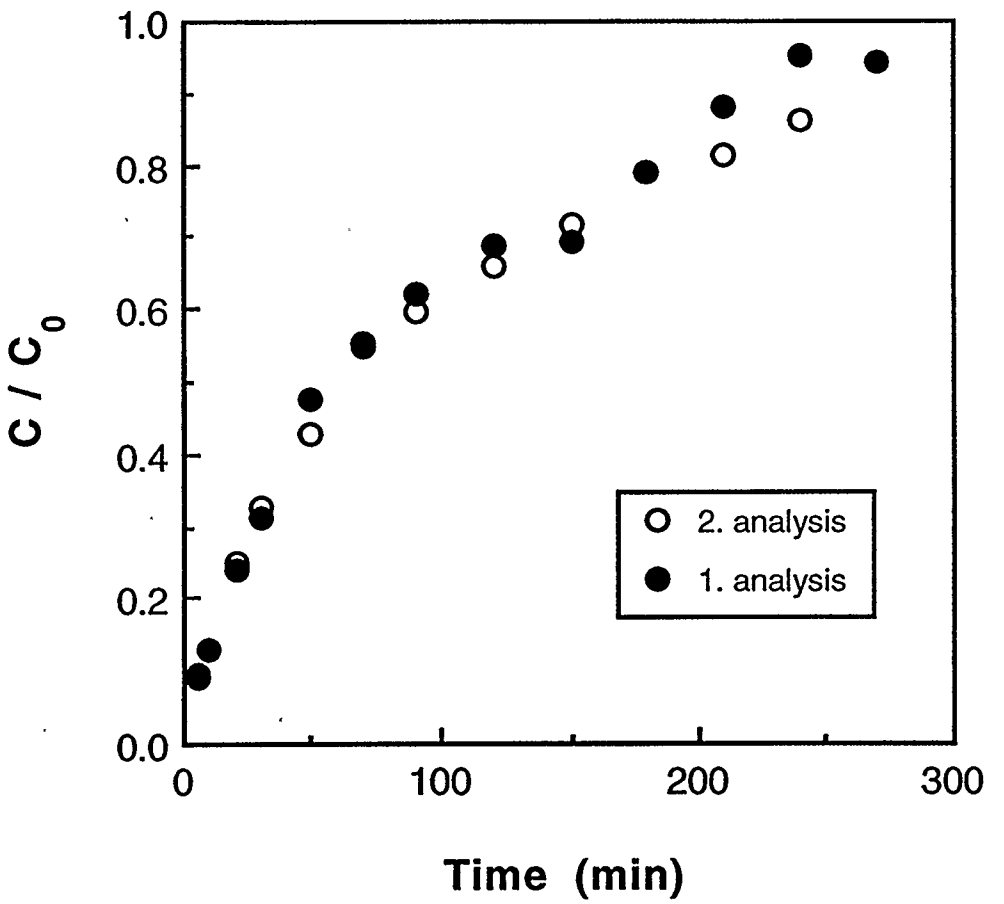


Figure 4.49 Comparison of the dimensionless DEA concentration curves resulted from analyses at two different times (Resin : Amberlyst A-27, Flowrate : 1.1 mL/min.)

the concentrations of the degradation products might be due to the continuing reactions after the samples were collected. Therefore, all the collected samples were re-analyzed. Some samples were analyzed for a third time and no concentration changes were detected. Hence, it was concluded that the samples became stable and all the results were based on the latest analysis of the samples.

It was planned to carry out similar experiments using another kind of basic ion-exchange resin. Amberlite IRA-400(OH) was chosen as the resin and one column experiment was carried out at a flowrate of 7.7 mL/min. The resin was left in the column overnight after the experiment as was done in the previous experiments. However, the column was found broken the next morning due to the swelling of the resin bed. The difference in the expansion capacity of the two resins can be due to their different structures. The first kind of resin used was macroreticular and the later was gel-type. As a result, the experiments with the second resin could not have been completed. Figure 4-50 shows the concentrations of DEA and the degradation products as functions of time for the experiment carried out with Amberlite IRA-400(OH) before column breakage. The two resins, Amberlyst A-27 and Amberlite IRA-400(OH), are compared in Figures 4.51-4.54 which show the concentrations of EG, BHEP, THEED and DEA plotted versus time. It can be seen that passing the solution through Amberlite IRA-400(OH) causes a higher decrease in the concentrations of all the compounds. This means that it has a higher capacity than Amberlyst A-27.

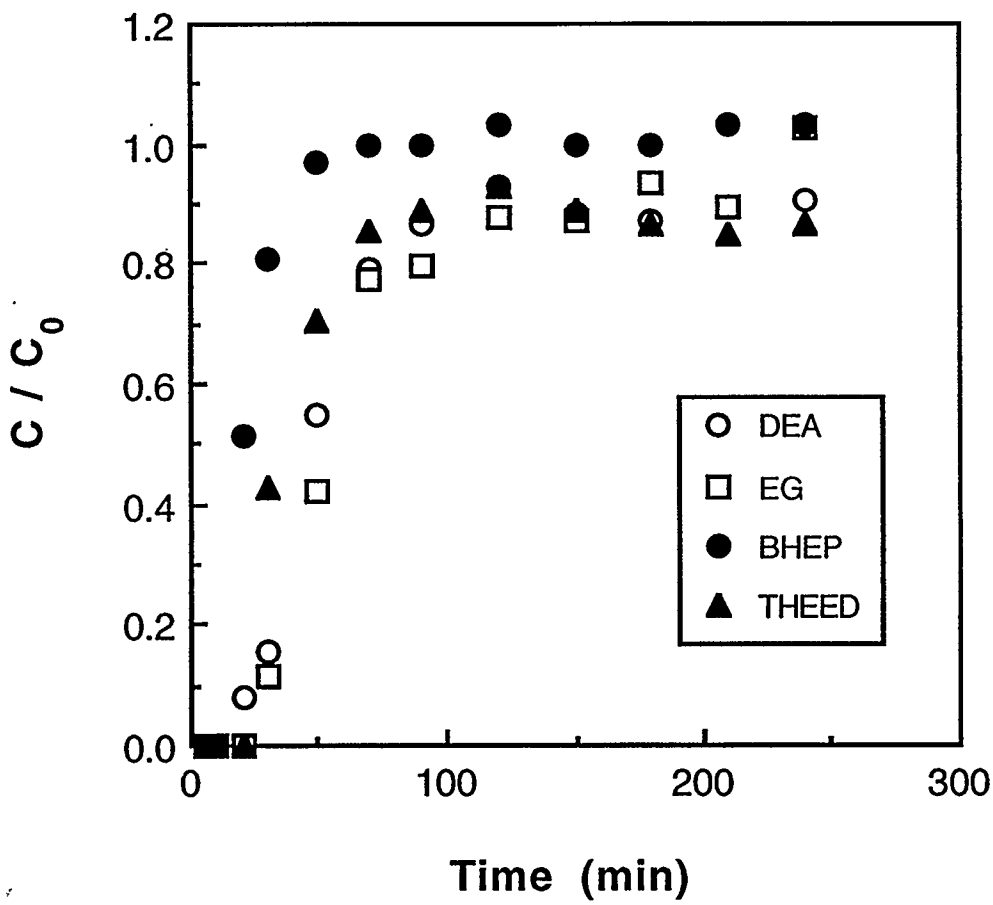


Figure 4.50 Dimensionless concentrations of DEA and its degradation products as functions of time
(Resin : Amberlite IRA-400(OH), Flowrate : 7.7 mL/min.)

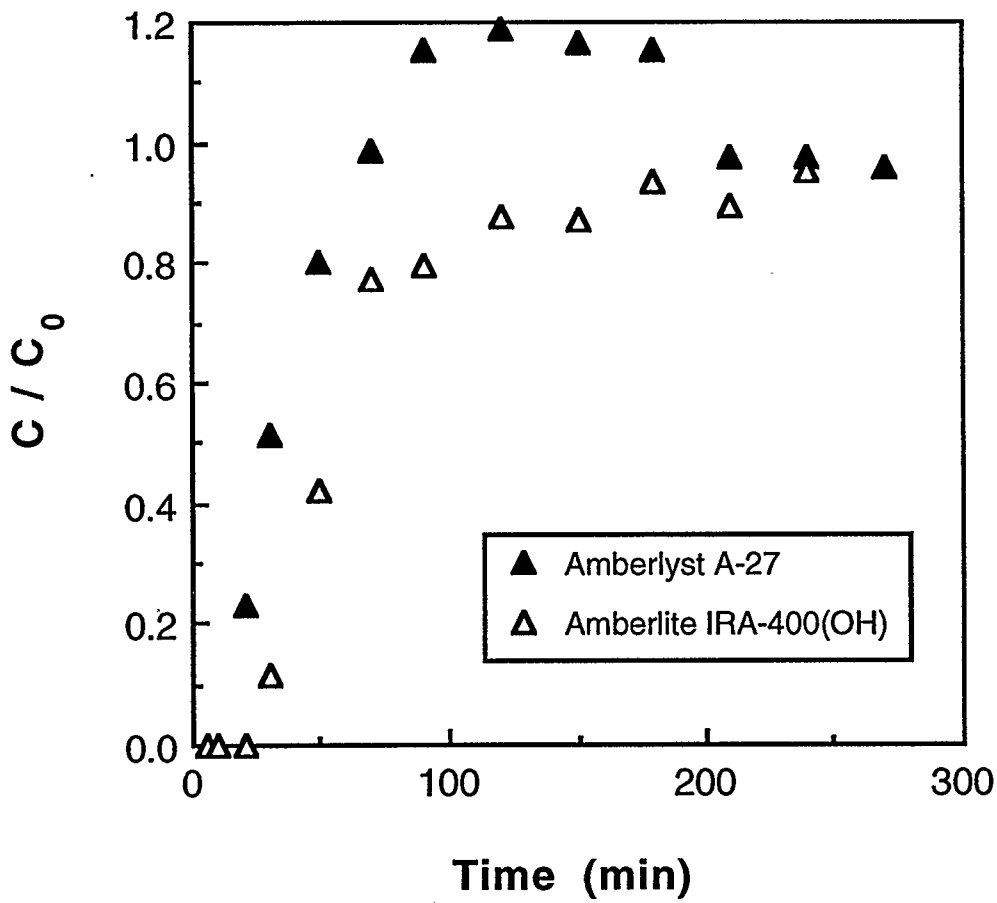


Figure 4.51 Comparison of the dimensionless EG concentration curves for two different resins (Flowrate : 7.7 mL/min.)

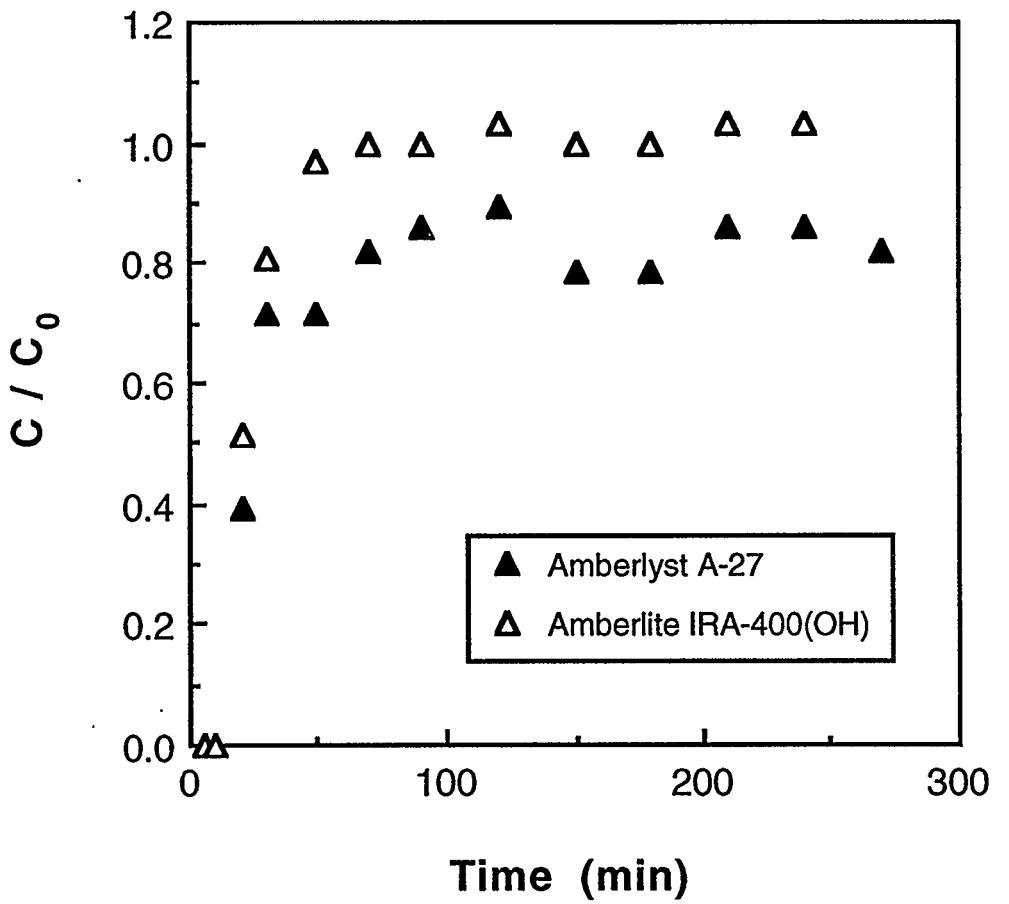


Figure 4.52 Comparison of the dimensionless BHEP concentration curves for two different resins (Flowrate : 7.7 mL/min.)

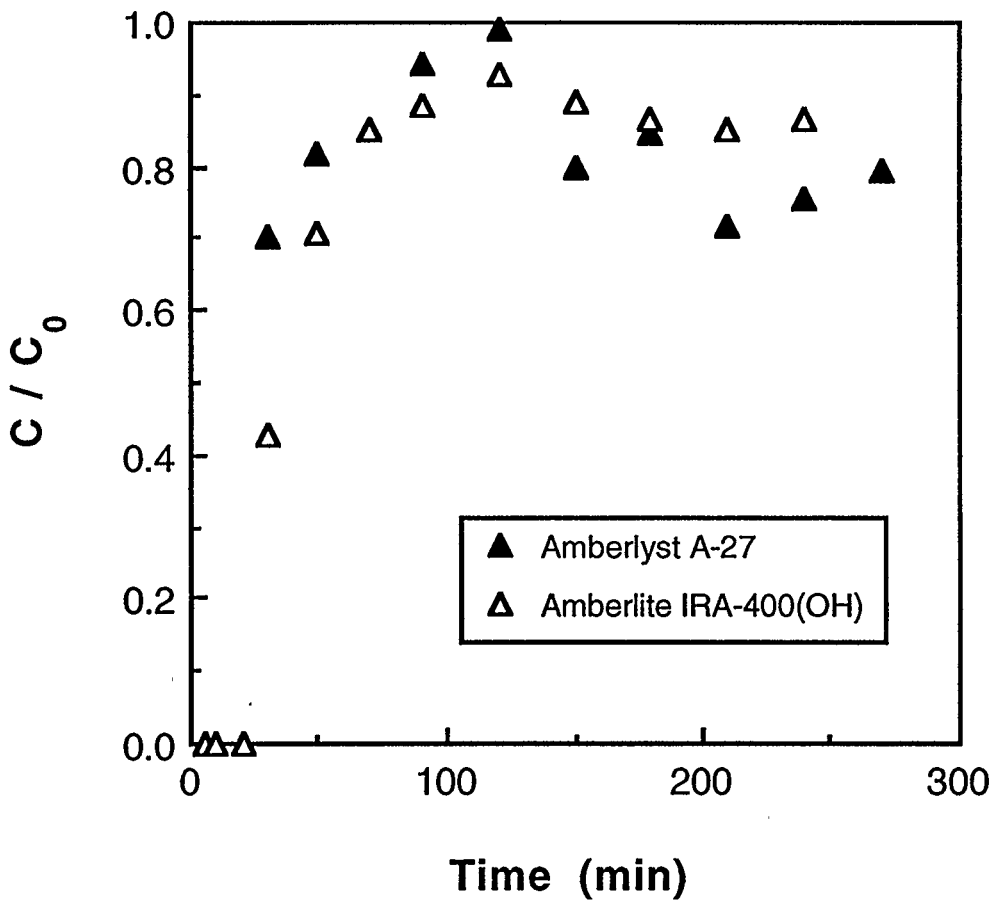


Figure 4.53 Comparison of the dimensionless THEED concentration curves for two different resins (Flowrate : 7.7 mL/min.)

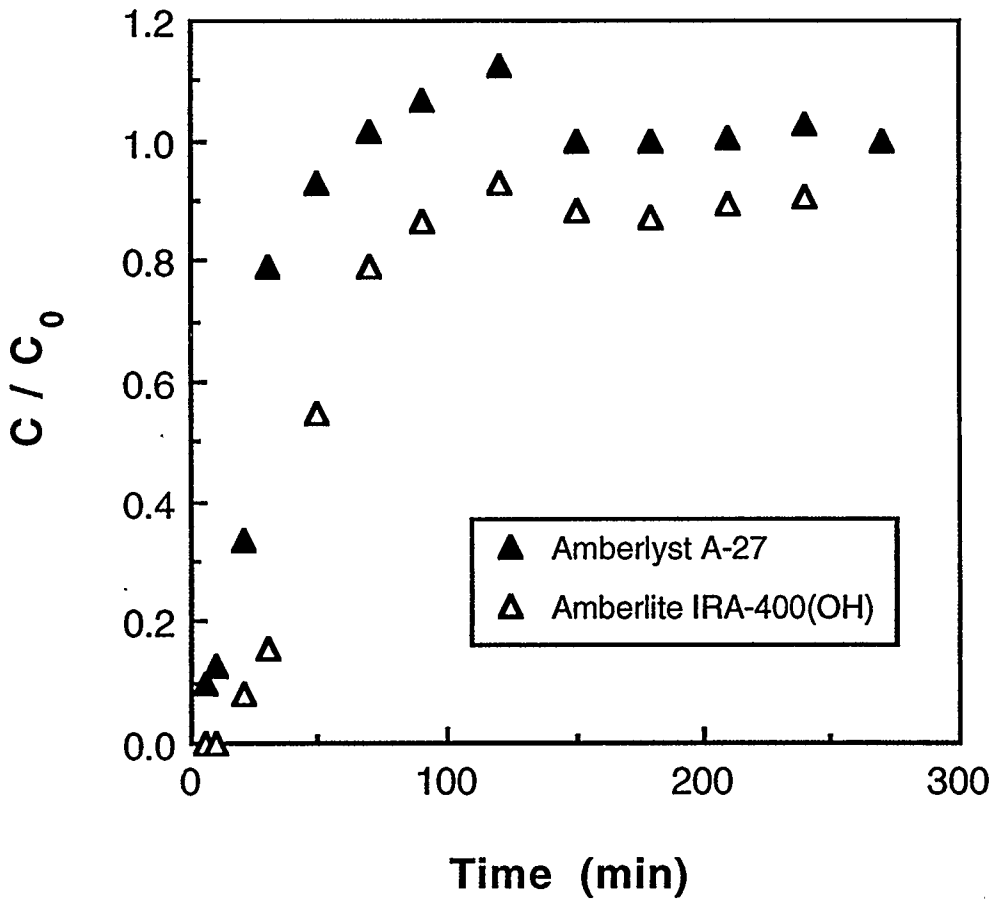


Figure 4.54 Comparison of the dimensionless DEA concentration curves for two different resins (Flowrate : 7.7 mL/min.)

CHAPTER 5

KINETIC MODEL FOR MIXED-SOLVENT DEGRADATION

Several kinetic models have been presented for the degradation of DEA and MDEA [17,18,40,41]. The degradation reactions are known to be extremely complex, involving several equilibrium, parallel and series reactions. The degradation of a mixed-solvent which is an aqueous mixture of MDEA and DEA is more complex and harder to describe. In the present study, an attempt was made to develop an overall kinetic model that would predict, quantitatively, the degradation of a mixed-solvent (50%MDEA-10%DEA) and the production of its major degradation compounds.

5.1 SIMPLIFIED DEGRADATION MECHANISM

Although many degradation products were detected as a result of the mixed-solvent degradation, the major degradation compounds were identified to be EG, DMAE, BHEP, HEOD and THEED, as stated earlier in Chapter 4. It was also mentioned in Section 4.1.2 that the gas chromatographic technique, used for the analysis, was not sufficient in detecting MDEA and DEA separately. Therefore, any quantitative information could not be obtained about the concentrations of MDEA and DEA individually, but the overall degradation of the mixed-solvent was followed. EG and DMAE are known to be the degradation products of MDEA. On the other hand, BHEP, HEOD and THEED are produced by both DEA and MDEA, but data collected in this study do not allow the

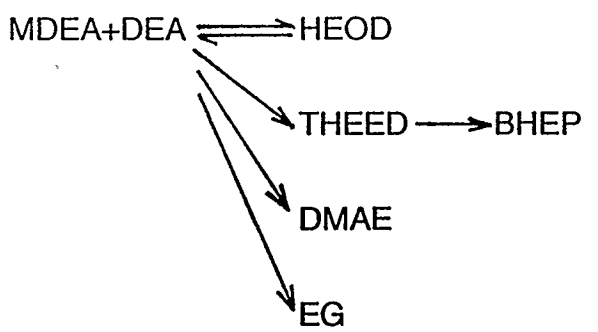
contribution of BHEP, HEOD and THEED from DEA and MDEA to be determined separately. Hence, a detailed mechanism describing the degradation of DEA and MDEA separately cannot be proposed based on the collected data, due to lack of information.

The reaction mechanisms proposed by Kennard [40] for DEA degradation and by Chakma [18] for MDEA degradation were taken as basis and combined to describe the mixed-solvent degradation. Kennard stated that HEOD was formed directly from DEA by a reversible reaction. It was also stated in his study that THEED was an intermediate product produced by DEA, and BHEP was a final degradation product produced by THEED. Although he suggested that an equilibrium existed between DEA and HEOD, Kennard considered the production of HEOD as an irreversible reaction to simplify the model. It was claimed that this simplification could have been justified since, at low temperatures the equilibrium between DEA and HEOD was established slowly and the plots of concentration of HEOD versus time did not level off. However, this could be due to the shortness of the time that the experiments were conducted in his study since a maximum could be observed in HEOD concentration versus time plots (see Section 4.1.2) in the present study.

MDEA degradation mechanism was studied and a complex kinetic model was proposed by Chakma [18]. Eleven major degradation products were taken into account in his model. DMAE was reported to be the first compound to be formed and followed by HMP (N-(hydroxyethyl) methyl piperazine) and TMA (Trimethyl amine). DMP (1,4 dimethyl piperazine), TEA (Triethanolamine), and TEHEED (Tetra-(hydroxyethyl) ethylenediamine) were the other degradation

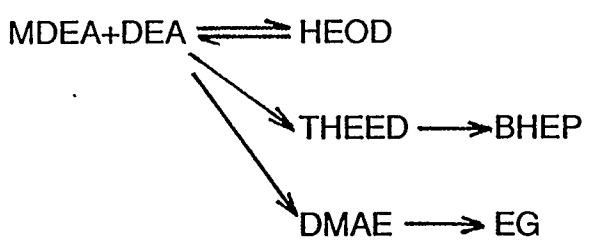
products included in the model. In his study, HEOD, THEED and BHEP were postulated to be produced by DEA via the same mechanism presented by Kennard [40]. DEA was believed to be formed from MDEA and the production of HEOD was assumed to be irreversible. DMAE was stated to come directly from MDEA and was suspected to be an intermediate product since its concentration initially increased and then decreased with time. Chakma carried out some degradation experiments with DMAE since it was observed to be the first degradation compound to be formed and also an intermediate compound. In his study, DMAE was degraded with CO_2 and it was concluded that EG was at least partly formed from DMAE.

All the information obtained from the two reaction mechanisms for DEA and MDEA degradation that are described above were combined to develop a mechanism for mixed-solvent degradation which would fit the experimental data. Although DMAE was stated to be an intermediate degradation product by Chakma [18], since its concentration constantly increases during a degradation run (see Figure 4.13) as opposed to the trend observed in his work, it seems to be an end product. Therefore, all the EG can be said to come from MDEA. Also, when the plot of HEOD concentration as a function of time is examined (see Figure 4.15), it can be seen that it passes through a maximum indicating that it is produced by a reversible reaction. Taking these observations into account, first the following reaction mechanism was formulated (see Appendix B for the chemical structures of the degradation compounds):



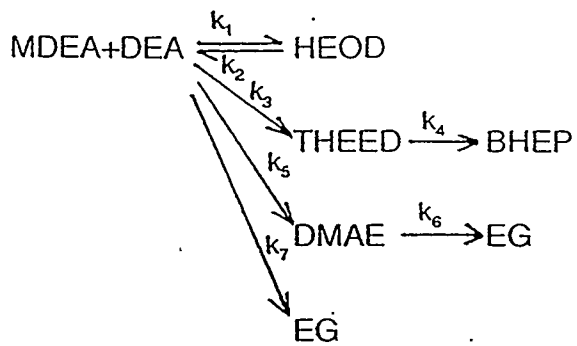
(5.1)

However, although DMAE concentration predictions based on this mechanism were in agreement with the experimental data, the predicted EG concentrations were much lower than the actual. These predictions are shown in the following section. Hence, based on the study by Chakma [18] showing that EG was at least in part formed from DMAE, the mechanism was changed as follows to see the effect:



(5.2)

This time, although EG concentration predictions fitted the experimental data, predicted DMAE concentrations showed a different trend than the actual. Therefore, it was decided to combine the two mechanisms shown by Equations 5.1 and 5.2. Finally, the following mechanism was developed to describe the degradation of the mixed-solvent:



(5.3)

5.2 KINETIC MODELING

A simple kinetic model that would describe the overall mixed-solvent degradation was developed, based on the reaction mechanism presented in the previous section (Equation 5.3). The following rate equations can be written depending on the proposed mechanism:

$$\frac{d[MDEA+DEA]}{dt} = -(k_3+k_5+k_7)[MDEA+DEA] - k_1[MDEA+DEA]^2 + k_2[HEOD]^2 \quad (5.4)$$

$$\frac{d[HEOD]}{dt} = k_1[MDEA+DEA]^2 - k_2[HEOD]^2 \quad (5.5)$$

$$\frac{d[THEED]}{dt} = k_3[MDEA+DEA] - k_4[THEED] \quad (5.6)$$

$$\frac{d[BHEP]}{dt} = k_4[THEED] \quad (5.7)$$

$$\frac{d[DMAE]}{dt} = k_5[MDEA+DEA] - k_6[DMAE] \quad (5.8)$$

$$\frac{d[EG]}{dt} = k_6[DMAE] + k_7[MDEA+DEA] \quad (5.9)$$

As can be seen in Equations 5.4 and 5.5, the forward and reverse reactions between [MDEA+DEA] and [HEOD] are accepted to be second order. Different magnitudes of reaction orders were tried and second order was

observed to be giving comparatively better HEOD concentration predictions with respect to the experimental data.

The rate constants were estimated and the concentrations of MDEA+DEA and the degradation products were calculated with a computer program using routines obtained from IMSL FORTRAN Libraries 2.0 that are installed in University of Calgary computer system. The IMSL routine IVPAG was used to solve the differential equations 5-4 to 5.9 as an-initial value problem applying backward differentiation formula, also called Gear's method. The IMSL optimization routine called BCLSJ which solves a nonlinear least squares problem subject to bounds on the variables using a modified Levenberg-Marquardt algorithm was utilized to estimate the rate constants.

The rate constants were calculated for four different temperatures ranging from 130 to 160 °C. The dependency of 'k' on temperature is known to follow Arrhenius equation which suggests that reaction rate rises exponentially with temperature. Assuming the applicability of Arrhenius equation to degradation reactions, the rate constants were plotted as functions of temperature and the following expressions were obtained:

$$k_1 = 3.76 \times 10^{-7} \exp \{ 26273 / RT \} \tag{5.10}$$

$$k_2 = 2.03 \exp \{ - 11004 / RT \} \tag{5.11}$$

$$k_3 = 3.20 \times 10^{14} \exp \{ - 146301 / RT \} \tag{5.12}$$

$$k_4 = 1.40 \times 10^{11} \exp \{ - 109254 / RT \} \tag{5.13}$$

$$k_5 = 2.98 \times 10^{10} \exp \{ - 111408 / RT \} \tag{5.14}$$

$$k_6 = 1.46 \times 10^4 \exp \{ - 53608 / RT \} \quad (5.15)$$

$$k_7 = 2.77 \times 10^{39} \exp \{ - 355947 / RT \} \quad (5.16)$$

The activation energy values in Equations 5.11-5.16 range from 11 to 356 kJ / mol depending on the temperature sensitivity of the reactions. On the other hand, the activation energy, which is usually defined as the minimum energy that must be possessed by the reacting molecules for the reaction to occur, has a negative value in Equation 5.10. Although the Arrhenius equation has been verified empirically to give the temperature behaviour of most reaction rate constants over fairly large temperature ranges, it is limited to elementary processes. Likewise, it is not valid if the reaction mechanism changes with temperature or thermal resistances are affecting the reactions. The activation energy, in the expression for k_1 (Equation 5.10), which has a negative value belongs to the formation reaction of HEOD, as can be seen in equation 5.3. As discussed in Section 4.1.2.1, HEOD production rate has an inverse relationship with temperature. Also, it has been stated before that degradation reactions are not elementary but complex reactions involving several steps. Therefore, obtaining a negative activation energy for such a reaction is not surprising but leads to the conclusion that Arrhenius law is not suitable for describing the temperature dependency of the specific rate constant in this case.

5.3 MODEL PREDICTIONS

Three different reaction mechanisms have been proposed in Section 5.1 (see Equations 5.1-5.3). The only difference between them is related to the production of EG. In the first mechanism, EG is assumed to be produced only by

the mixed-solvent. In the second one, it is supposed to come from DMAE. The concentrations of the degradation products were predicted depending on both of the reaction mechanisms. Although no alteration was observed in the concentration trends of BHEP, HEOD and THEED; the change in mechanism had a significant effect on DMAE and EG concentrations. Figures 5.1 and 5.2 show the concentration predictions of DMAE and EG as functions of time according to the two different mechanisms. As can be seen in Figure 5.1, the mechanism proposed in Equation 5.1 fits the experimental data obtained for DMAE, but the other one deviates significantly. On the other hand, it can be seen in Figure 5.2 that the situation is just the opposite for EG. The mechanism given in Equation 5.2 which presumes EG coming from DMAE is in better agreement with the experimental data for EG. Therefore, the third mechanism, which is a combination of the first two as shown in Equation 5.3, has been accepted and used for the model predictions.

Figures 5.3-5.6 show the model predictions and experimental data as functions of time for MDEA+DEA at different temperatures. The model predictions can be said to be in good agreement with the experimental data for the mixed-solvent concentration.

Experimental and predicted DMAE concentrations are plotted versus time at different temperatures in Figure 5.7. The model predictions deviate from the actual DMAE concentrations with increasing time, since predicted DMAE concentrations level off while the experimental ones keep increasing. This implies that DMAE may not be an intermediate product as proposed by the mechanism as discussed earlier.

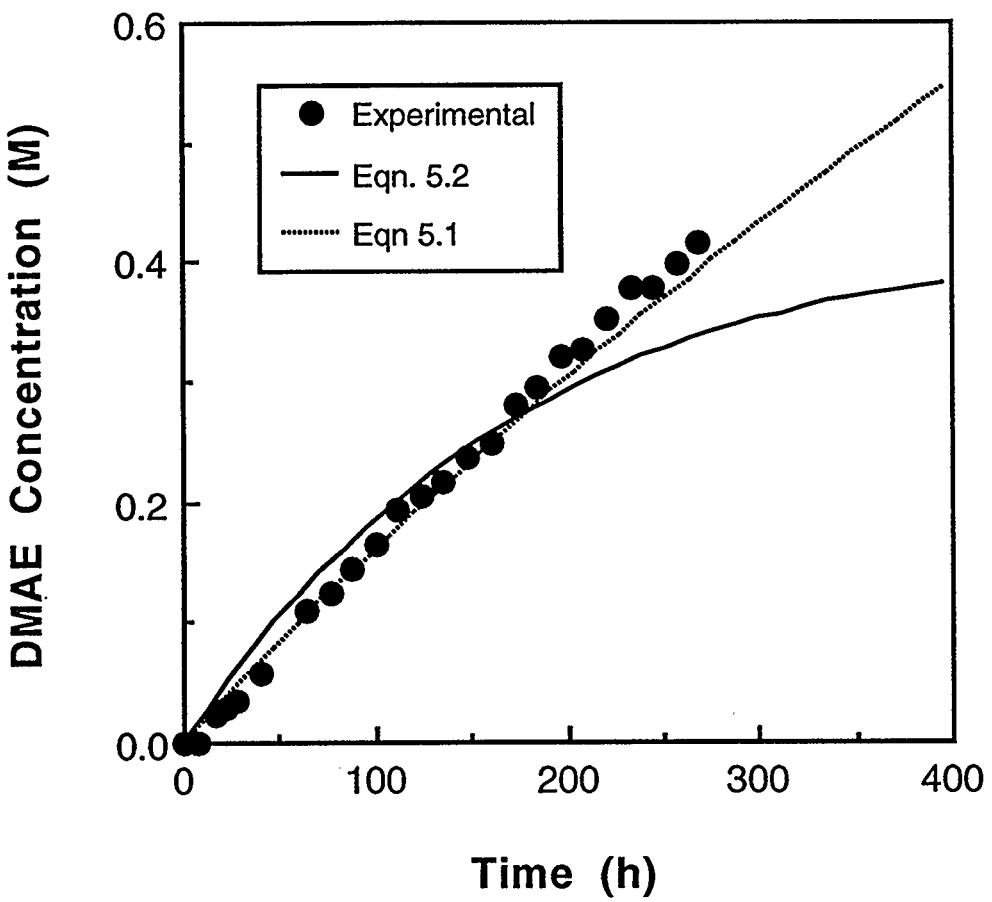


Figure 5.1 Comparison of the DMAE concentrations predicted by two different mechanisms with the experimental data (50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2, 150 °C)

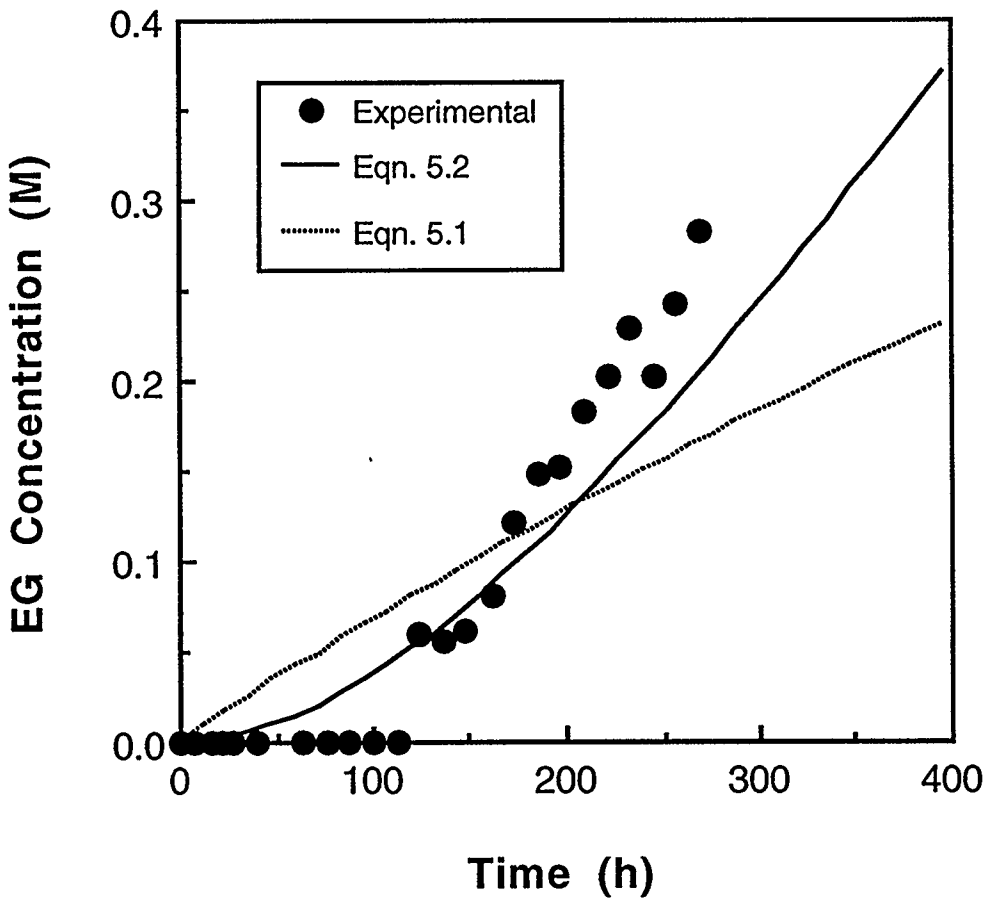


Figure 5.2 Comparison of the EG concentrations predicted by two different mechanisms with the experimental data (50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2, 150 °C)

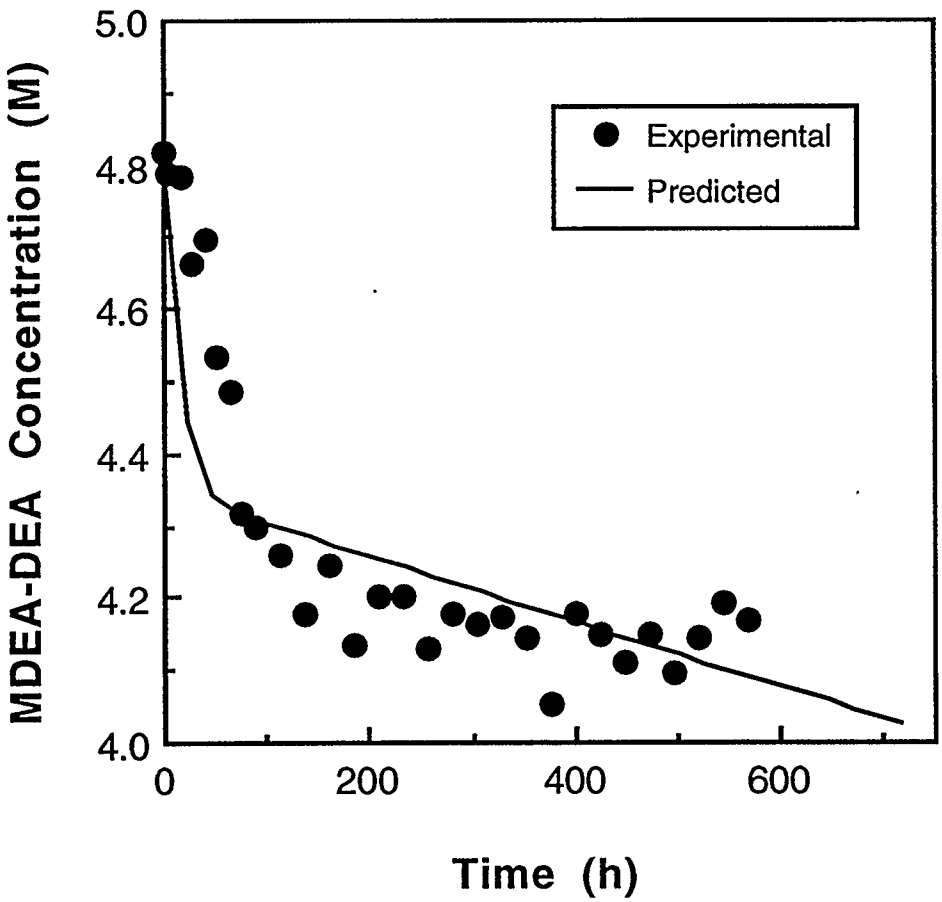


Figure 5.3 Experimental and predicted MDEA+DEA concentrations as functions of time at 130 °C
(50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

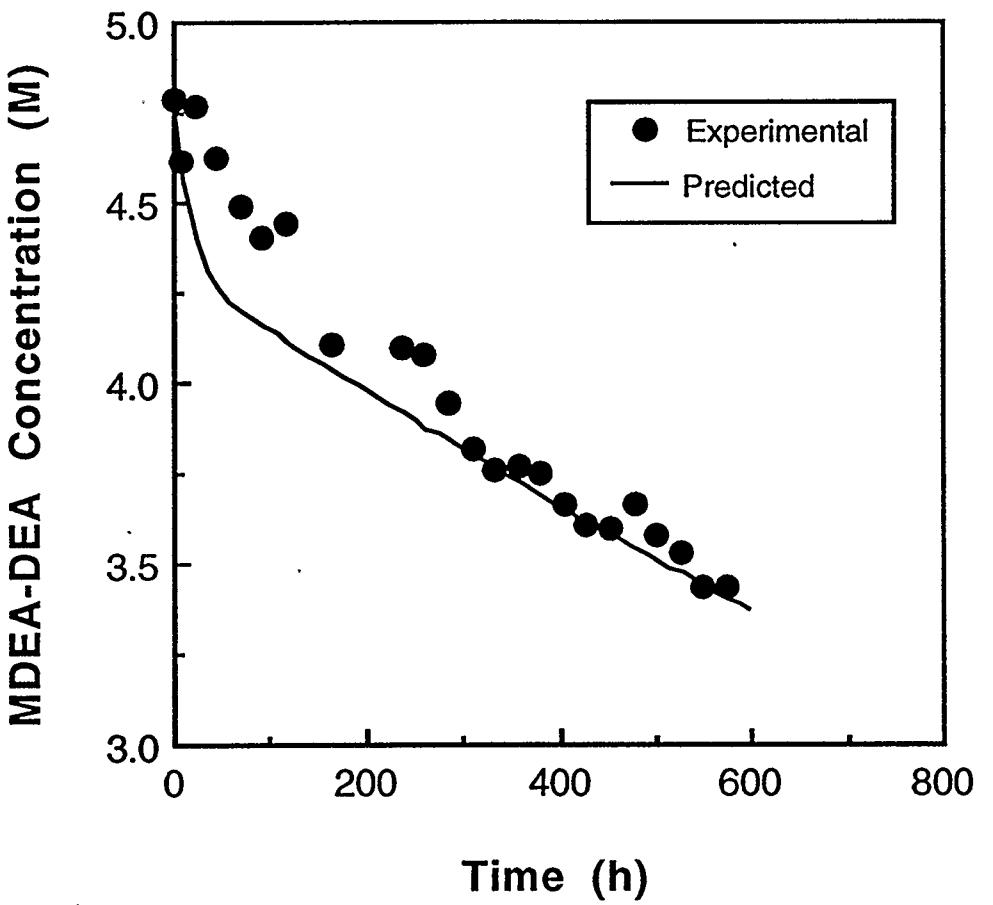


Figure 5.4 Experimental and predicted MDEA+DEA concentrations as functions of time at 140 °C
(50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

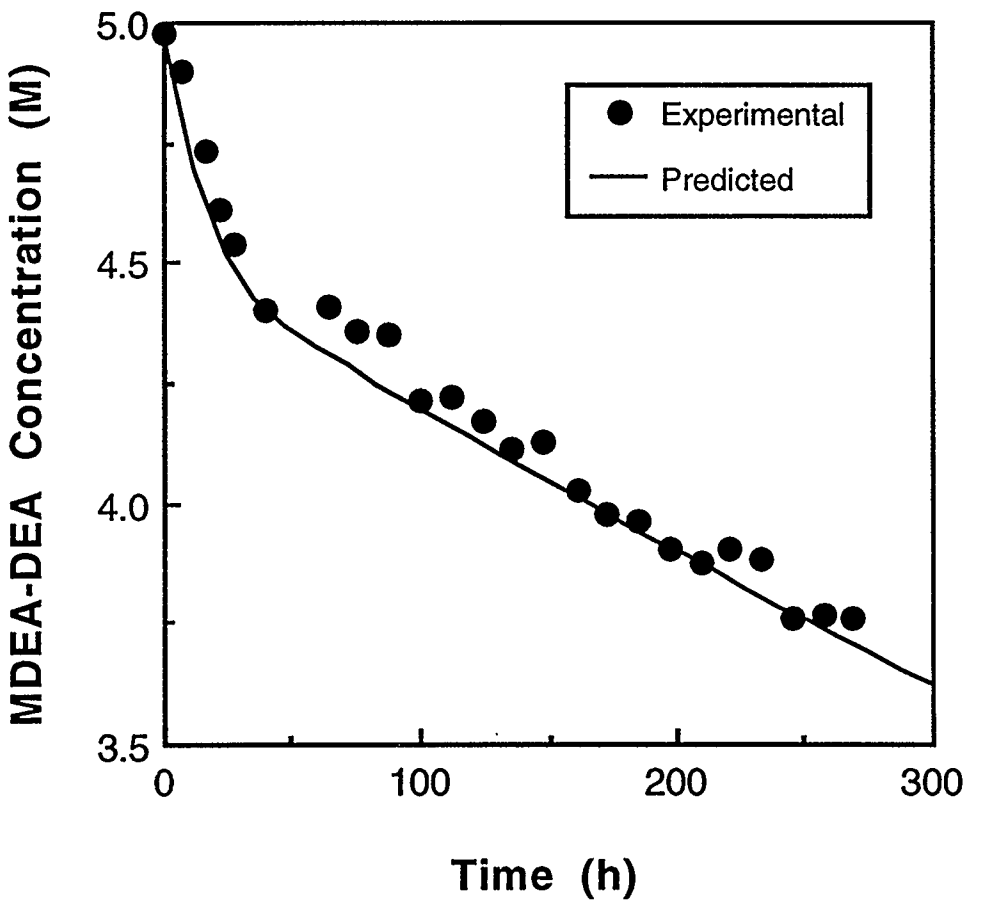


Figure 5.5 Experimental and predicted MDEA+DEA concentrations as functions of time at 150 °C
(50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

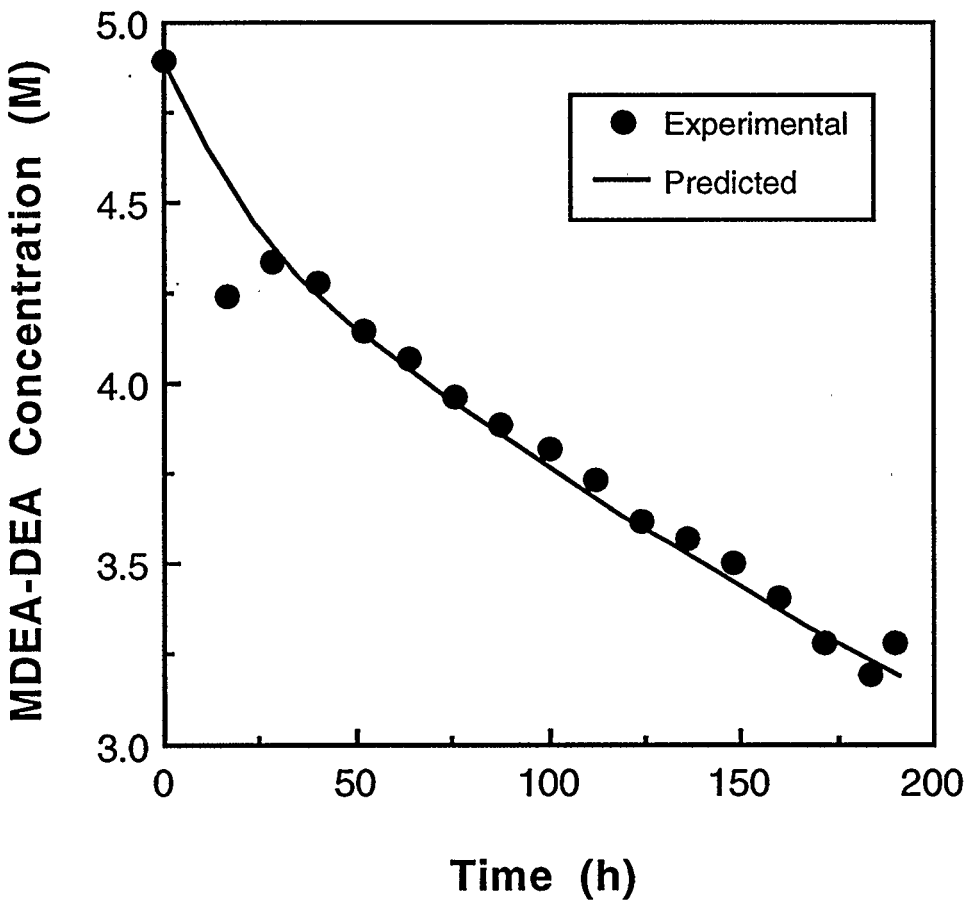


Figure 5.6 Experimental and predicted MDEA+DEA concentrations as functions of time at 160 °C
(50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

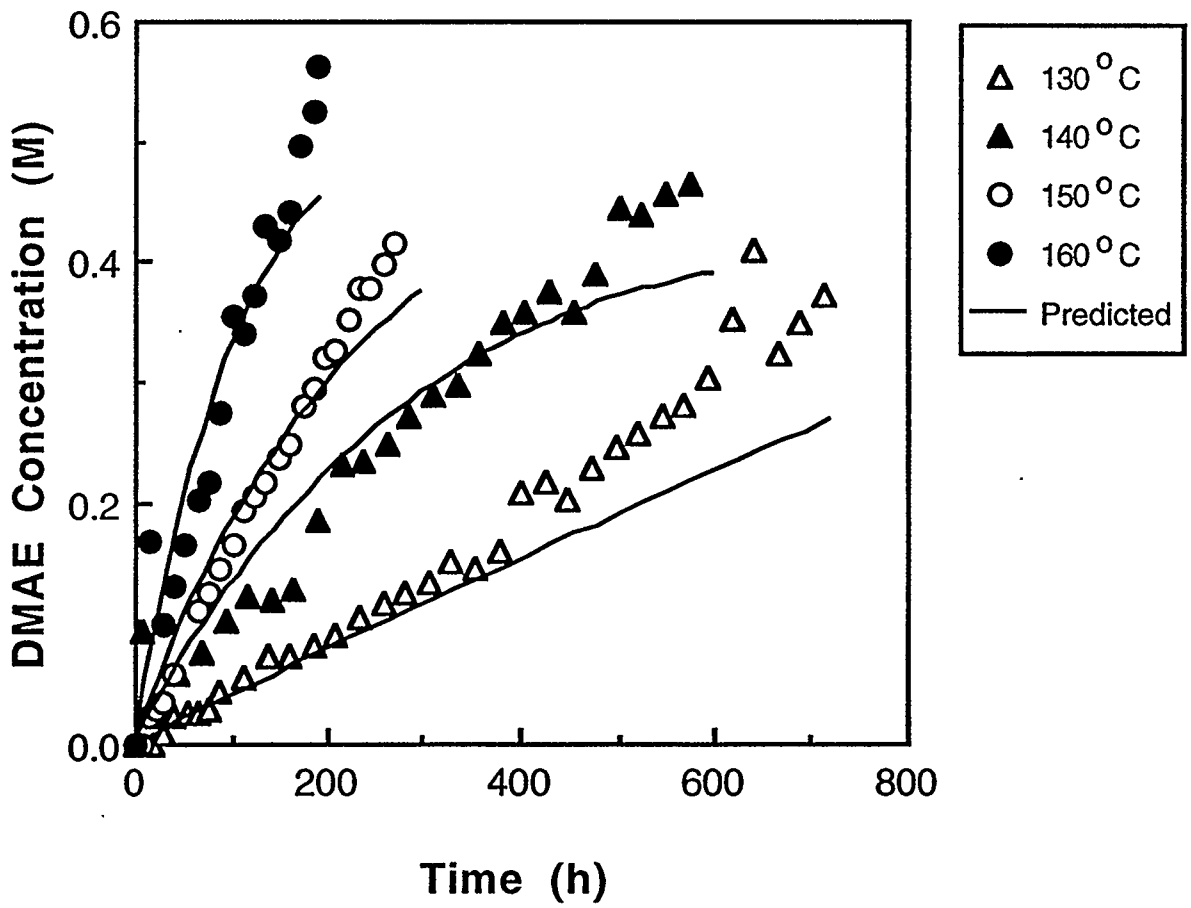


Figure 5.7 Experimental and predicted DMAE concentrations as functions of time and temperature (50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

Figure 5.8 shows the comparison of experimental and predicted EG concentrations at different temperatures. As can be seen, model predicts lower EG concentrations at lower temperatures, but the predictions fit the experimental data better at high temperatures.

Figures 5.9 and 5.10 show the actual and predicted THEED and BHEP concentrations as functions of time and temperature. The model predictions are lower than the experimental values at low temperatures as in the case of EG but the deviations are larger for THEED and BHEP than for EG.

The model predictions of HEOD concentration show a different trend from the experimental data as can be observed in Figure 5.11. The model predictions are much lower than the experimental values and level off with time while the experimental HEOD concentration reaches a maximum and then decreases, implying that it could be an intermediate product. This means that a different reaction mechanism than the suggested one exists for the HEOD production. Also, two different mechanisms may exist for the formation of HEOD from MDEA and DEA or the interactions between MDEA and DEA may change the mechanism. Another reason which is valid for the deviations of the model predictions from experimental data for all the degradation products is that while converting the GC peak areas to concentrations for MDEA+DEA peak, the calibration chart of MDEA was used since it was known that percentage of MDEA was much higher than DEA. However, this should not cause a significant divergence, since MDEA and DEA have similar calibration curves.

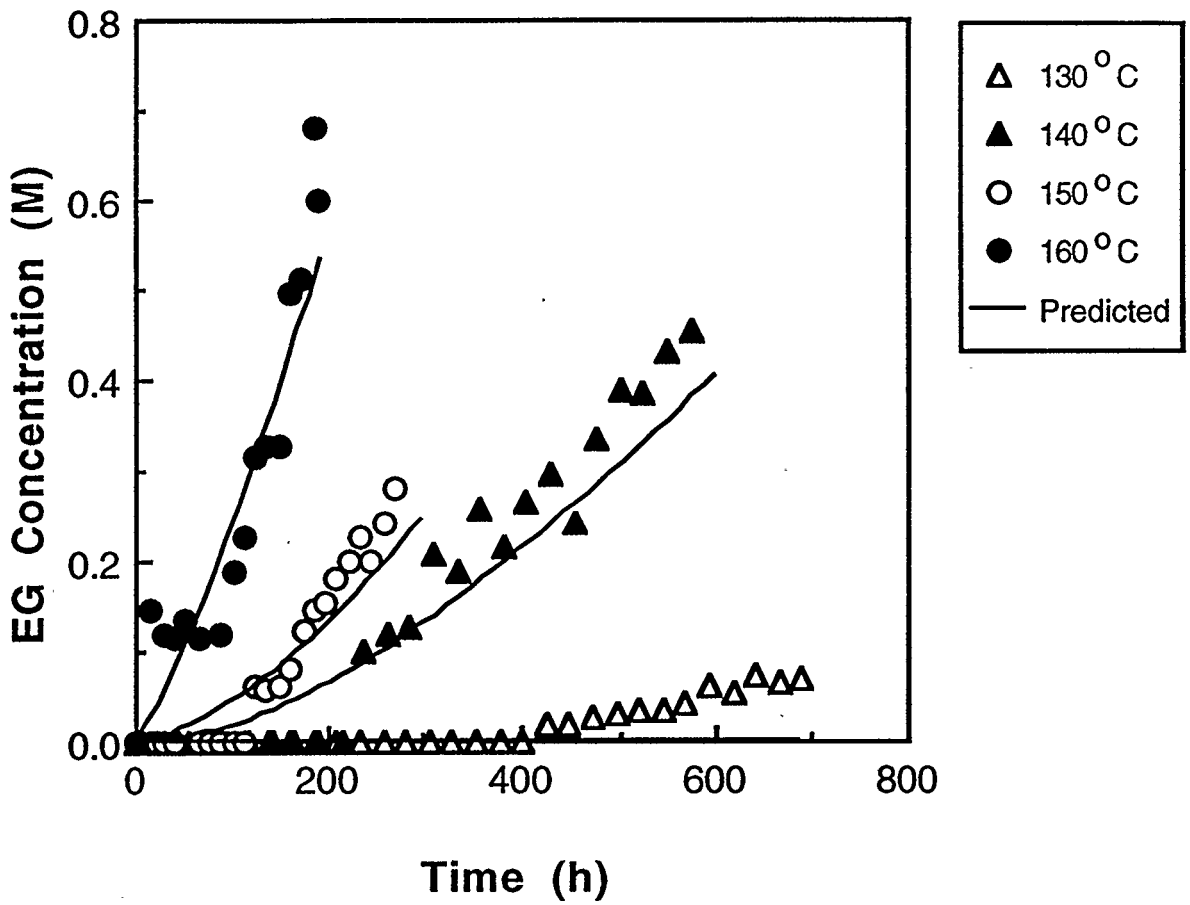


Figure 5.8 Experimental and predicted EG concentrations as functions of time and temperature
(50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

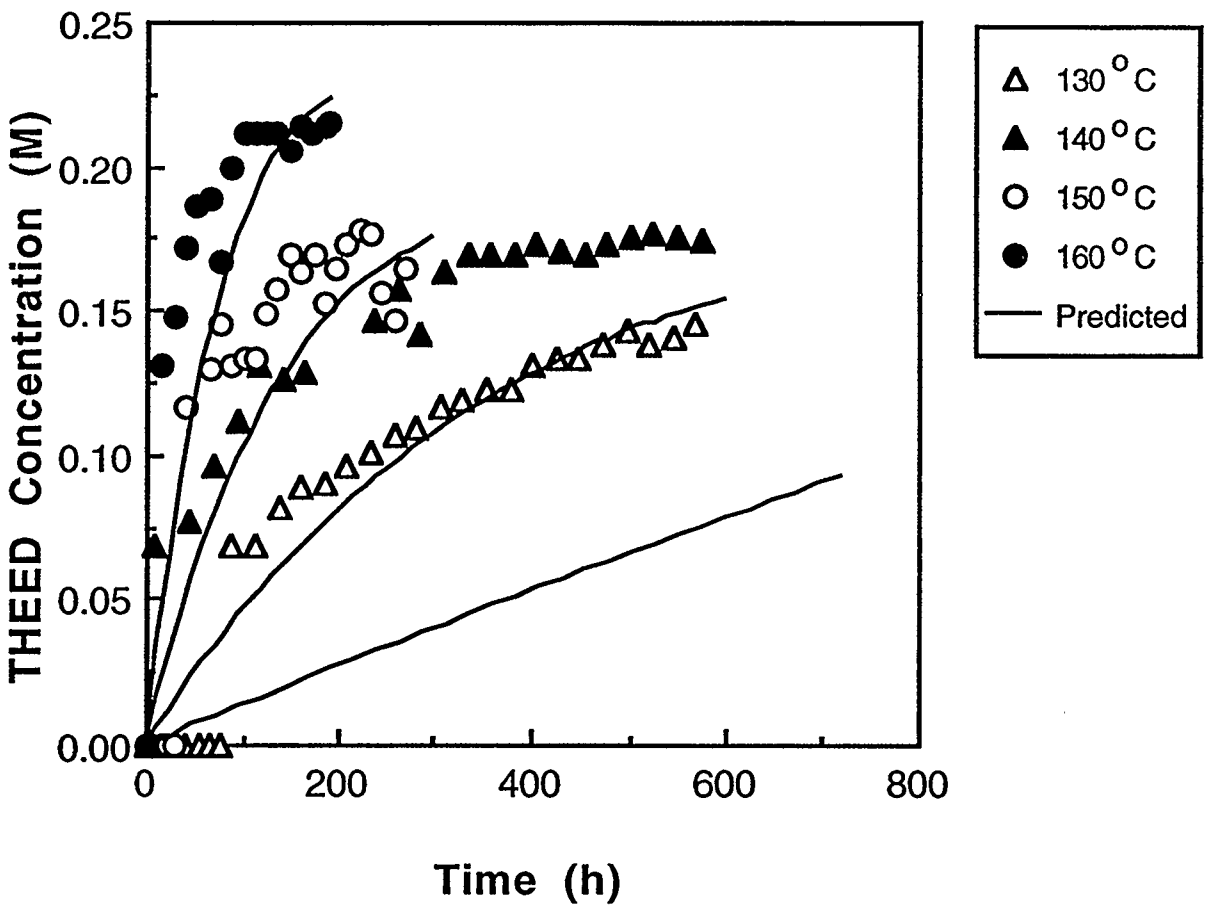


Figure 5.9 Experimental and predicted THEED concentrations as functions of time and temperature (50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

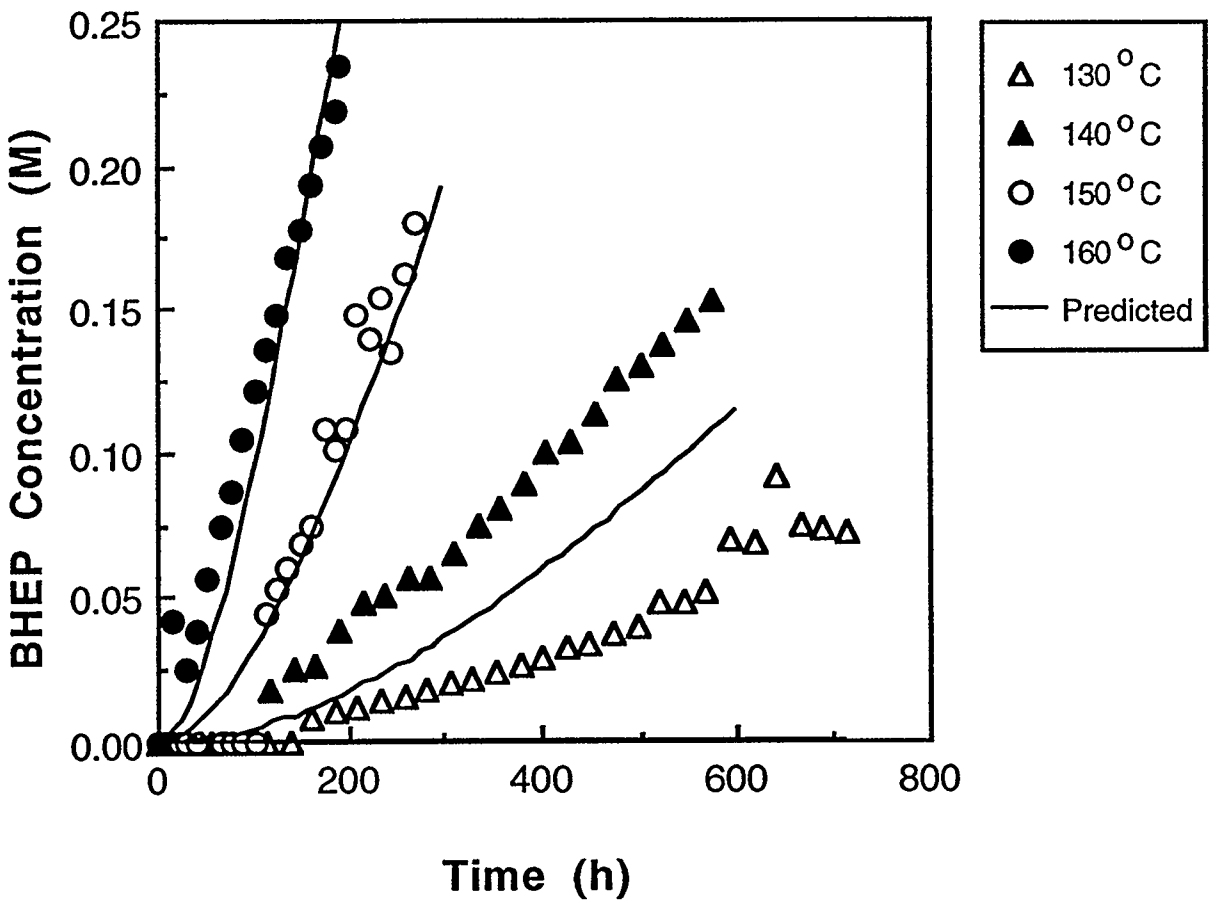


Figure 5.10 Experimental and predicted BHEP concentrations as functions of time and temperature (50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

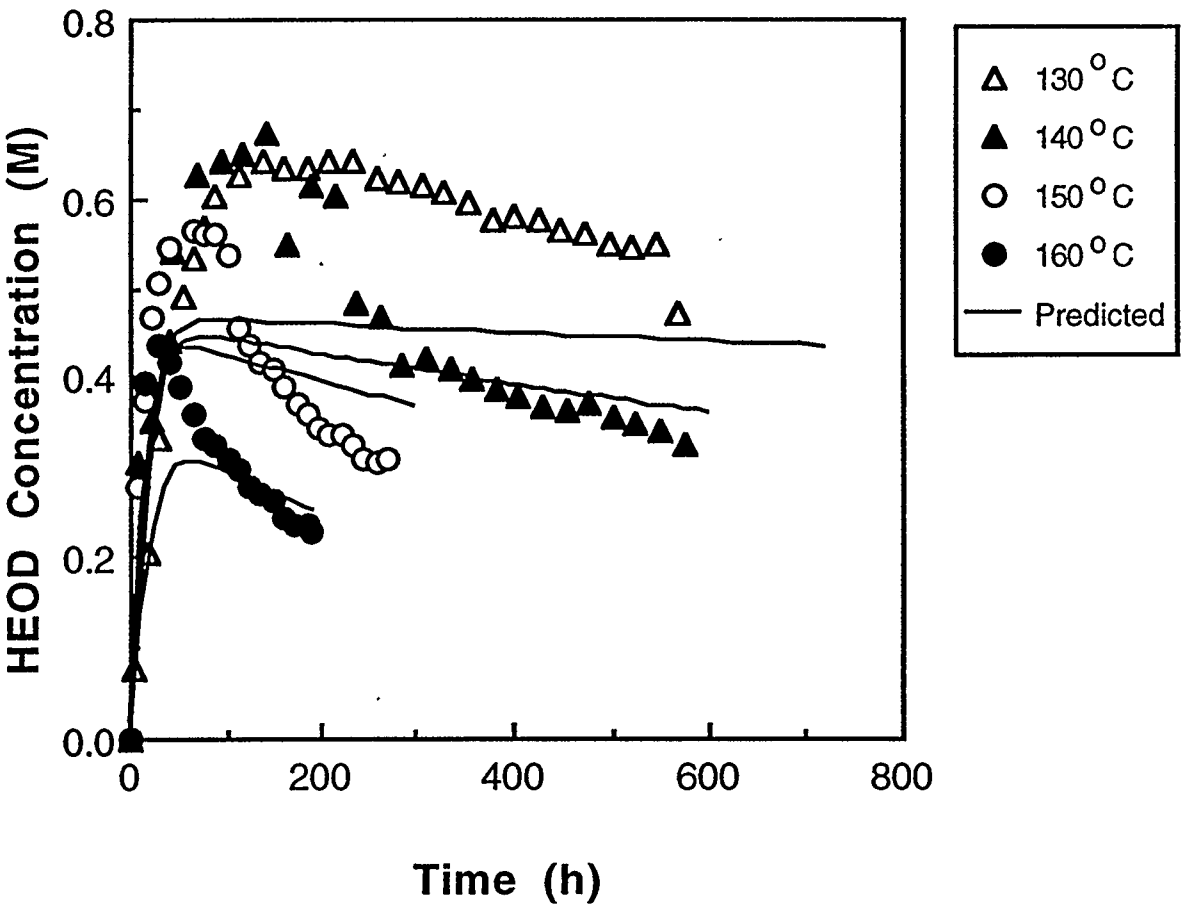


Figure 5.11 Experimental and predicted HEOD concentrations as functions of time and temperature (50 wt% MDEA-10 wt% DEA, 4137 kPa CO_2)

As a result, it can be concluded that the model is successful in predicting the concentration of the mixed-solvent at different temperatures. Being able to predict the solvent concentration correctly is important industrially in foreseeing the extent of degradation and estimating the solvent losses. The model predictions of DMAE, EG, THEED and BHEP are satisfactory, especially at high temperatures. However, the HEOD concentration predictions are not in good agreement with the experimental data. Nevertheless, the model can overall be considered to be sufficient in describing mixed-solvent degradation.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The main conclusions can be summarized as follows :

- The degradation products of MDEA-DEA mixtures are the same as MDEA degradation products.
- The major degradation compounds are EG, DMAE, BHEP, HEOD and THEED.
- EG and DMAE are produced by MDEA, but BHEP, HEOD and THEED are the common degradation products of MDEA and DEA.
- The degradation rate of MDEA-DEA mixtures has a strong dependence on temperature.
- The production rates of all the degradation compounds, except for HEOD, increase with increasing temperature.
- The overall amount of HEOD produced decreases at high temperatures.
- The degradation rate increases with increasing CO_2 partial pressure.
- The degradation reactions between MDEA-DEA mixtures and CO_2 are complex and can not be described by simple stoichiometric equations.

- The simple kinetic model, presented to describe the degradation of MDEA-DEA mixture with CO_2, is quite satisfactory in predicting the concentrations of the degradation compounds, especially at high temperatures.
- H_2S does not cause degradation, also it does not have any effect such as hindering the degradation of DEA with CO_2.
- Addition of NaOH to degraded DEA solutions decreases the HEOD and THEED concentrations, but it has no significant effect on BHEP.
- Vacuum distillation is not effective in purification of degraded DEA solutions.
- Passing industrially degraded solutions through a bed of basic ion-exchange resin (Amberlyst A-27) causes the disappearance of HEOD and a decrease in the concentrations of DEA, EG, BHEP and THEED.

6.2 RECOMMENDATIONS

The degradation of MDEA-DEA mixtures has been explored in the present study at temperatures ranging from 130 to 160 °C and CO_2 partial pressures of 689 to 4137 kPa. A more detailed experimental program can be devised in order to have a better insight into the degradation mechanism of the mixed-solvent. Also, the degradation of amine mixtures consisting of various amines can be studied.

The gas chromatographic technique used for the analysis of the degraded solutions can be modified or another technique can be proposed, to be able to separate MDEA and DEA.

Degradation experiments can be carried out with other common contaminants present in raw natural gas, such as COS and CS_2 instead of CO_2.

Although it is known to be difficult, it is worthwhile to focus on the purification of degraded amine solutions. Experiments can be carried out with different kinds of ion-exchange resins, or new, more effective methods, such as membrane systems, can be searched.

Finally, efforts might be directed to finding a way to prevent degradation, which seems quite impossible for the time being.

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APPENDIX A

GAS CHROMATOGRAPHIC TECHNIQUE

The gas chromatographic technique, presented by Kennard and Meisen [37] for the quantitative analysis of degraded DEA solutions and modified by Chakma and Meisen [14] for analyzing degraded MDEA solutions, has been used throughout this study. Although the technique was determined to be effective for degraded DEA and MDEA samples, it was not as satisfactory for MDEA-DEA mixtures. MDEA and DEA could not be separated using this technique since they have very similar structures and physical properties. The technique was tried to be improved by using different kinds of GC columns and packing materials, and trying to optimize the operating conditions, but the separation of MDEA and DEA could not be achieved for solutions with low DEA concentration relative to MDEA content. However, it was reliable and satisfactory in the detection of the degradation products.

Analytical Equipment

- Gas Chromatograph (Model HP 5890 Series II, Hewlett Packard)
- Integrator (Model HP 3396A, Hewlett Packard) connected to the GC
- Chromatographic column of 3.18 mm. OD and 1.83 m. long, made of stainless steel
- Packing material, Tenax G.C. 60/80 mesh

- 20 μL syringe (Model 7102KN, Hamilton Co.) with 2 μL fixed needle and Chaney adapter

Operating Conditions

Temperature programming was used in order to get a good separation of the degradation compounds, since they are known to have different molecular weights and polarities [14,37]. The operating conditions can be summarized as follows:

- Carrier gas - Helium
- Carrier gas flowrate - 30 mL/min.
- Detector - Thermal conductivity
- Detector port temperature - 300 °C
- Injection port temperature - 280 °C
- Column temperature - Isothermal at 100 °C for 3.0 min., then temperature increased at 20 °C/min. to 280 °C

Sample Injection

A 20 μL precision syringe (Model 7102KN, Hamilton Co., Reno, NV) fitted with a Chaney adapter and a 2 μL needle (Model 7102RN, Hamilton Co.) was used for sample injection. The injected sample size was 0.5 μL. The analysis took about 35 min., including the cooling down period since the column had to be cooled from 280 °C to 100 °C after each run. Each sample was injected at least three

times and the peak areas of the components were averaged. The septum was replaced with a new one regularly to prevent leakage.

Calibration

A direct calibration was used for MDEA, DEA and BHEP which could be purchased in pure form. Known concentrations of MDEA, DEA and BHEP were injected into the chromatograph and the peak areas were noted. At least five injections were made for each concentration and the average of the peak areas was taken. The calibration plots for the rest of the degradation products were obtained by adapting the calibration charts presented in Chakma's research [18]. The calibration charts of MDEA, DEA and BHEP were compared with the ones obtained by Chakma and the necessary modifications were made on the calibration charts of the other compounds assuming that the same trends of differences would be observed. Figures A.1 to A.7 show the calibration plots of concentration versus peak area for different compounds.

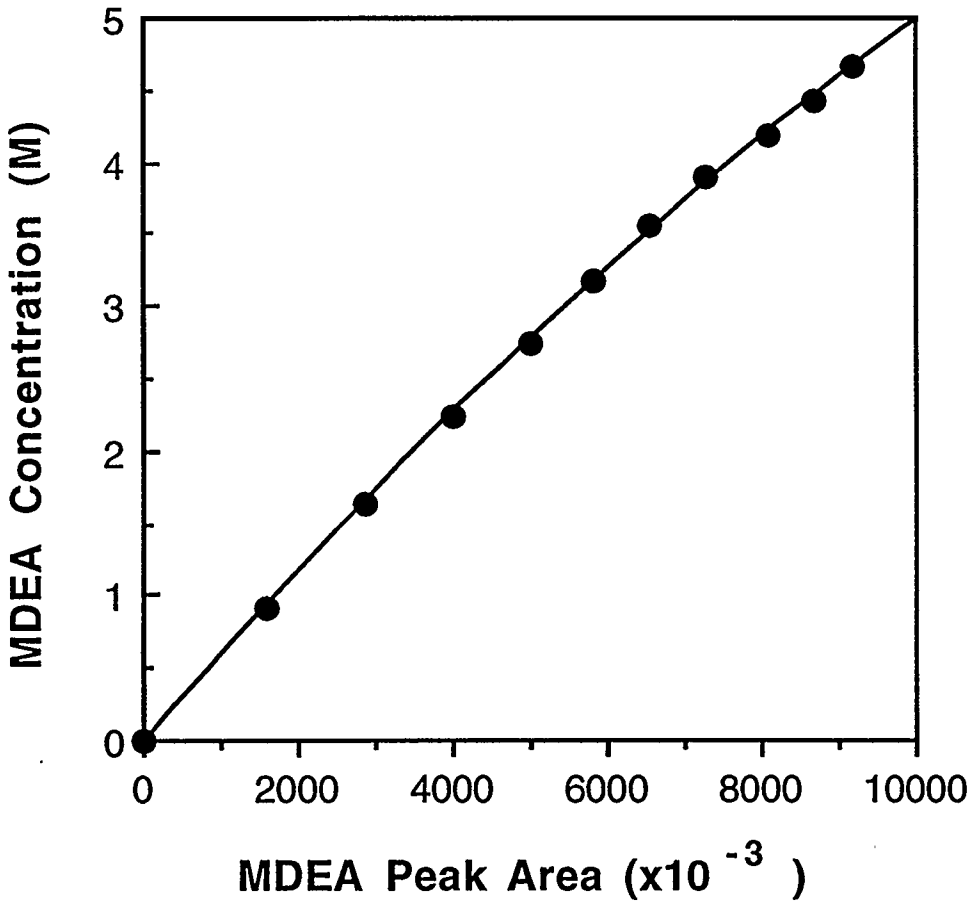


Figure A.1 Calibration plot for MDEA

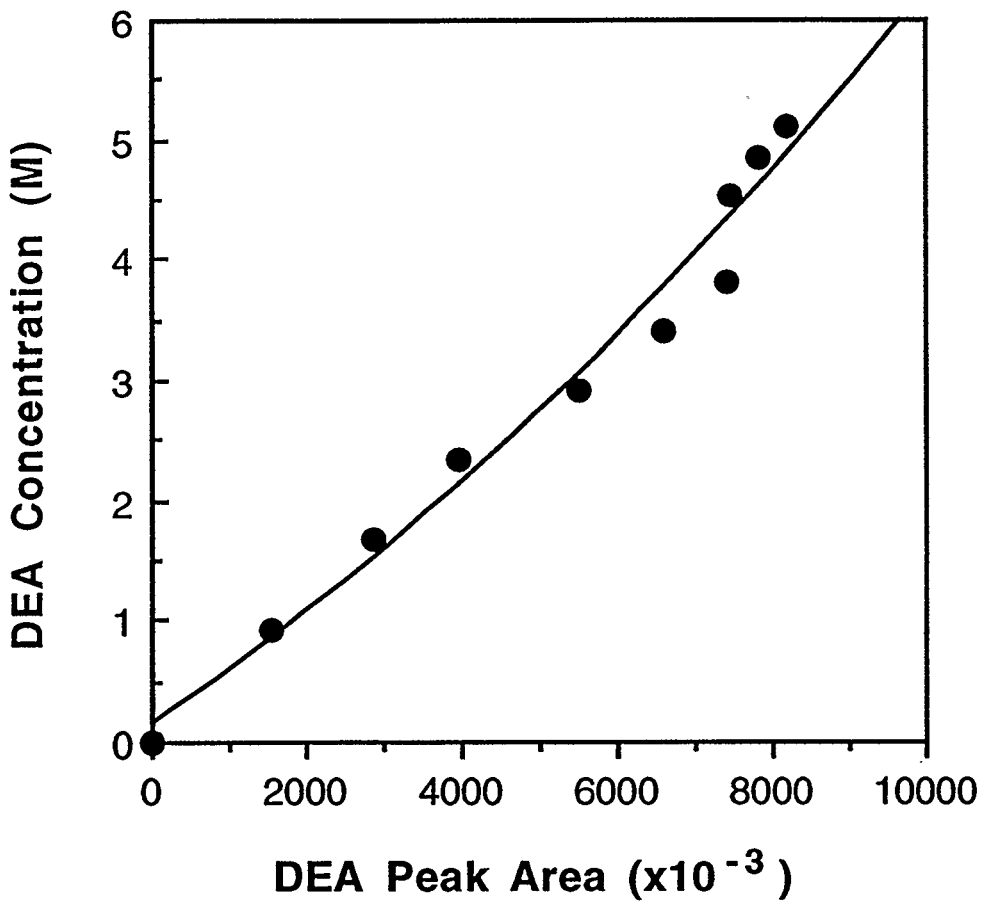


Figure A.2 Calibration plot for DEA

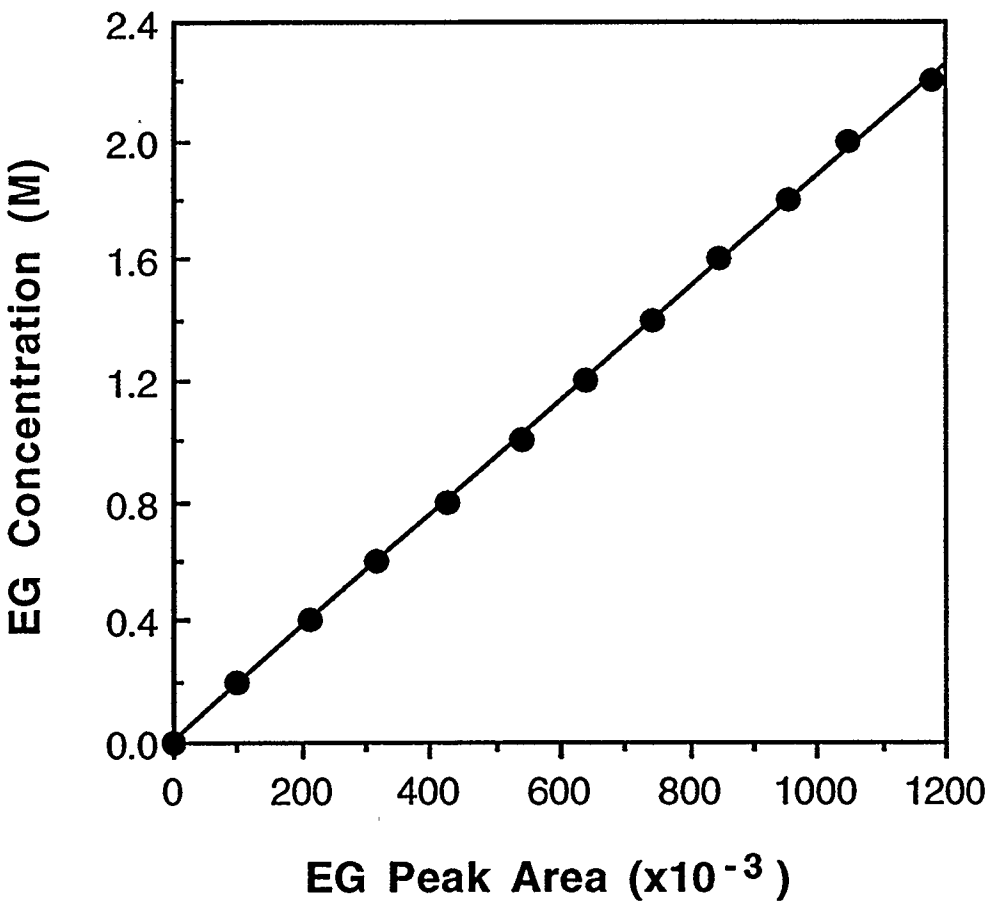


Figure A.3 Calibration plot for EG

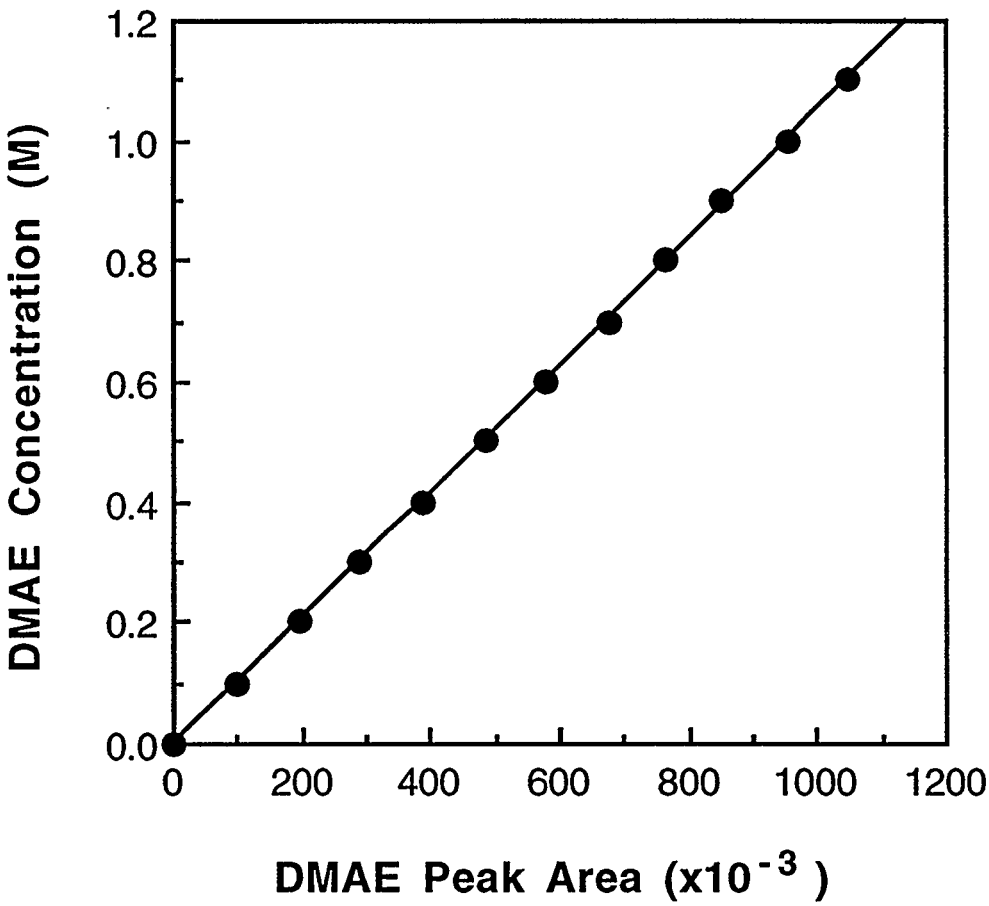


Figure A.4 Calibration plot for DMAE

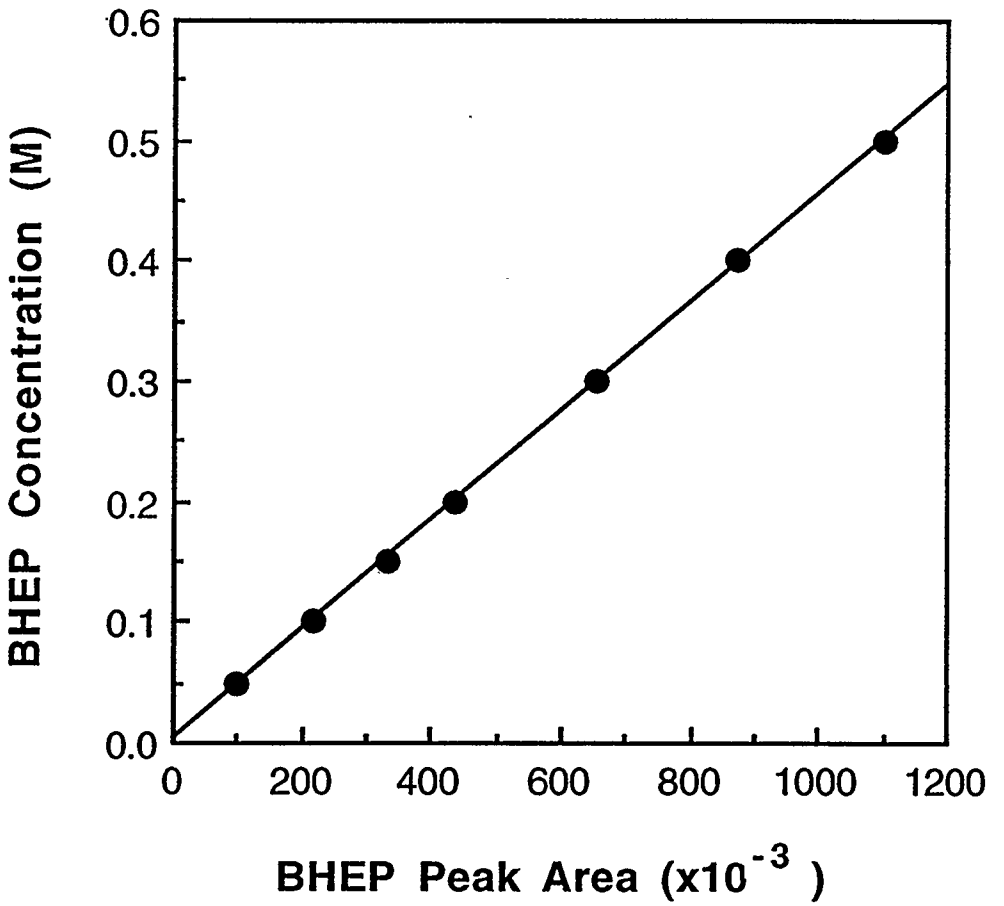


Figure A.5 Calibration plot for BHEP

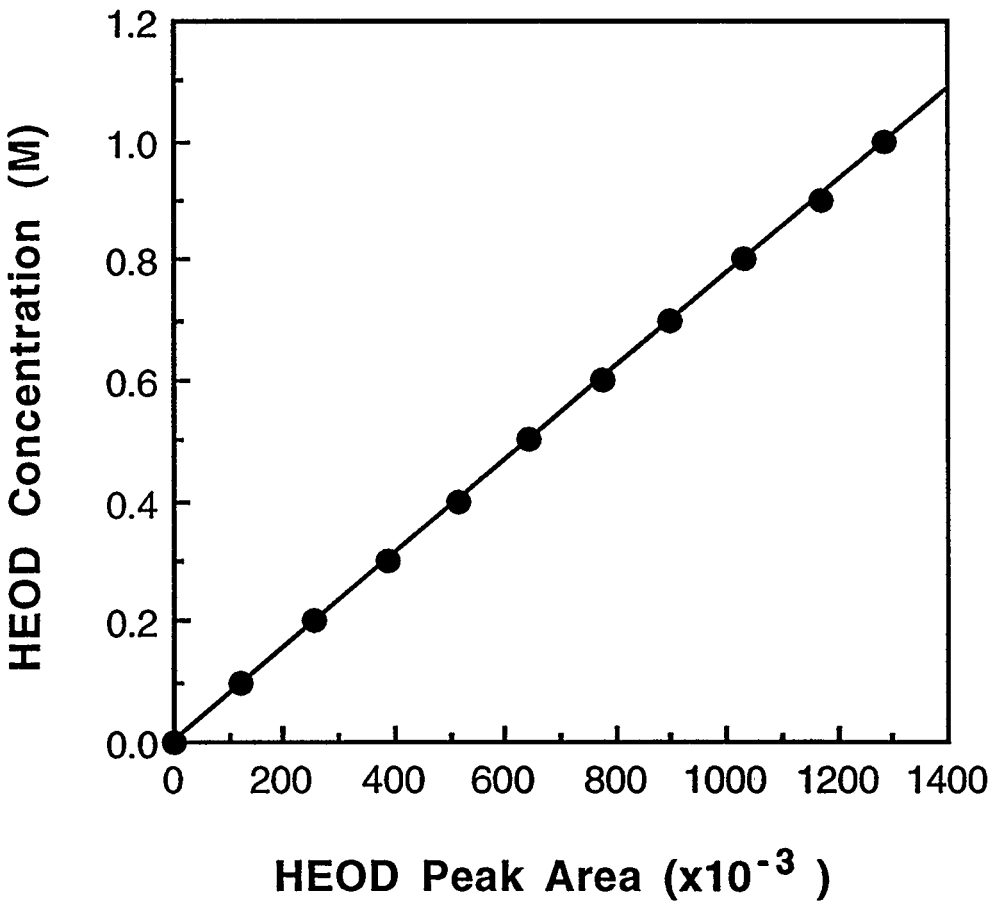


Figure A.6 Calibration plot for HEOD

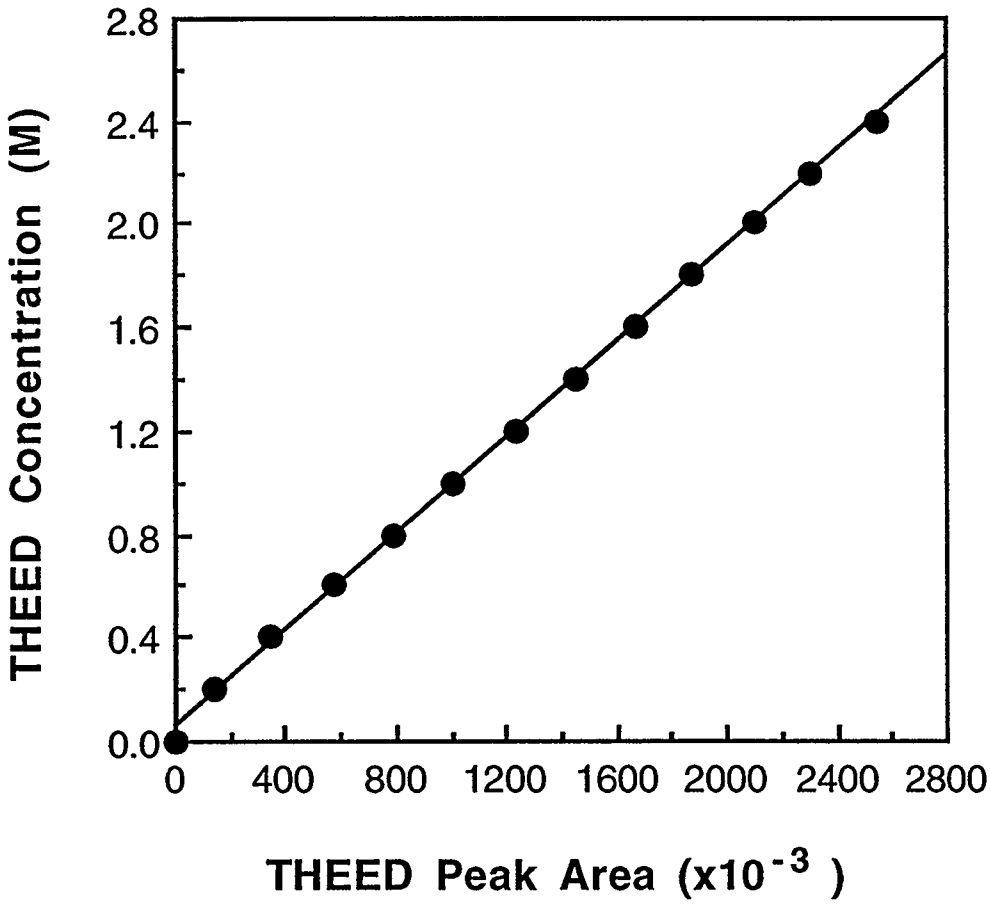


Figure A.7 Calibration plot for THEED

APPENDIX B

CHEMICAL STRUCTURES OF MAJOR MDEA-DEA DEGRADATION PRODUCTS

The chemical structures and molecular weights of MDEA, DEA and the major degradation products detected in degraded MDEA-DEA mixtures are tabulated below:

Table B.1 : Chemical structures of major MDEA-DEA degradation products

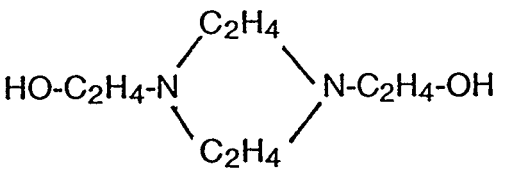
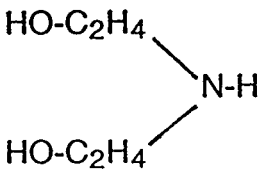
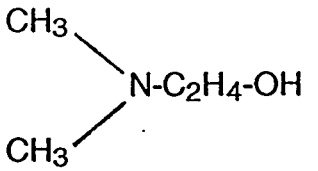
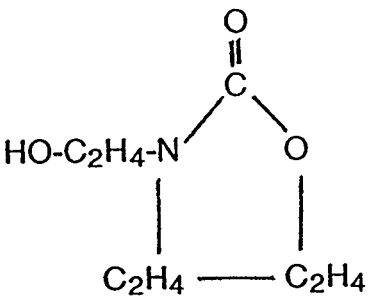
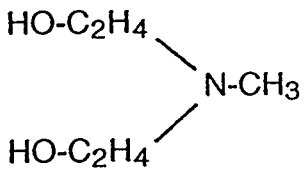
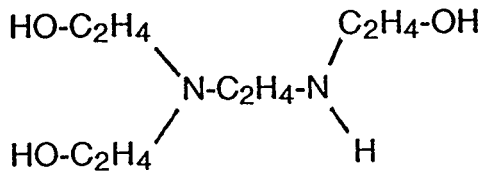
Compound	Chemical Structure	M.W.
BHEP N,N-bis(hydroxyethyl) piperazine		174
DEA Diethanolamine		105
DMAE 2-(dimethylamino) ethanol		89

Table B.1 (cont'd.)

Compound	Chemical Structure	M.W.
EG Monoethylene glycol	$HO\text{-}C_2H_4\text{-}C_2H_4\text{-}OH$	90
HEOD 3-(hydroxyethyl)-2-oxazolidone		131
MDEA Methyldiethanolamine		119
THEED N,N,N-tris(hydroxyethyl) ethylenediamine		192