CHARACTERISTICS OF ABSORPTION WITH REACTION IN PACKED COLUMN

Essam K. Halabia*, Ahmed M. Al-Barifcani, and Farah T. Jassem***

*Chemical Engineering Department – University of Technology – Iraq

**State Company for Engineering Designing and Consultation - Iraq

ABSTRACT

Absorption of carbon dioxide from gaseous mixture (nitrogen, carbon dioxide) was studied by using chemical absorbent in a counter current packed column (0.15m inside diameter x 1.5m height), packed with glass raschig rings of 1.8cm inside diameter to a depth of 1.1 m. The absorbent used is mainly diethanolamine solution.

The effect of several parameters on the absorption of carbon dioxide were studied using central composite rotatable design method for designing the experiment , namely, liquid flow rate (1 – 5)l/min, absorbent concentration (8.5 – 25) wt% and liquid temperature (30 – 75) ℃ at constant gas condition (21.04 mole/min.m^2 flow rate and 55℃ of temperature). , and also to find the optimum operating condition.

The relationships between the above mentioned variables and the objective functions (percentage conversion and absorption rate) for diethanolamine solution could be established. The relationship represented by second order polynomial mathematical models. From these mathematical models ,the mass transfer coefficients (K_La, K_Ga) and reaction rate constant of carbon dioxide are estimated.

The results of optimization show that the optimum operating conditions for absorption of carbon dioxide in diethanolamine solution is found at:liquid flow rate =3.86 l/min,diethanolamine concentration =25 wt% and liquid temperature = 66℃. which give a maximum absorption rate = 12.485 mMol / min.

From the experimental result it is concluded that the percentage conversion of diethanolamine solution decreases with increasing liquid flow rate and absorbent concentration, and increasing with increasing liquid temperature up to 66℃ then decreasing gradually with further increasing of temperature.

The absorption rate of carbon dioxide and mass transfer coefficients (K_Ga, K_La) were found to be largely influenced by liquid flow rate, absorbent concentration and liquid temperature, which increased and reaches the maximum values at optimum operating conditions. And decreases when liquid flow rate and temperature exceed the optimum value.

INTRODUCTION

Removal of carbon dioxide from gaseous mixtures is of vital importance in the natural gas and petroleum processing industry .In principle, many processes are employed for the removal of carbon dioxide, but the use of liquid solvents is economically attractive [1].The solvent should therefore have a high absorption capacity for absorbing the solute without building up appreciable equilibrium back pressure, quickly absorbed acid gas, and release it easily in the desorber [2]. Diethanolamine has a resistance to degradation from COS and CS_2, has low vapour pressure operations as vaporization losses are quite negligible and diethanolamine solutions are less corrosive than monetholamine solutions and other amines solutions. In addition, the decomposition products from side reactions are essentially noncorrosive. Diethanolamine and each of ethanolamines have at least hydroxyl group and amino group. In general, it can be considered that the hydroxyl group serves to reduce the vapour pressure and increase the water solubility, while the amino group provides the necessary alkalinity in water solutions to cause the absorption of acidic gases [3].

An earlier investigation on absorption carbon dioxide in diethanolamine solutions was been carried out by Mason et al [4]. They studied the rate of absorption of carbon dioxide in diethanolamine solutions at different temperatures and concentrations.

Cryder et al [5] investigated the absorption coefficient K_Ga of carbon dioxide by diethanolamine solutions at various liquid flow rate and temperature up to 55°C in packed column. The results obtained that the absorption coefficient K_Ga is higher than published valued for the absorption of carbon dioxide in water or carbonate solutions.

Danckwerts et al [6,7] measured the rates of absorption of carbon dioxide at very low pressure into aqueous solutions of diethanolamine in a stirred cell at 25°C. They showed that the results were compatible with reaction scheme suggested by Danckwerts [8].

Experimental data are presented on the reaction of carbon dioxide and eqeous diethanolamine solutions at 228 K by versteeg et al [9] for determining the solubility and diffusivity by means of the CO_2-N_2O analogy [7] and a modified Stokes-Einsten relation respectively.

A rigorous computer model was developed by DE Leye et al [10] for the simulation of absorption of diethanolamine in packed or plate column. It allows the computation of the concentration and pressure profile along the column and of the concentration profile in both the gas and liquid film at any height in the column.

Also, Versteeg et al [11] developed another model, which can be used to calculate rapidly absorption rates of carbon dioxide enhancement factors and concentration profile in aqueous solutions of MEA-DEA-MDEA mixtures.

Weiland [12] measured the diffusion coefficient of carbon dioxide in diethanolamine solution.

Nielsen et al [13] reviewed the fundamental aspects of LPG amine treaties, and includes guidelines, design consideration and alternatives for static mixers, jet educator mixers and columns with structured packing random packing and sieve trays. Amines used in this study monoethanolamine, diethanolamine and methyldiethanolamine solutions.

EXPERIMENTAL WORK

Experimental Equipment

A schematic diagram of the experimental apparatus employed throughout this work is shown in Fig. (1).

Absorption column is the principal parts of the apparatus used in the present work. It was constructed from stainless-steel pipe of i.d. 15cm x height 1.5cm (of adequate ratio of column diameter to packing 8 to 1).The packed was made from a glass Rasching rings (20mm o.d x 19mm i.d x 20mm long), 110 cm height of packing was used.The packing support was a perforated stainless-steel with 64 holes of 0.9 cm diameter.

The liquor and gaseous mixture flow rates introduced at the top and bottom of the column respectively through the distributors were located at the top and bottom of the packed section .A spider type liquid distributor was used which made from carbon steel as shown in Fig. (2). This distributor gives a good distribution of liquid at low and high flow rates . For the gases distributor a perforated ring type gas distributor was used of 18 holes, each hole is of 1mm diameter. This distributor had concentric copper ring with 9 cm diameter. The ring was a pipe of 1 cm o.d and length equal to its circumference.

The spent absorbent discharge from bottom of the column through a pipe connected to a three way valve which is manually operated and the samples for the spent absorbent were taken from the column through this sampling device. The gases left the column at the top through a pipe to the atmosphere. A U-tube manometer was used for pressure drop measurement across the packing.

Gaseouse flow rate and liquor flow rates were measured by a calibrated rotameters. The temperature of the prepared liquor was measured by K-type thermocouple and controlled at this temperature by controller.The temperature of gaseous mixture and inlet liquor to the absorber was measured by K-type thermocouple and the reading was done by a digital reader of ELC .

Two stainless-steel cylindrical vessels of 0.1 m^3 were used in the present work. The first one was used as a liquor receiving vessel for the spent absorbent discharged from the absorber. The second vessel was used for the preparation of feed absorbent solution, it was equipped with two immersion heaters (3000 watt) for heating the liquor to the desired temperature and motor driven stirrer. Using of the motor driven stirrer gave a homogeneous liquor concentration and temperature throughout the vessel.

The bottom of the second vessel had two lines: one for feeding the liquor from the first one (receiving vessel) and the other connected with rotary pump (type Mohno pump) through three-way valve, for pumping the solution to the absorber.The excess liquid was recycled into the second liquor vessel. The inlet liquor samples were taken from another side of the valve.

Gas-mixer was used to mix the gases, carbon dioxide and nitrogen before entering the absorption column in order to obtain the desired concentration. The gas mixer was a stainless-steel pipe of 0.75m i.d x 1.5m height, packed with 1cm i.d x 1cm long glass Rasching rings of 120 cm height packing.

Electrical heating element (4500 watt) and tape heaters (800 watt) connected in parallel around the gas mixer and tube between gas mixer and absorption column for heating the gaseous mixture to the desired temperature set by a thermostat ranging from 0 – 90 C°.

RESULTS AND DISCUSSION

1.Absorption rate of carbon dioxide Calculated from the material balance with chemical reaction.

2.DEA Conversion % = $\dfrac{CO_2 \text{ absorbed}}{[\text{DEA}]_{\text{Inital}}}$

3. Overall mass transfer coefficients K_Ga, K_La

a. Overall mass transfer coefficients are based on gas phase K_Ga can be calculated from the equation[14]:

$$K_Ga = \frac{N}{S(\Delta P)L_m}$$

$(\Delta P)L_m$ = is the logmean terminal partial pressure driving force atm.

$$= \frac{P_1 - P_2}{\ln \dfrac{P_1}{P_2}}$$

b. The overall mass transfer coefficient for liquid phase K_La is obtained from equation [15]:

$$K_La = H\ K_Ga$$

Hanry's law constant for CO_2 – DEA solution can be determined as follows[16]:

$$\ln\frac{H}{Ho} = 1.0406\times10^{-4} + 6.8433\times10^{-3}m + 1.33633\times10^{-2}m^2 - 1.1549\times10^{-3}m^3$$

Where H^0 is Henry's law constant of CO_2 in water can be obtained as follows [15]:

$$\text{Log}\left[H^o\right]^{-1} = -4.3856 + \frac{867.4932}{T}$$

The reaction rate constant for CO_2-alkaline solution system (ethaolamine) has been well correlated by Saraf et al [15]and Astarita et al[17] as

$$\log k_2 = 13.635 - \frac{2895}{T} + 0.08\,Ii$$

Ionic strength for diethanolamine can be determined as follows[17]:

$$Ii = m\,y$$

Absorption of Carbon Dioxide Results

The arrangements of the three parameters studied are shown in Table (1) with the response accomplished by the experimental work.

The complete regression results for the second order response surface of the objective function (percentage conversion and absorption rate) have been achieved by using Statistic- Software Windows release 5, 1995 as a function of process variables gave the following equation:

$$\text{DEA conversion \%} = 57.11155 - 10.8861X_1 - 6.5338X_2 + 5.2826X_3 - 3.49832X_1^2 - 1.7568X_2^2 - 4.9811X_3^2 + 5.12136X_1X_2 - 0.70088X_1X_3 - 0.36938X_2X_3 \qquad (1)$$

Correlation coefficients = 0.9443

Absolute average error = 4.5%

Absorption rate of carbon dioxide mMol/min = $10.47501 + 0.776127X_1 + 0.580129X_2 + 0.371042X_3 - 0.937039X_1^2 + 0.135857X_2^2 - 0.36658X_3^2 + 0.305044X_1X_2 + 0.155046X_1X_3 - 0.013716X_2X_3$ (2)

Correlation coefficients = 0.948

Absolute average error = 4.5%

The mathematical models (1 to 2) of the absorption rate of carbon dioxide percentage conversion describe adequately the real behavior of the system. Therefore, from these mathematical models the mass transfer coefficients (K_Ga, K_La) rate of reaction and rate constant can be estimated.

The results of optimization technique corresponding to a maximum absorption rate of carbon dioxide is: liquid flow rate =3.86 l/min,diethanolamine concentration =25 wt% and liquor temperature = 66°C. which give a maximum absorption = 12.485 mMol / min.

Effect of Liquid Flow Rate

Fig.(3) show the effect of liquid flow rate on the absorption rate of carbon dioxide in DEA solution at constant temperature of 72°C and different concentrations in the range of (8.5 - 25) wt%. Also, this effect is shown in Fig.(4) at constant concentration of 25wt% and different temperatures in the range of (30 - 75) °C. Similar effect of liquid flow rate on the mass transfer coefficients (K_Ga, K_La) are shown in Figs.(5) and (6).

It is clear that absorption rate and mass transfer coefficients increase markedly with increasing liquid flow rate up to a value of 3.86 l/min. This is due to decrease effective liquid film thickness, hence the concentration gradient of free carbon dioxide in the liquid will be greater, leading to increase the rate of absorption and mass transfer coefficients.

With further increasing liquid flow rate, a slow decreases in the absorption rate of carbon dioxide can be noticed. This is due to forming of some ripples and new patterns will be established which will cause maldistribution which accordingly decrease the mass transfer area and the absorption rate of carbon dioxide and the reaction rate of diethanolamine solution is not great enough for the dissolved carbon dioxide molecules to be destroyed chemically in a thin region near the interface.

Increasing absorption rate and mass transfer coefficients as liquid flow rate increases and decreasing with further increasing of liquid flow rate indicates that carbon dioxide absorption can be regarded as mainly diffusion and reaction controlled process. This is in agreement with the work of Yih et al [18] , and Cryder et al [19] .

Fig. (7) show the effect of liquid flow rate on percentage conversion of diethanolamine solution into carbonate and bicarbonate. It is clear that the percentage conversion decreases gradually when the liquid flow rate increases.

Effect of Absorption Concentration

The effect of absorbent concentration on absorption rate of carbon dioxide and mass transfer coefficients (K_Ga, K_La) at constant temperature of 72°C and different liquid flow rate are shown in Figs. (8) and (9).Similarly are shown in Figs. (10) and (11) at constant liquid flow rate of 4.36 l/min and for different temperature.

From these figures indicate that the absorption rate of carbon dioxide and mass transfer coefficients increase rapidly with increasing of dithanolamine concentration, however an increase in concentration the viscosity of solution increase which accordingly decrease the diffusivity of carbon dioxide and the absorption rate. The reason for this increasing is mainly attributed to the fact that the amino group increases which provides the necessary alkalinity in water solutions to cause the absorption acidic gases ,the zone of reaction approach the gas-liquid interface rapidly which decreasing the thickness of the liquid film through the solute must diffuse ,and also the reaction rate constant of carbon dioxide increases as shown in Fig.(12). Therefore absorption rate and overall mass transfer coefficients increased . These results are in agreement with results of Yih et al [18] , Cryder et al [19] and Blanc et al [16].

Increasing of absorbent concentration has an adverse effect on the percentage conversion as shown in Fig. (13) . This is due to increasing the bicarbonate concentration. It should be noted that dilute solution has lower carbon dioxide absorption rate and higher percentage conversion as shown in Table (1).

Effect of Liquor Temperature

Figs.(14) and (15) show the effect of liquid temperature on the absorption rate of carbon dioxide and mass transfer coefficients at constant concentration of 25 wt% and different liquid flow rates. This is also shown in Figs.(16) and (17)at constant liquid flow rate of 4.36 l/min and different concentrations.

It is clear that liquid temperature has a significant effect on rate of absorption and mass transfer coefficients of carbon dioxide up to 66°C. This is attributed to the fact that in theory for endo chemical reaction, an increase in temperature would presumably decrease the solubility of carbon dioxide in the absorbent and leads to decrease in the absorption rate it will also increase the rate of chemical reaction and decrease the viscosity of the solution, which leads to increase in absorption rate. This in agreement with the present work because the reaction of carbon dioxide with diethanolamin solution is endo chemical reaction.

Furthermore, the reaction rate constant of carbon dioxide increases with increasing liquid temperature as shown in Fig.(18).

Further increasing of liquor temperature a slow decrease in absorption rate and mass transfer coefficient is observed. This implies that second effect predominates and further supports the theory that the absorption of carbon dioxide is diffusion and reaction controlled process.

The reason for decreasing absorption rate and mass transfer coefficient is attributed to firstly volatilization of diethanolamine at higher temperature which cause the loss of diethanolamine and secondly chemical degraded from side reaction of diethanolamine solution with carbon dioxide. These results in agreement with results of Benson et al [15,20] , and Yih et al [18]

The effect of liquid temperature on percentage conversion of diethanolamine solution into carbonate and bicarbonate is shown in Fig. (19) . The percentage conversion increases gradually with increasing liquor temperature up to 66 °C. This is related to the same reasons for decreasing the absorption rate and mass transfer coefficient when liquor temperature exceeds 66 °C.

CONCLUSIONS

The following points are concluded from present work:

1. The percentage conversion of diethanolamine decreases with:
   - i. Increasing liquid flow rate.
   - ii. Increasing absorbent concentration.

   And increasing with increasing liquor temperature up to 66°C, then decreasing gradually with further increasing of temperature.
2. The absorption rate of carbon dioxide and mass transfer coefficients (K_Ga, K_La) increases with:
   - i. Increasing liquid flow rate.
   - ii. Increasing absorbent concentration
   - iii. Increasing liquor temperature.

   which reaches the maximum values at optimum operating conditions.
3. Absorption rate and mass transfer coefficient decrease when liquid flow rate and temperature exceed the optimum value.
4. The optimum operating conditions for the absorption of carbon dioxide in diethanolamine solution are 3.86 l/min, 25 wt% of diethanolamine concentration and 66°C liquor temperature, which gave a maximum absorption rate is 12.485 mM/min.
5. The results show that the absorption of carbon dioxide using diethanolamine in which a reversible reaction in liquid phase is carried out the diffusion and reaction in liquid phase are controlling in this system .

NOMENCLATURE

Symbol	Definition	Unit
H	Henry's law constant in the active solution	atm.m^3/kmol
H_0	Value of H in pure solvent	atm.m^3/kmol
I_i	Ionic strength	kmol/m^3
K_Ga	Overall mass transfer coefficient, Based on gas side	kmol/atm.m^2.min
K_La	Overall mass transfer coefficient on liquid basis	m/min
k_2	Reaction rate constant	m^3/kmol.s
m	Molarity	kmol/m^3
N	Molar rate of transfer of gas with chemical reaction per unit time	mMol/min

Symbol	Definition	Unit
P_{lm}	Logarithmic Mean Value of Partial Pressure of inert gas	atm
P_1	Partial pressure of inlet gas	atm
P_2	Partial pressure of outlet gas	atm
s	Cross-sectional area of bed	m^2
T	Temperature	K
y	Fractional conversion of X	(-)

REFERENCES

1. Maddox, R.N., J.M. Gilbert, and A.R. Mahmud, Ind. Eng. Chem. Res., 26 ,P.77, (1987) .
2. Linek, V., J. Sinkule, and P. Vavelka, Ind. Eng. Chem. Res., 33,P. 2731, (1994) .
3. Kohl, A.L., and F.C. Riesenfeld, "Gas Purification", 3rd ed., Houston, Texas, (1979).
4. Mason, J.W. and B.F. Dodge, Trans. Am. Inst. Chem. Engrs., 32 , P. 27-48, (1936).
5. Cryder, D.S., and J.O. Maloney, Trans. Am. Inst. Chem. Engrs., 37, P. 827-852, (1941) .
6. Danckwerts, P.V., Chem Eng. Sci., 34 , P. 443-446, (1979).
7. Danckwerts, P.V., and S.S. Laddha, Chem Eng. Sci., 36 , P. 479, (1981) .
8. Danckwerts, P.V., and S.S. Laddha, Chem Eng. Sci., 37, P. 475-475, (1982).
9. Versteeg, G.F., and M.L. Oyevaar, Chem Eng. Sci., 44 , P.1264, (1989) .
10. Deleye L. and G. F. Fromert, Computers and Chem. Eng.,10, P.493, (1986) .
11. Versteeg, G.F., J.A.M. Kuipers, F.P.H. Van beckum, and W.P.M. van Swaaij, Chem. Eng. Sci., 45. P. 183, (1990).
12. Weiland, R.H., Report from internet, (1993).
13. Nielsen, R.B., J. Rogers, J.A. Bullin, and K.J. Duewall, Hydrocarbon processing, 9, P. 49, (1997) .
14. Benson, H.E., J.H. Field, and R.M. Jimeson, Chem. Eng. Progr., 54 , P.433, (1956).
15. Saraf, D.N., N. Vasishtha, and D. Sanyal, Ind. Eng. Chem. Res., 27, P. 2149, (1988).
16. Blanc, C., and G. Demarais, Int. Chem. Eng., 24, P. 43, (1984) .
17. Astarita, G., D.W. Savage, and A. Bisio, "Gas Treating with Chemical Solvents", Wiley, New York, (1983) .
18. Yih, S.M., and C.C. Sum, Can. J. Chem. Eng., 65, P.581-588 ,(1987).
19. Cryder, D.S., and J.O. Maloney, Trans. Am. Inst. Chem. Engrs., 37, P. 827, (1941) .
20. Benson H. P., J. H. Field and R. M. Jimeson, Chem. Eng. Prog., 50 , P.356-364, (1954).

Table (1) Results of experimental planned according to composite rotatable design for diethanolamine.

No. of exp.	Coded variables			Real variables			DEA solution			
	X_1	X_2	X_3	X_1	X_2	X_3	DEA conversion%	CO2 absorbed		y_1
				Liquid flow rate l/min	Conc. wt%	Liquid Temp. °C		Mol/liter	mMol / min	
1	-1	-1	-1	1.84	11.98	39.5	61.575	0.7012	7.876	0.0751
2	1	-1	-1	4.15	11.98	39.5	30.254	0.3445	8.723	0.06196
3	-1	1	-1	1.84	21.5	39.5	50.148	1.0349	9.078	0.0568
4	1	1	-1	4.15	21.5	39.5	35.119	0.724	10.75	0.034
5	-1	-1	1	1.84	11.98	65.5	72.409	0.8245	9.257	0.0545

6	1	-1	1	4.15	11.98	65.5	34.091	0.3882	9.887	0.0455
7	-1	1	1	1.84	21.5	65.5	55.311	1.1415	10.009	0.0438
8	1	1	1	4.15	21.5	65.5	41.861	0.8638	11.456	0.0259
9	-1.732	0	0	1	16.75	52.5	66.236	1.0603	5.327	0.1093
10	1.732	0	0	5	16.75	52.5	36.285	0.5808	9.408	0.0522
11	0	-1.732	0	3	8.5	52.5	87.834	0.7075	10.074	0.0366
12	0	1.732	0	3	25	52.5	44.337	1.0687	11.098	0.0279
13	0	0	-1.732	3	16.75	30	33.419	0.5349	8.556	0.0642
14	0	0	1.732	3	16.75	75	60.627	0.9705	9.6015	0.0496
15	0	0	0	3	16.75	52.5	56.886	0.9106	10.475	0.0374
16	0	0	0	3	16.75	52.5	56.884	0.9106	10.475	0.0374
17	0	0	0	3	16.75	52.5	56.881	0.9106	10.475	0.0374
18	0	0	0	3	16.75	52.5	56.885	0.91052	10.475	0.0374
19	0	0	0	3	16.75	52.5	56.884	0.91052	10.475	0.0374
20	0	0	0	3	16.75	52.5	56.881	0.91052	10.475	0.0374

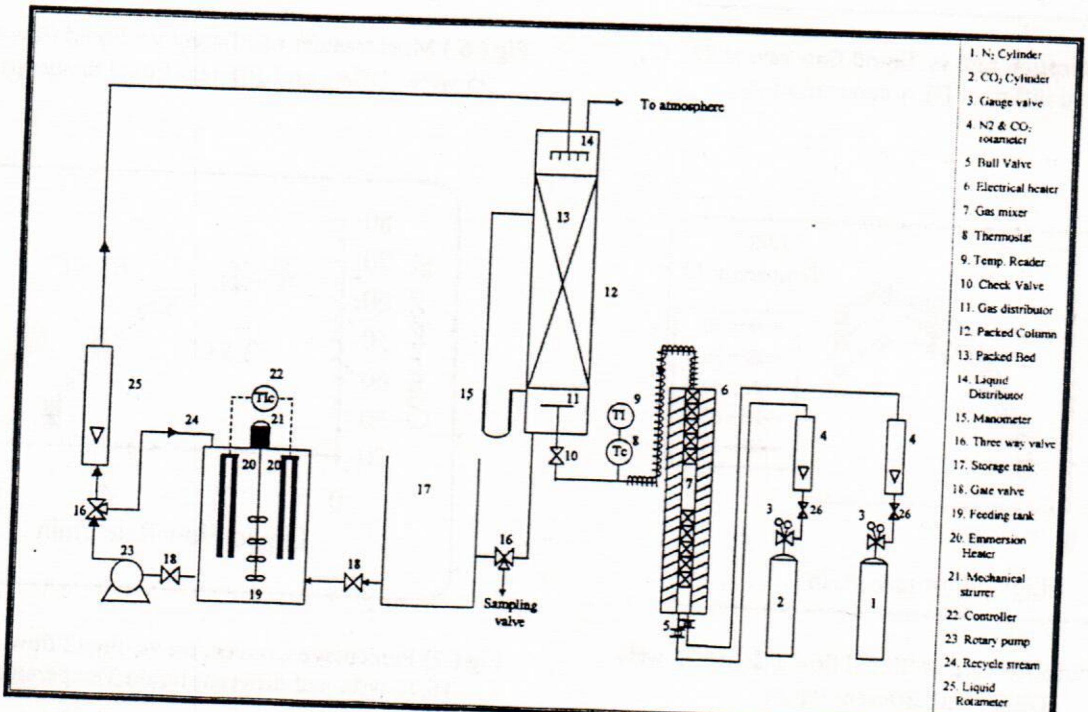

Fig. (1) Schematic diagram of experimental apparatus

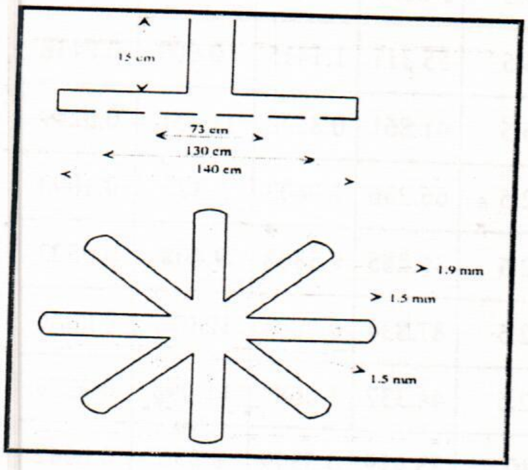

Fig. (2) Liquid distributor

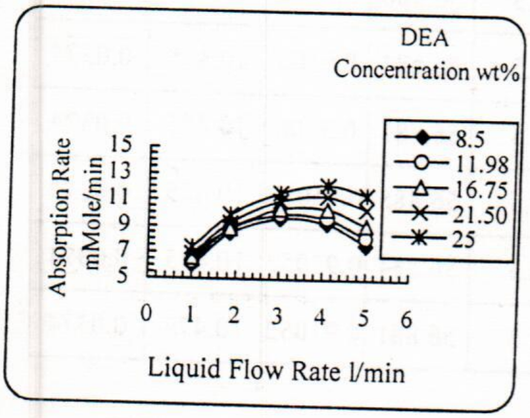

Fig.(3) Absorption rate vs. liquid flow rate at 72 C, and different DEA concentration

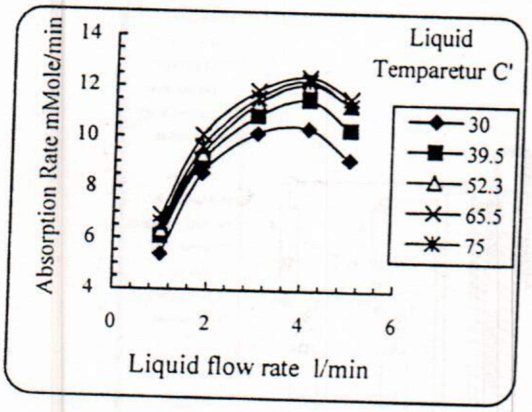

Fig.(4) Absorption rate vs. liquid flow rate at 25 wt% DEA, and different liquid

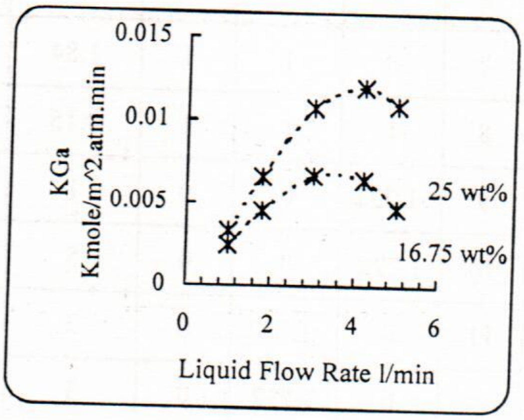

Fig.(5) Mass transfer coefficient vs. liquid flow rate at 72 C, and different DEA concentration

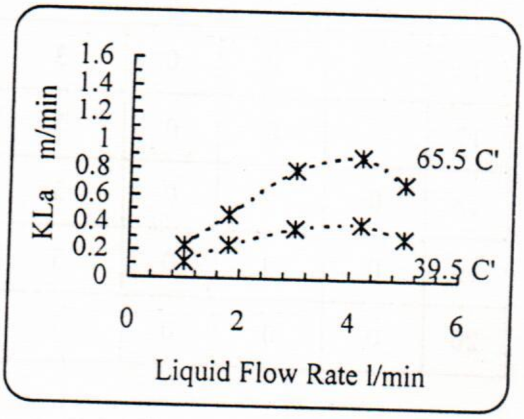

Fig.(6) Mass transfer coefficient vs. liquid flow rate at 25 wt% DEA, and different liquid temperature

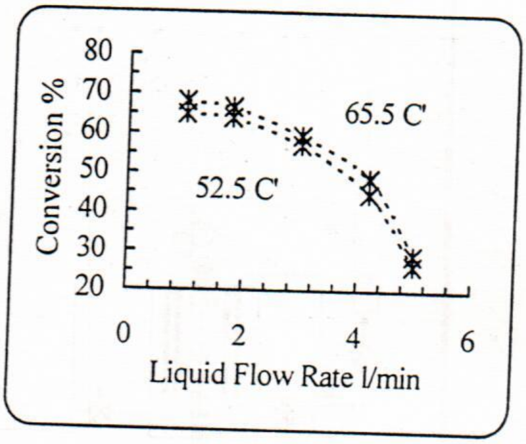

Fig.(7) Percentage Conversion vs. liquid flow rate at 16.75 wt% and different liquid Temperature

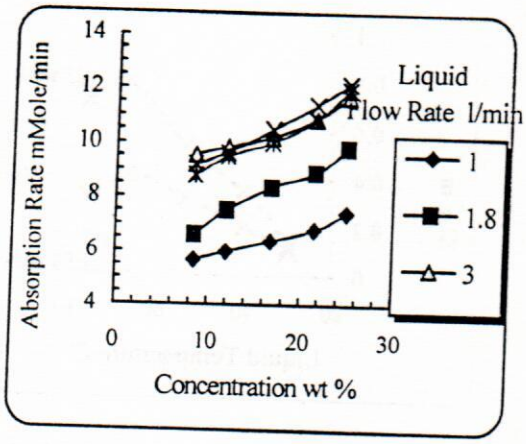

Fig.(8) Absorption rate concent- ration vs. at 72 C , and different liquid flow rate

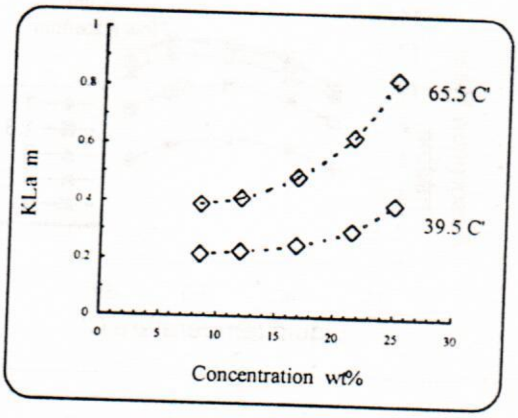

Fig.(11) Mass transfer coefficient vs. concentration at 25 wt% ,and different liquid temperature

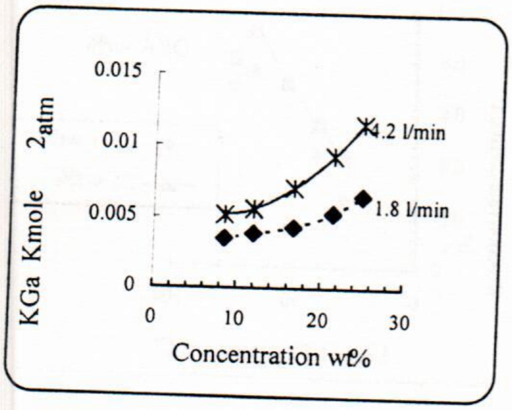

Fig.(9) Mass transfer coefficient vs. concentration at 72 C , and different liquid flow rate

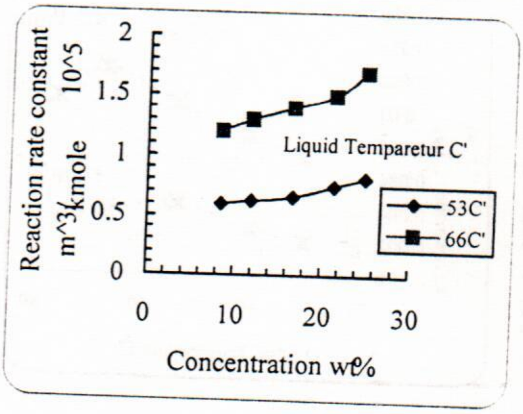

Fig.(12) Reaction rate constant vs. concentration at 4.36 l/min and different liquid temperature

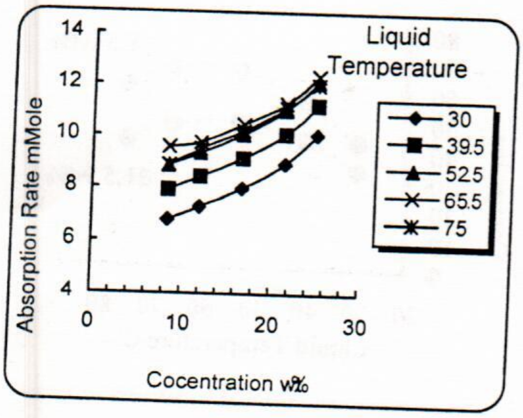

Fig.(10) Absorption rate vs. concentration at 25 wt% ,and different liquid temperature

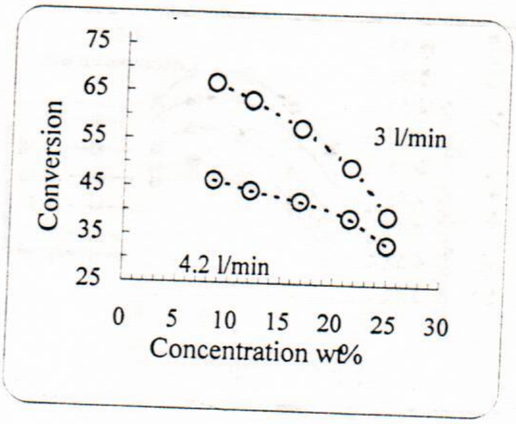

Fig.(13) Percentage Conversion vs. concentration at 1.8 l/min and different liquid temperature

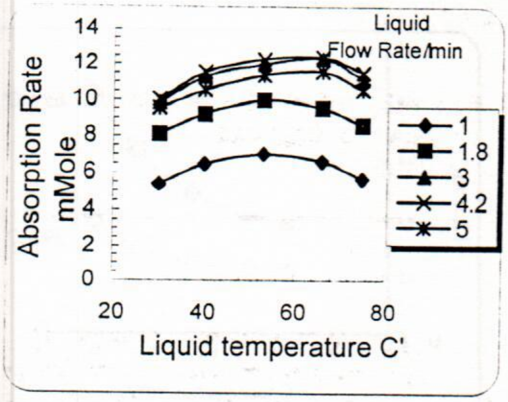

Fig. (14) Absorption rate vs. liquid temperature at 25 wt%, and different liquid flow rate

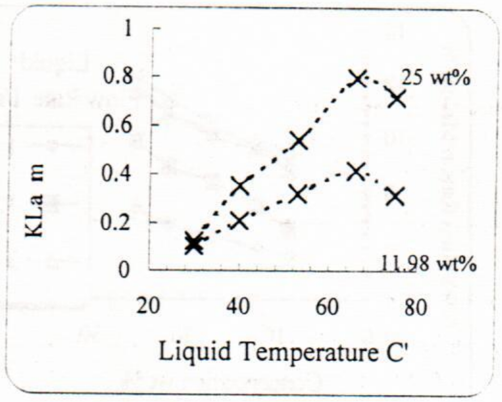

Fig. (17) Mass transfer coefficient Vs. Liquid temperature at 4.36 l/min,and different concentration

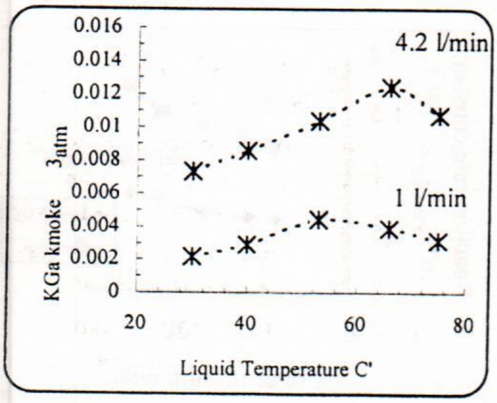

Fig.(15) Mass transfer coefficient Vs. . Liquid temperature at 25 wt%, and different liquid flow

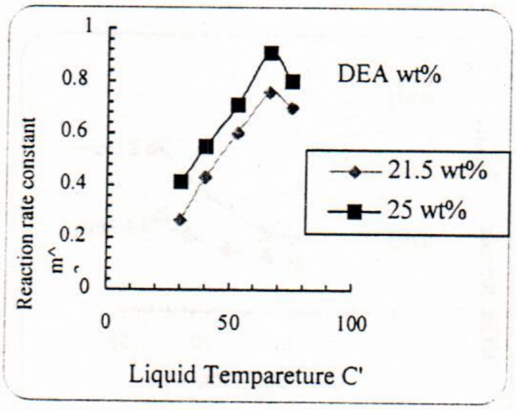

Fig. (18) Reaction rate constant vs. liquid temperature at 3 l/min and different concentration

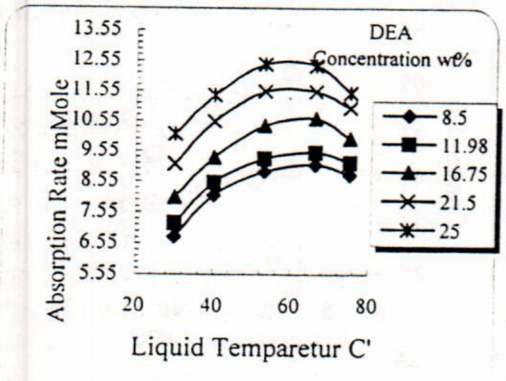

Fig. (16) Absorption rate vs. liquid temperature at 4.36 l/min,and different concentration

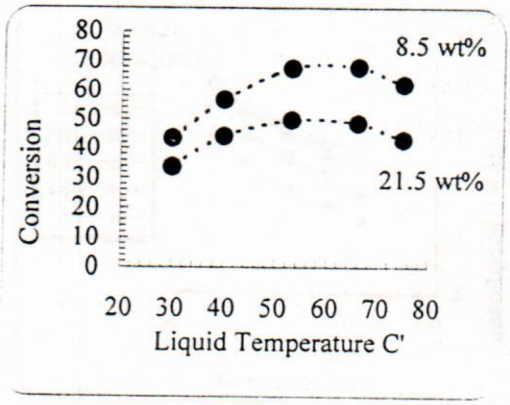

Fig. (19) Percentage Conversion vs. liquid temperature at 1.8 l/min and different concentration