

Modeling of carbon dioxide separation processes from natural gases

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Abstract:

Background: The increase in environmental temperatures and the transition of nature to two seasons, requires the making of some crucial decisions to ensure sustainability in the future. That is precisely why the European Union, through the Net-Zero Directive, proposed accelerating the transition towards climate neutrality, by imposing the elimination of the use of fossil fuels. For the transition to the use of energy fuels with CO₂ emissions reduced to zero, the use of natural gas was accepted as fuel transition. Under these conditions, the consumption of natural gas will increase in the future, as it is necessary to exploit condensate and impure gas deposits. Currently, the methods of removing CO₂ from natural gas include processes of chemical adsorption, physical adsorption, condensation and the use of separation membranes. Classical methods of carbon dioxide removal are energy-consuming and also require chemicals that must be reprocessed later. Due to the need to improve energy efficiency and conservation (protection) of the environment, the use of supersonic separators has been proposed. Through the analysis carried out in this article, I will describe how to treat carbon dioxide from extracted natural gases with amines.

Materials and Methods: Data collected by several researchers were able to determine a correlation between CO₂ partial pressure and amine loading capacity (moles CO₂/moles amine).

Results: In the present paper I have obtained relationships for each research carried out and also compare it with the results obtained in the experiments carried out in this PhD thesis, so that we can define the partial pressure of CO₂ versus the amine loading capacity (moles CO₂/mole amine).

Conclusion: So the simulation method chosen in the present paper demonstrates that amines are strongly absorbing substances in the range 0-500 kPa, then the absorption curve is flattened.

Key Word: amines, carbon dioxide, numerical modeling, amine treatment.

I. Introduction

Absorption of acid gases into alkanol amines is a process that has been used in old industrial applications. Despite this, several new factors keep this process in the attention of researchers and designers. The emergence of new alkanol amines continues to improve this process.

Alkanolamines are chemicals that have at least one hydroxyl group and one amino group.

It is believed that the hydroxyl group reduces the vapor pressure and increases the amines' solubility in water, while the amino group provides the amines' aqueous solutions with the alkalinity necessary to absorb acid gases.

Amines of commercial interest in the field of acid gas purification are:

- monoethanolamide (MEA),
- diethanolamine (DEA),
- methyl diethanolamine (MDEA),
- diisopropanolamine (DIPA),
- diglycolamine (DGA).

Substances that have two hydrogen atoms directly bonded to a nitrogen atom, as in MEA and DGA, are certain primary amines and have the highest alkalinity.

The secondary amines, DEA and DIPA, have hydrogen atoms directly bonded to nitrogen atoms.

Diisopropanolamine was used in the 1960s and 1970s in the ADIP and Sulfinyl processes [1].

This was replaced by methyl ethanolamine.

In MDEA, no hydrogen atom is bonded to the nitrogen anymore, so we are dealing with tertiary amine.

The chemical structures of the main primary, secondary, and tertiary amines are shown in Figure 1 [2].

In the design of gas treatment plants, it is essential to know the relationship between the concentration of acid gases in amine solutions and their partial pressure in the gas phase, i.e., solubility data (or liquid-vapor equilibrium data).

Usually, the concentration in the liquid phase is expressed as moles of acid gas per mole of amine and is called the amine loading or amine absorption capacity.

These values vary with the partial pressure of the acid gas (more precisely with the fugacity), with the temperature, the type of amine, the concentration of the amine in the solution, and the nature and concentration of other components present in the solution [3].

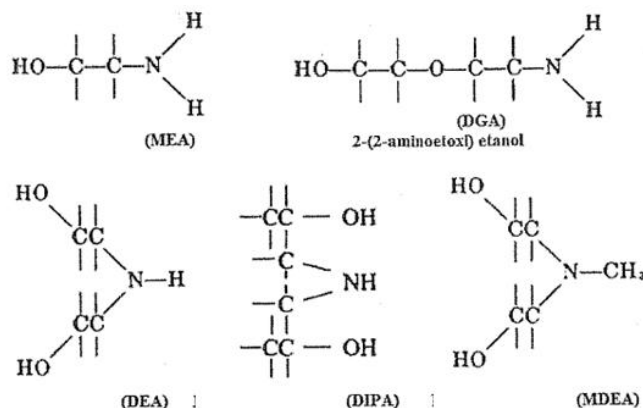


Figure 1. Structural formulas of traditional alkanolamines used in acid gas purification [2].

In gas purification processes, the choice of absorbent depends on the pressure and temperature conditions at which the impure gas is available, the composition and concentration of the components in the gas, and the purity required of the treated gas.

Aqueous MEA solutions are preferred for absorbing hydrogen sulfide and carbon dioxide from gases with low relative concentrations and free of COS (carbon oxysulfide) and CS₂ (carbon disulfide) [3].

This is especially true when treating gases at low pressures and when a maximum degree of H₂S and CO₂ recovery is desired.

Due to its stronger basic character than other amines, MEA has as its main advantage the high absorption rate of acid gases, with favorable consequences on the dimensions (height) of the absorption column.

MEA has the lowest molar mass and consequently has the highest absorption capacity (mass) at moderate concentrations.

Despite these considerable advantages, aqueous MEA solutions have a number of disadvantages.

One of them is the formation of irreversible reaction products with COS and CS₂, which leads to important amine losses, especially at high concentrations of these compounds.

MEA reacts with COS by the same mechanism as CO₂.

Another disadvantage of monoethanolamine solutions is much greater corrosion than other amines, especially at MEA concentrations above 20% mass and at high acid gas loadings.

The introduction of corrosion inhibitors can support the increase of MEA concentration even above 30 masses %, but only in the case of CO₂ absorption [3].

The choice of the concentration of MEA in aqueous solution is based more on the experience of operating the facilities.

A major disadvantage of MEA is that its reactions with CO₂ or H₂S are strongly exothermic [3]. Heats of reaction of MEA are approximately 30% higher than those of DEA with H₂S or CO₂.

Aqueous DEA solutions are frequently used for the purification of refinery gases that contain, in addition to H₂S and CO₂, other sulfur compounds such as COS and CS₂.

The lower vapor pressure of DEA than MEA gives it the advantage of lower vaporization losses [4]. In aqueous solution, the DEA concentration can reach up to 20-35% mass without the need for the use of corrosion inhibitors.

A disadvantage is that degradation products of DEA solutions can be removed from the system by vacuum fractionation [4].

When treating gases with a high CO₂ content, DEA leads to numerous irreversible reactions with CO₂ resulting in corrosive degradation compounds.

An advantage of DEA over MEA is the lower heat of reaction.

Aqueous solutions of MDEA have, until recently, only been used for the selective absorption of H₂S from gas streams with high CO₂ content.

The kinetic selectivity of MDEA over H₂S is based on the fact that its reaction rate with CO₂ is relatively low.

Selective absorption of H₂S from streams containing both acid gases is achieved by sizing the absorbers so that its contact area allows the reaction and absorption of H₂S, but is insufficient for a significant proportion of the CO₂ to be absorbed. Purified gases with a content of less than 4 ppm volume H₂S can thus be obtained.

Several qualities of MDEA have increased interest in its use even for the absorption of CO₂ from gases.

Thus, MDEA can be used in aqueous solutions at concentrations above 50-55% mass without producing corrosion, it has a very low vapor pressure and therefore negligible losses through vaporization, it has a low degradation rate.

From the point of view of CO₂ absorption, compared to primary or secondary amines, MDEA does not form carbamate, but bicarbonate.

Due to this reaction mechanism, the heat of reaction with CO₂ is much lower than that of other traditional amines, and therefore the consumptions for regeneration are much lower.

A major disadvantage of CO₂ absorption in aqueous MDEA solutions is, as previously mentioned, the low rate of absorption.

In the case of high CO₂ content, to compensate for the low absorption rate, the absorption and regeneration columns are equipped with a greater number of trays or higher packing heights than in the case of MDEA or DEA.

A comparison between the physical properties of the main amines used in gas purification and used in the experiments carried out in this work is presented in table 1.

Table 1. Physical properties of common alkanolamines [5]

PROPERTY	MDEA	DEA	MDEA	DIPA	DGA
Molar mass	61,09	105,14	119,17	133,19	105,14
Density at 20°C, g/mL	1,012	1,097	1,038	1,004	1,05150
Boiling point,					
	171	271	247,2	248,7	221
	100	187	164	167	-
	69	150	133	133	-
Pressure at 760 mmHg	0,36	0,01	0,01	0,01	0,01
Pressure at 50 mmHg	10,5	28,0	-21,0	42,0	-9,5
Pressure at 10 mmHg	full	96,4	full	87	full
Vapor pressure, mmHg at 20°C	1,4539	1,477	1,4694	1,4615-1,4635	1,4598

II. Material And Methods

Data collected by several researchers were able to determine a correlation between CO₂ partial pressure and amine loading capacity (moles CO₂/moles MEA) [6]

In the present paper I propose relationships for each research carried out and compare it with the results obtained in the experiments carried out in this PhD thesis, so that we can define the partial pressure of CO₂ versus the amine loading capacity (moles CO₂/moles MY).

The method used is the method of least squares.

Also, relations will be written for the absorption of CO₂ in aqueous solution of DEA 2M and 4M and for the absorption of CO₂ in aqueous solution of MDEA.

Table 2. Equilibrium data for 15.3% mass at 40°C [6]

Shen and Li		Jones		Lee		Less ş.a.	
Pressure P_{CO_2} , kPa	Amine loading, X $\frac{mol\ CO_2}{mol\ MEA}$	Pressure P_{CO_2} , kPa	Amine loading, X $\frac{mol\ CO_2}{mol\ MEA}$	Pressure P_{CO_2} , kPa	Amine loading, X $\frac{mol\ CO_2}{mol\ MEA}$	Pressure P_{CO_2} , kPa	Amine loading, X $\frac{mol\ CO_2}{mol\ MEA}$
15,7	0,561	0,3	0,412	2,0	0,460	1,0	0,437
24,1	0,609	2,0	0,485	3,9	0,502	3,2	0,488
35,3	0,619	2,3	0,495	19,9	0,562	10,0	0,538
55,6	0,641	22,0	0,599	132,3	0,684	31,6	0,595

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89,4	0,685	22,5	0,602	137,9	0,678	100,0	0,673
120,7	0,722	75,1	0,684	245,4	0,748	316,0	0,772
139,9	0,734	76,0	0,685	365,0	0,800	1000,0	0,902
563,0	0,873	120,7	0,713	446,0	0,797	316,0	1,090
1000	0,900	-	-	488,0	0,808	-	-
1370	0,942	-	-	929,0	0,897	-	-
1900	-	-	-	1639,0	0,989	-	-
2100	1,022	-	-	2873,0	1,072	-	-
2550	1,049	-	-	-	-	-	-

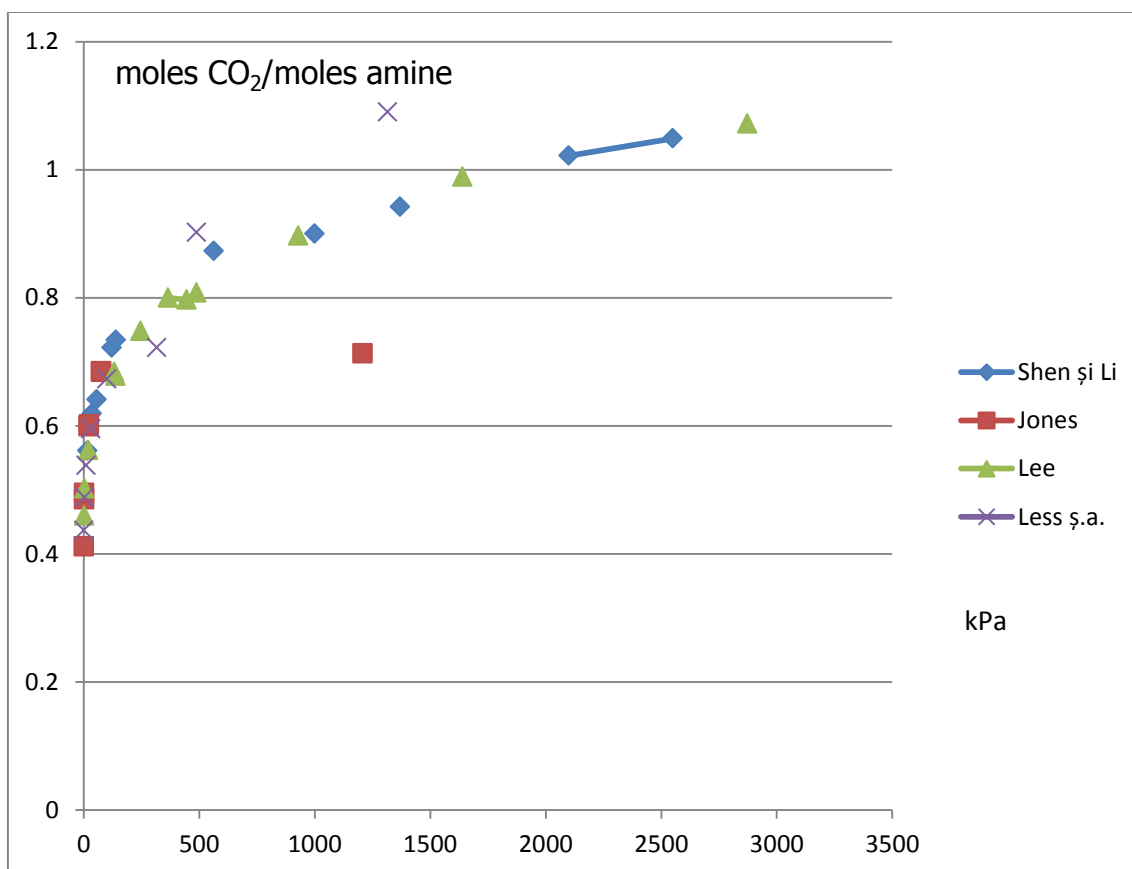


Figure 2. Amine loading MEA as a function of CO₂ partial pressure

Table 3. Equilibrium data for CO₂ absorption in aqueous solution of DEA 2M and 4M, at a temperature of 40°C [6]

DEA 2M		DEA 4M	
Pressure p_{CO_2} , kPa	Amine loading, X $\frac{moli CO_2}{mol DEA}$	Pressure p_{CO_2} , kPa	Amine loading, X $\frac{moli CO_2}{mol DEA}$
0,1	0,172	0,1	0,091
0,5	0,278	0,9	0,281
1,0	0,32	5,3	0,441
5,3	0,459	10,4	0,499
10,7	0,538	31,0	0,561
32,1	0,597	52,6	0,599
53,8	0,662	102,1	0,639
104,7	0,727	-	-

Table 4. Equilibrium data for the absorption of CO₂ in aqueous solution of MDEA 45% by mass, at the temperature of 40°C. [6]

Pressure p_{CO_2} , kPa	Amine loading, X $\frac{moli CO_2}{mol MDEA}$	pressure, bar	y , molar fraction	Y , $\frac{mol CO_2}{mol air}$
106	0,71	1,0464	0,872	6,812
83,4	0,7	0,8237	0,6861	2,186

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13,3	0,285	0,1313	0,1094	0,1229
2,67	0,136	0,02635	0,0219	0,02246
0,703	0,0609	0,00694	0,00578	0,00582
0,0310	0,0104	0,000297	0,000248	0,000248
0,109	0,0057	0,000108	8,79E-05	6,31E-05
0,00767	0,00381	7,57E-05	6,31E-05	6,31E-05
0,0231	0,00202	2,28e-05	1,9E-05	1,9E-05

Table 5. Density of aqueous solutions of MDEA [6]

MDEA concentration (% masă)	Temperature (°C)	Density (kg/m ³)
20	20	1017
	30	1013
	50	1005
30	20	1027
	30	1023
	50	1013
40	20	1038
	30	1033
	50	1021
50	20	1045
	30	1039
	50	1027

III. Result

„The equations of dynamic modeling of the density of aqueous MDEA solutions as a function of MDEA concentration (% mass), determined, following the realization of the experiments, are of the form:

$$\text{Density} = a + b * \text{temperature} \quad (1)$$

The values of parameters a and b were determined by the method of least squares, the program being written in Mathcad and are given in table 6.

Table 6. The parameter values of Eq 1.

MDEA concentration (% masă)	Value at a	Value at b	Mean value quoted	Mean value determined	Mean error, %
20	1025	-0,4	1012	1012	0
30	1037	-0,471	1021	1021,3	0,003
40	1050	-0,571	1031	1030,6	0,006
50	1057	-0,6	1037	1037	0

The density equations of the density of aqueous solutions of MDEA as a function of MDEA concentration (% mass) are presented in table 7.

Table 7. The dynamic model equations

MDEA concentration (% masă)	Value at a	Value at b	Equation
20	1025	-0,4	D=1025-0,4*t
30	1037	-0,471	D=1037-0,471*t
40	1050	-0,571	D=1050-0,571*t
50	1057	-0,6	D=1057-0,6*t

The equations determined for Dynamic Modeling of CO₂ Absorption in Aqueous Solution by MEA are of the form:

$$\ln(\text{partial } p) = a + b * \text{the loading capacity of the amine} \quad (2)$$

The values of parameters a and b were determined by the method of least squares, the program being written in Matchad and are given in table 8.

Table 8. The values of the parameters of equation 2, CO₂ absorption in aqueous solution by MEA according to the correlations in the specialized literature

Equation	Value at a	Value at b	Mean value quoted	Mean determined value	Mean error, %
Jones	0,458	0,051	0,779	0,686	0.0093
Less ş.a.	0,37	0,081	0,532	0,733	-0.00201
Shen and Li	0,285	0,093	0,711	0,702	0.00009
Lee	0,352	0,078	0,686	0,701	-0.00015

Table 9. Parameter values of equation 2, CO₂ absorption in aqueous solution of DEA 2M and 4M

Solution type	Value at a	Value at b	Mean value quoted	Mean determined value	Mean error, %
DEA 2M	0,337	0,08	0,469	0,695	-0.00226
DEA 4M	0,289	0,08	0,444	0,647	-0.00203

Table 10. Parameter values of equation 2, CO₂ absorption in aqueous solution of MDEA 45%

Solution type	Value at a	Value at b	Mean value quoted	Mean determined value	Mean error, %
MDEA	0,216	0,081	0,2126	0,5749	-0.00362

The data obtained from the laboratory analyzes allowed us to create numerical modeling equations.

Through the modeling equations developed by me I tried to determine which amine solution is more useful (absorbs more CO₂) (table 11, figures 3 and 4).

Table 11. Mathematical equations of CO₂ absorption in aqueous solutions of amines

Chemical model	Ecuation	Observation
aqueous solution of MEA	Ln P=0,458+0,051 X	Jones
aqueous solution of MEA	Ln P=0,37+0,081 X	Less ş.a.
aqueous solution of MEA	Ln P=0,285+0,093 X	Shen ş Li
aqueous solution of MEA	Ln P=0,352+0,078 X	Lee
aqueous solution of DEA 2M	Ln P=0,337+0,08 X	
aqueous solution of DEA 4M	Ln P=0,289+0,08 X	
MDEA 45%	Ln P=0,216+0,081 X	

where:

- P is partial pressure of CO₂, p_{CO₂}, kPa,
- X is amine loading $\frac{moli CO_2}{mol MDEA}$,

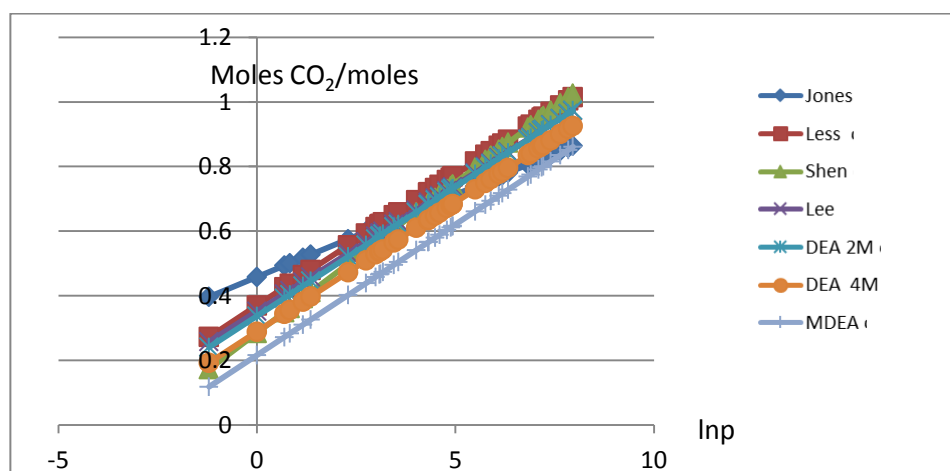


Figure 3. The calculated logarithmic values of the partial pressure of CO₂ depending on the amine loading

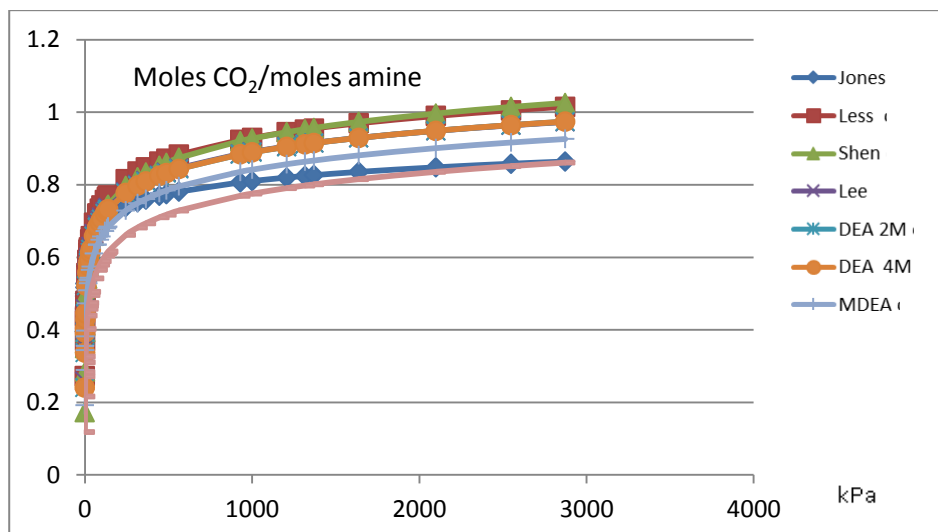


Figure 4. The tabulated values of the partial pressure of CO₂ depending on the amine loading

IV. Discussion

After analyzing the specialized literature and experimental modeling, we found the following:

- a. between 0 and 10 kPa, absorption is better described by Jones' relationship,
- b. in the range of 0-10 kPa, the best absorption has the MEA solutions,
- c. between 10 and 2873 kPa the best absorption is presented by the MEA solutions, but the relationship closest to reality is the one described by Lee's experiment,
- d. DEA 2 M solutions are more absorbent than DEA 4 M solutions,
- e. MDEA solutions are less absorbent but are the cheapest,
- f. to mention that all the experiments were carried out at 40 °C, so the results are comparable,
- g. it is also observed that at the partial pressure of 2873 kPa it is possible for the absorption to be 1/1 mol CO₂/mol amine.

V. Conclusion

So the simulation method chosen in the present paper demonstrates that amines are strongly absorbing substances in the range 0-500 kPa, then the absorption curve is flattened.

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