SOLUBILITY OF CO_2 IN AQUEOUS MIXTURES OF DIETHANOLAMINE WITH METHYLDIETHANOLAMINE AND 2-AMINO-2-METHYL-1-PROPANOL.

Florentino Murrieta-Guevara, Ma. Esther Rebolledo-Libreros, Ascención Romero-Martínez and Arturo Trejo*

Instituto Mexicano del Petróleo, Subdirección de Transformación Industrial, Gerencia de Investigación Aplicada de Procesos, Eje Central Lázaro Cárdenas # 152, 07730 México, D.F. (México)

ABSTRACT

Using the static method with recirculation of the vapor phase, experimental data of the solubility of CO_2 in aqueous solutions of mixtures of diethanolamine (DEA) with methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) has been obtained in the pressure range 3-3000 kPa. The data for DEA-MDEA were obtained at 313.15 and 393.15 K and are reported at four different compositions : 10 wt.% DEA-15 wt.% MDEA, 10 wt.% DEA-20 wt.% MDEA, 20 wt.% DEA-10 wt.% MDEA and 10 wt.% DEA-35 wt.% MDEA, while the data for DEA-AMP were obtained at 313.15 and 393.15 K and are reported at two different compositions: 25 wt.% DEA-5 wt.% AMP and 20 wt.%DEA-10wt.%AMP. The results are given as the partial pressure (p) of CO_2 against its mol rate α (mol CO_2/mol alkanolamine), in the range of temperature studied. The solubility of CO_2 decreases with temperature and increases with pressure and is a strong function of the composition of the alkanolamines. The mixture of AMP 10 wt. % at 313.15 K shows higher

capacity to absorb CO_2 than the others mixtures studied here. From these results, exothermic values of the enthalpy of the solutions ΔH_s were derived.

Keywords : alkanolamine, 2-amino-2-metil-1-propanol, aqueous mixtures, carbon dioxide, data, diethanolamine, experimental method, gas solubility

INTRODUCTION

The removal of carbon dioxide (CO_2) is of great importance in refining, gas-processing and petrochemical industry. The current industrial process for acid-gas (e.g. H_2S and CO_2) removal is to absorb the acid gas in an aqueous solution of alkanolamine, traditionally diethanolamine (DEA). Mixtures of primary (monoethanolamine, MEA) or secondary alkanolamine (DEA) with tertiary (e.g. MDEA) alkanolamines have been used to improve the energy efficiency of the process, [1,2] in fact, aqueous mixtures of alkanolamines formulated in base of MDEA or sterically hinder alkanolamines have been extensively used to treat gas streams contaminated with acid gases, [3].

The selection of the best aqueous mixtures of alkanolamines is based on the very well known reactions mechanism with the acid gases, for CO_2 this depends on the type of alkanolamine. Primary and secondary alkanolamines can react quickly with CO_2 trough the carbamate reaction and therefore exhibit high rates of acid gas removal, tertiary alkanolamines cannot form the carbamate and must undergo the much slower acid-base reaction, for this, are able to effect a high total CO_2 removal but at much lower rates. Sterically hinder alkanolamines, like AMP, are characterized by the presence of a bulky substituent group near the nitrogen atom, with a hinder alkanolamine the carbamate can

form but it is unstable . The formation of a stable carbamate causes a stoichiometric loading limitation of 0.5 mol of CO_2/mol of alkanolamine, so, the goal when using an aqueous mixture of alkanolamines has been to maximize the desireable qualities of the individual alkanolamines, that is, retain much of the high absorption rates of primary or secondary alkanolamines, offer low regeneration costs and to decrease both corrosion and circulation rates. Therefore, the experimental investigation of equilibrium solubilities of selected acid gas/aqueous mixtures of alkanolamines systems is of fundamental importance for reaching this goal.

Reported experimental data on the solubility of CO_2 in mixtures of alkanolamines of industrial importance are not plentiful, some solubility data in aqueous mixtures of MEA or DEA with MDEA have been reported by [4-7]. In this work experimental data of the solubility of CO_2 in aqueous solutions of mixtures of DEA with MDEA and AMP have been obtained in the pressure range 3-3000 kPa. The data for DEA-MDEA were obtained at 313.15 and 393.15 K and are reported at four different compositions : 10 wt.% DEA-15 wt.% MDEA, 10 wt.% DEA-20 wt.% MDEA, 20 wt.% DEA-10 wt.% MDEA and 10 wt.% DEA-35 wt.% MDEA, while the data for DEA-AMP were obtained at 313.15 and 373.15 K and are reported at two different compositions: 25 wt.% DEA-5 wt.% AMP and 20 wt.%DEA-10wt.%AMP. The results are given as the partial pressure (p) of CO_2 against its mol rate α (mol CO_2/mol alkanolamine). From these results, values of the enthalpy of the solution ΔH_s were derived.

EXPERIMENTAL

Materials

The MDEA and AMP were from Aldrich with a quoted purity of 99 mol % and 95 mol %, respectively. The sample of DEA was obtained from Merck with a reported purity of 98 mol %. Each of the three alkanolamines was further purified by repeated fractionation in a stream of dried nitrogen under controlled reduced atmosphere in an all-glass still and then stored over molecular sieve in order to eliminate any traces of water during handling of the samples. The purified samples were analyzed by gas-liquid chromatography which showed no impurities using a lower limit of detection of 0.05 mol %, the water used to prepare the mixtures was bidestilled. The sample of CO_2 was the same as that used in previous work [8,9], its minimum purity was 99.7 mol %.

Apparatus and procedure

The experimental apparatus used in the present study is the same as that described in detail in previous works by [10-12]. Equally, comprehensive information on the measurement procedure is given in the mentioned works from this laboratory.

The temperature at equilibrium was controlled within ± 0.4 K in the range studied, and the equilibrium total pressure was measured with an accuracy of ± 3.5 kPa.

RESULTS AND DISCUSSION

In order to establish the accuracy of the experimental data, the solubility of CO_2 in an aqueous solution of 30 wt. % DEA at 313.15 and 373.15 K was measured, an estimate of the error was obtained by comparing our results with interpolated literature values, [13].

Figure 1 presents the comparison, it may be observed that there exists good agreement especially at 313.15 K, the total average deviation was 8 %.

Experimental equilibrium solubilities were obtained for CO_2 in the aqueous mixtures of 25 wt.% DEA-5 wt.% AMP and 20 wt.%DEA-10wt.%AMP at 313.15 and 373.15 K. Figure 2 shows the results obtained. In order to clearly establish the effect of the addition of a sterically hinder alkanolamine (AMP) in a DEA solution, solubility data of CO_2 in an aqueous solutions of 30 wt. % DEA, obtained in this work, are also included in figure 2. Within the temperature and pressure ranges studied here it may be observed that the solubility of CO_2, for a given composition of the alkanolamines, changes regularly, that is, it increases with an increase in pressure and decreases as the temperature increases. The effect of changing by 5 wt. % the composition of the AMP in the alkanolamine mixture is very important, since at the same partial pressure, for example 500 kPa, α is 0.862 for the mixture with 5 wt. % AMP and 0.912 for the mixture with 10 wt. % AMP, also, it is quite clear that the solubility of CO_2 in any of the mixtures of DEA-AMP is higher than in the DEA solution, both results are consistent with the well known reaction mechanism between CO_2 and hindered alkanolamines and essentially they could be explained as due to the decrease in the formation of a stable carbamate.

Figure 3 shows the experimental results for the four aqueous mixtures of DEA-MDEA at 313.15 K. It is evident that the solubility of CO_2 is a strong function of the overall composition of the alkanolamine in the mixtures. Within the pressure range investigated, the choice of DEA or MDEA in the mixture for a constant composition (30 wt. %) did not make any difference in the equilibrium solubility of CO_2.

A comparison between the solubility of CO_2 in the aqueous mixtures of DEA-MDEA, DEA-AMP and the aqueous solution of DEA for a total composition of alkanolamines of 30 wt. %, at 313.15 K, is given in figure 4. The role that is playing the sterically hinder alkanolamine AMP on the solubility of CO_2 is in agreement with the reaction mechanism of this gas with secondary and tertiary alkanolamines : it is known that the reactivity for the CO_2 is in the order primary > secondary > tertiary alkanolamines, the reactivity of CO_2 with sterically hinder alkanolamines is comparables to that with primary or secondary alkanolamines without formation of a stable carbamate, this fact, allows to achieve the high thermodynamic absorption capacity of 1 mol of CO_2/mol of alkanolamine. From the figure, the mixture with 5 wt. % AMP has lower absorption capacity than the mixtures with MDEA, however the mixture with 10 wt. % AMP has a higher capacity.

Knowledge of the enthalpy of solution, ΔHs, in the aqueous mixtures of alkanolamines is of particular interest when considering heat input for the design of energy efficient heat transfer equipment in a gas treating process. Thus, we have obtained values of ΔHs from the experimental solubility data reported here using the procedure discussed in detail in previous work [11]. The exothermic ΔHs values are consistent with the negative temperature coefficients of solubility for CO_2. Our results of ΔHs for CO_2 in DEA 30 wt. %, DEA 10 wt. %-AMP 20 wt. % and DEA 20 wt. %-MDEA 10 wt. % are shown graphically in figure 5. It can be seen that, the enthalpy of the solution is almost a linear function of α for the solution with DEA, while for the mixtures with DEA-MDEA and DEA-AMP is a strong function of α.

CONCLUSIONS

Although aqueous mixtures of alkanolamines formulated with tertiary or sterically hinder alkanolamines are extensively used in the purification of gas streams contaminated with acid gases, solubility data of acid gases reported in these systems are scarce. Hence in this work, data for the solubility of CO_2 in aqueous mixtures of secondary (DEA) with tertiary (MDEA) and sterically hinder alkanolamines (AMP) have been obtained over ranges of temperature and pressure of industrial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial help from Fideicomiso para la Investigación con Instituciones de Educación Superior (FIES) del Instituto Mexicano del Petróleo, under Project FIES-95F-141-II.

REFERENCES

[1] T. Chakravarty, U.K. Phukan and R.H. Weiland, Reaction of the acid gases with mixtures of amines, Chem. Eng. Prog, 1985, 81 (4), pp. 32-36.

[2] L. Katti and R.A. Wolcott, Fundamental aspects of gas treating with formulated amine mixtures, 1987, Presented at the AICHE National Meeting, Minneapolis, MN.

[3] M.D. Anderson, M.J Hegarty and J.E. Jhonson, Flexible selective solvent design, Proceedings Annual Convention Gas Processors Association, 1992, 71, pp. 292-309.

[4] D.A. Glasscock, J.E. Critchfield and G.T. Rochelle, CO_2 absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine, Chem. Eng. Sci., 1991, 46, pp. 2829-2845.

[5] F.J. Jou, F.D. Otto and A.E. Mather, Vapor-liquid equilibrium of carbon dioxide in aqueous mixtures of monoethanolamine and methyldiethanolamine, Ind. Eng. Chem. Res., 1994, 33, pp. 2002-2005.

[6] O.F. Dawodu and A. Meisen, Solubility of carbon dioxide in aqueous mixtures of alkanolamines, J. Chem. Eng. Data, 1994, 39, pp. 548-552.

[7] D.P. Hagewiesche, S.S. Ashour, H.A. Al-Gawas and O.C. Sandall, Absorption of carbon dioxide into aqueous blends of monoethanolamine and n-methyldiethanolamine, Chemical Engineering Science, 1995, 50, pp. 1071-1079.

[8] F. Murrieta-Guevara, E. Rebolledo-Libreros and A. Trejo, Gas solubility of carbon dioxide and hydrogen sulfide in mixtures of sulfolane with monoethanolamine, Fluid Phase Equilibria, 1993, 86, 225-231.

[9] F. Murrieta-Guevara, E. Rebolledo-Libreros and A. Trejo, Gas solubility of hydrogen sulfide and carbon dioxide in mixtures of sulfolane with diethanolamine, Fluid Phase Equilibria, 1994, 95, pp. 163-174.

[10] E. Rebolledo-Libreros, Study on the solubility of carbon dioxide and hydrogen sulfide in mixtures of sulfolane with alkanolamines, M.Sc. Thesis, National Polytechnic Institute of Mexico, 1990, Mexico City, (in spanish).

[11] F. Murrieta-Guevara, E. Rebolledo-Libreros and A. Trejo, Solubility of carbon dioxide in binary mixtures of N-methylpyrrolidone with alkanolamines, J. Chem. Eng. Data, 1992a, 37, pp. 4-7.

[12] F. Murrieta-Guevara, E. Rebolledo-Libreros and A. Trejo, Solubility of hydrogen sulfide in mixtures of N-methylpyrrolidone with alkanolamines, Fluid Phase Equilibria, 1992b, 73, pp. 167-174.

[13] J.I. Lee, F.D. Otto and A.E. Mather, Solubility of carbon dioxide in aqueous diethanolamine solutions at high pressures, J. Chem. Eng. Data, 1972, 17, pp. 465-468.

LIST OF SYMBOLS

α	mol CO_2/mol alkanolamine
p	pressure
ΔH_s	enthalpy of solution

CAPTION TO FIGURES.

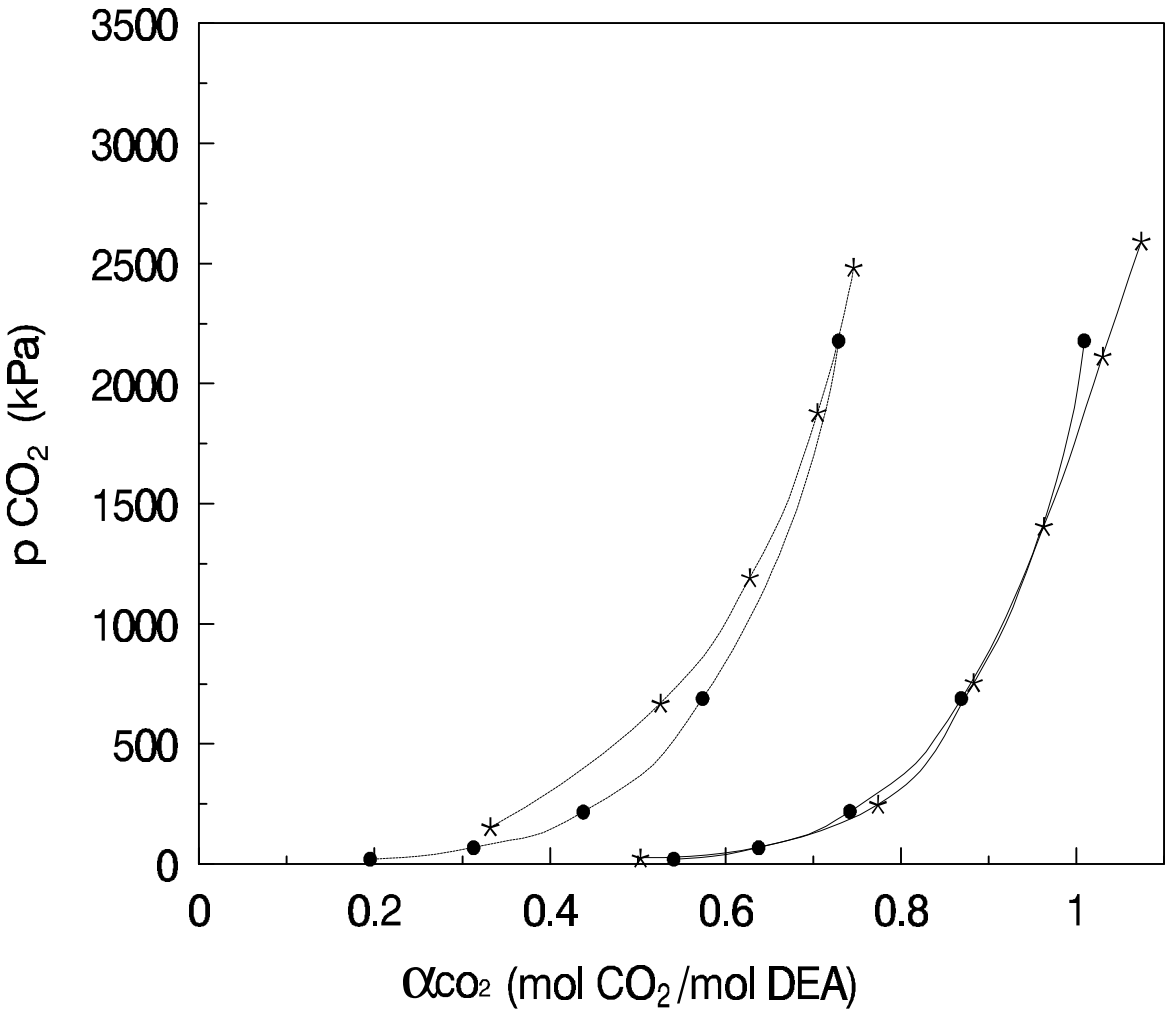
Figure 1. Comparision of solubility data for CO_2 in aqueous solution of DEA 30 wt. %: ∏, this work and , literature. The full lines are at 313.15 K and the dash lines are at 373.15 K.

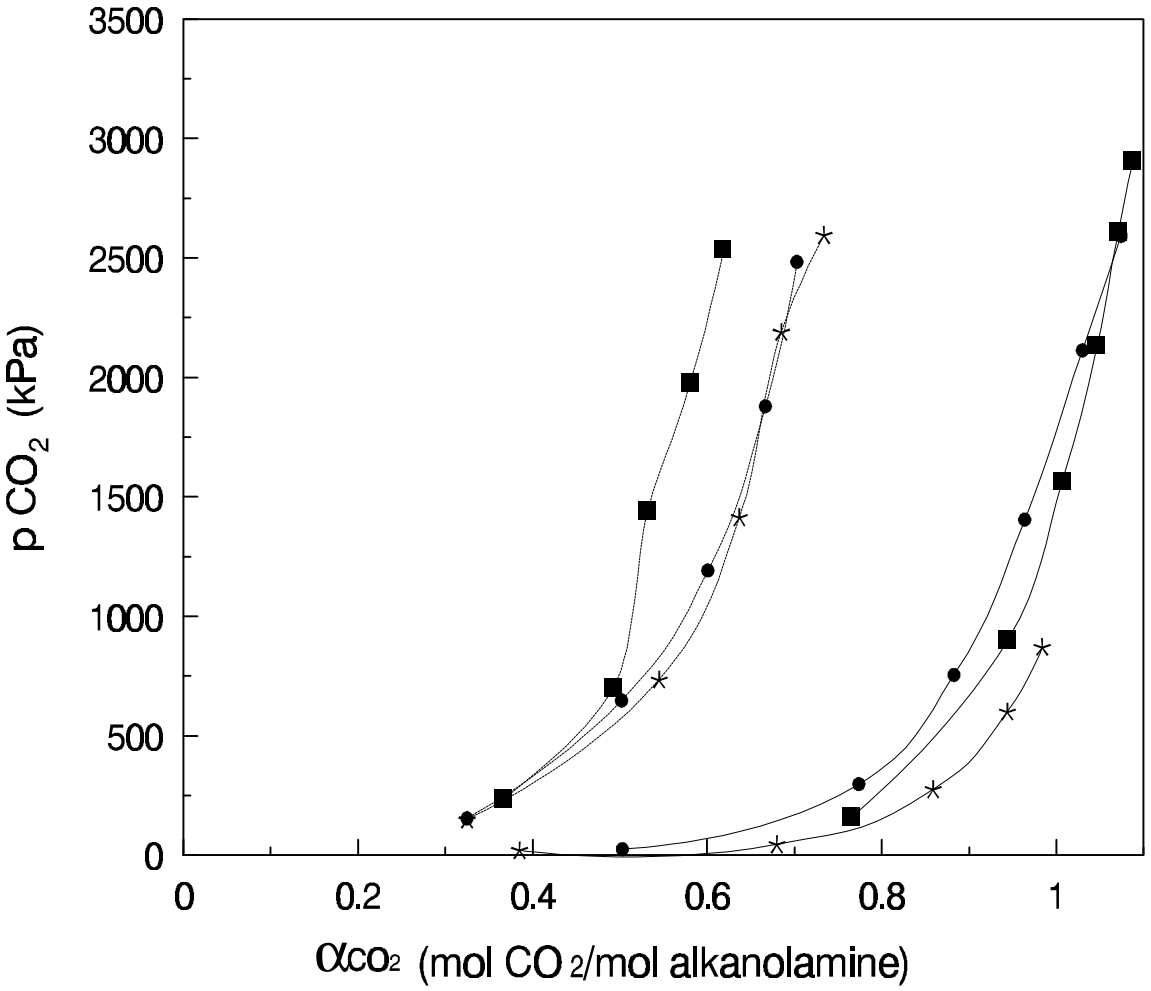
Figure 2. Solubility of CO_2 in aqueous mixtures of DEA with AMP: , DEA 30 wt. %, ■, DEA 25 wt. % - AMP 5 wt. % and ∏, DEA 20 wt.% - AMP 10 wt.%. The full lines are at 313.15 K and the dash lines are at 373.15 K.

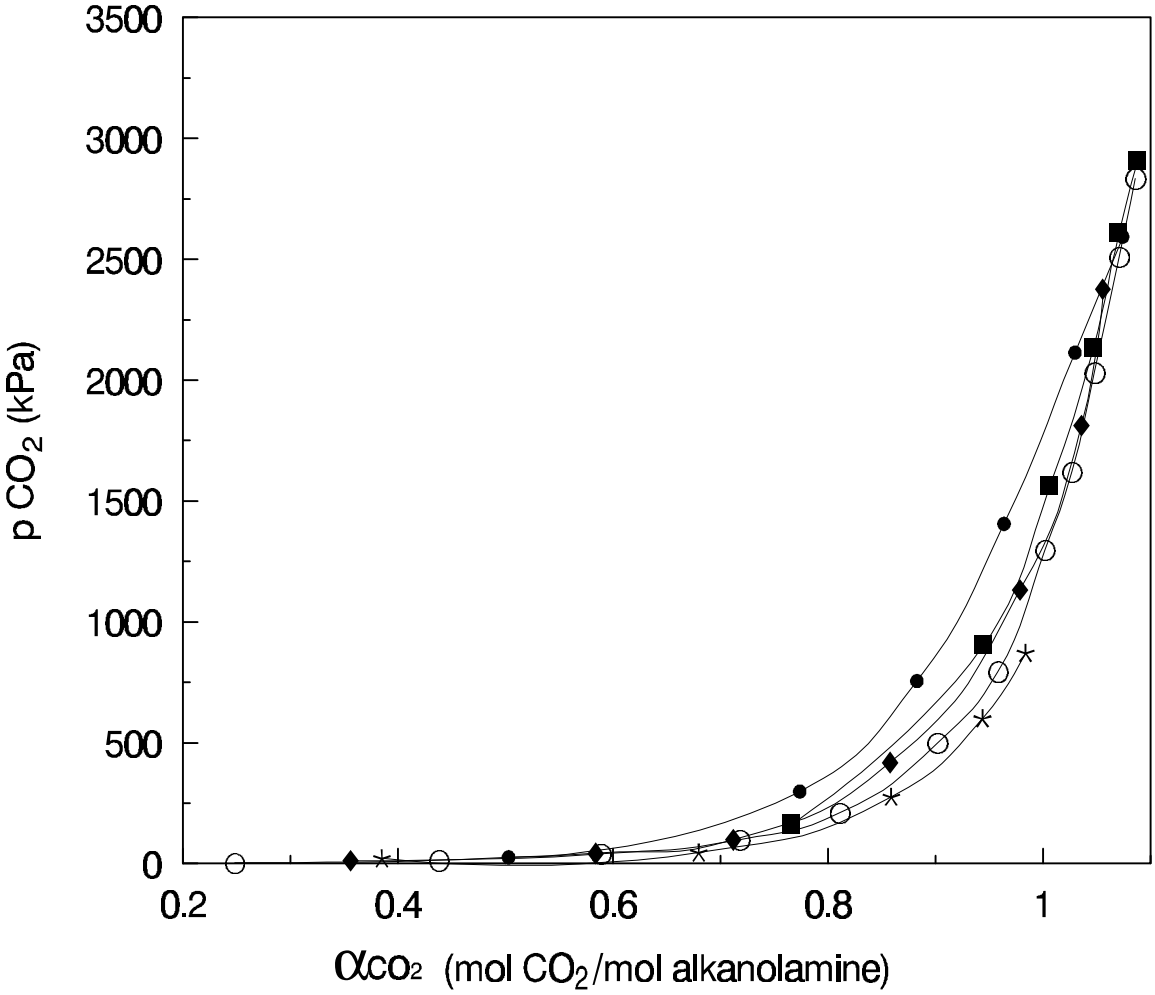
Figure 3. Solubility of CO_2 in aqueous mixtures of DEA with AMP and with MDEA at 313.15 K: , DEA 30 wt. %, ■, DEA 25 wt. % - AMP 5 wt. %, ∏, DEA 20 wt.% - AMP 10 wt.%, ◆, DEA 20 wt. % - MDEA 10 wt. % and DEA 10 wt.% - MDEA 20 wt.%.

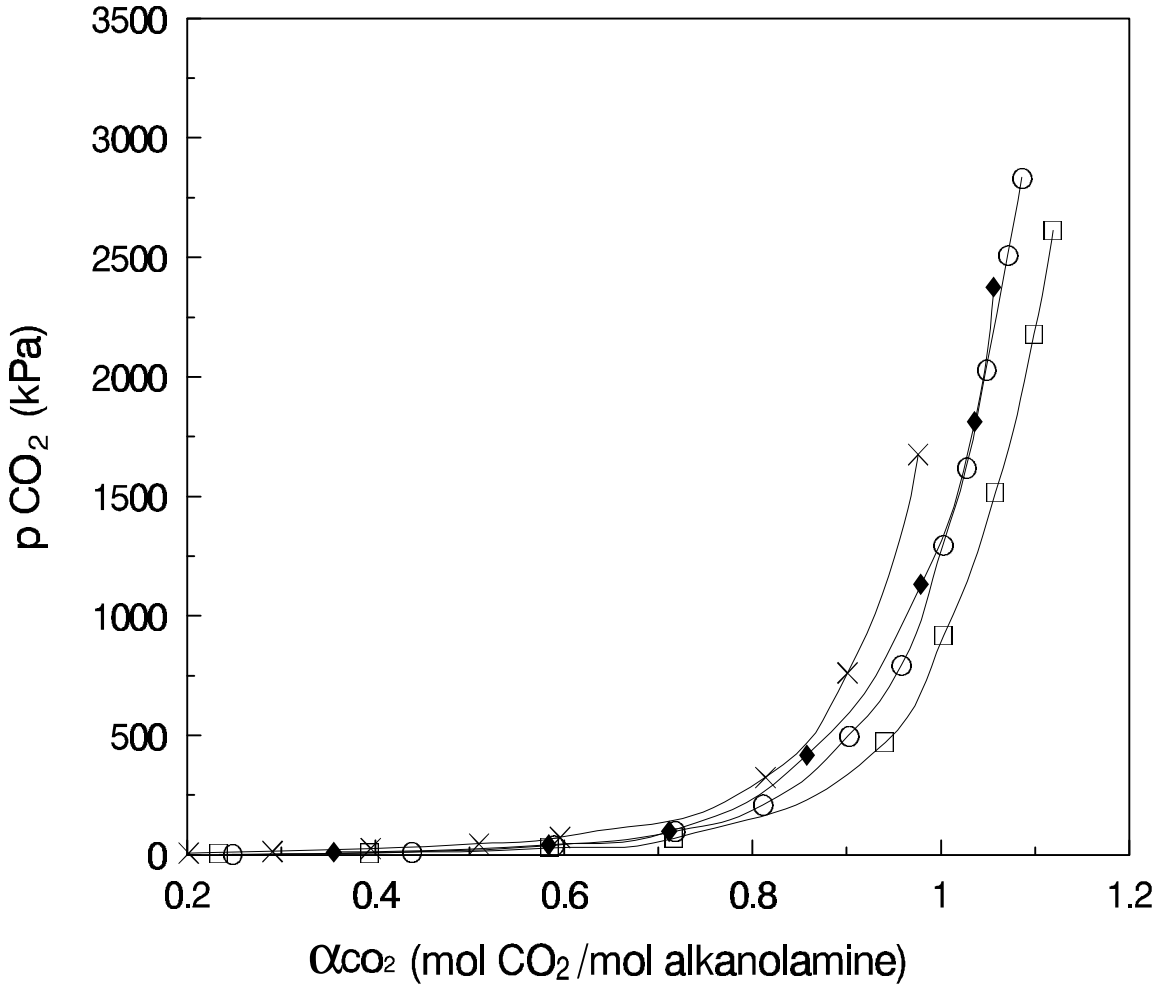
Figure 4. Solubility of CO_2 in aqueous mixtures of DEA with MDEA at 313.15 K: ◆, DEA 20 wt. % - MDEA 10 wt. %, , DEA 10 wt. % - MDEA 15 wt. %, , DEA 10 wt.% - MDEA 20 wt.%, and ⊆, DEA 10 wt.% - MDEA 20 wt.%

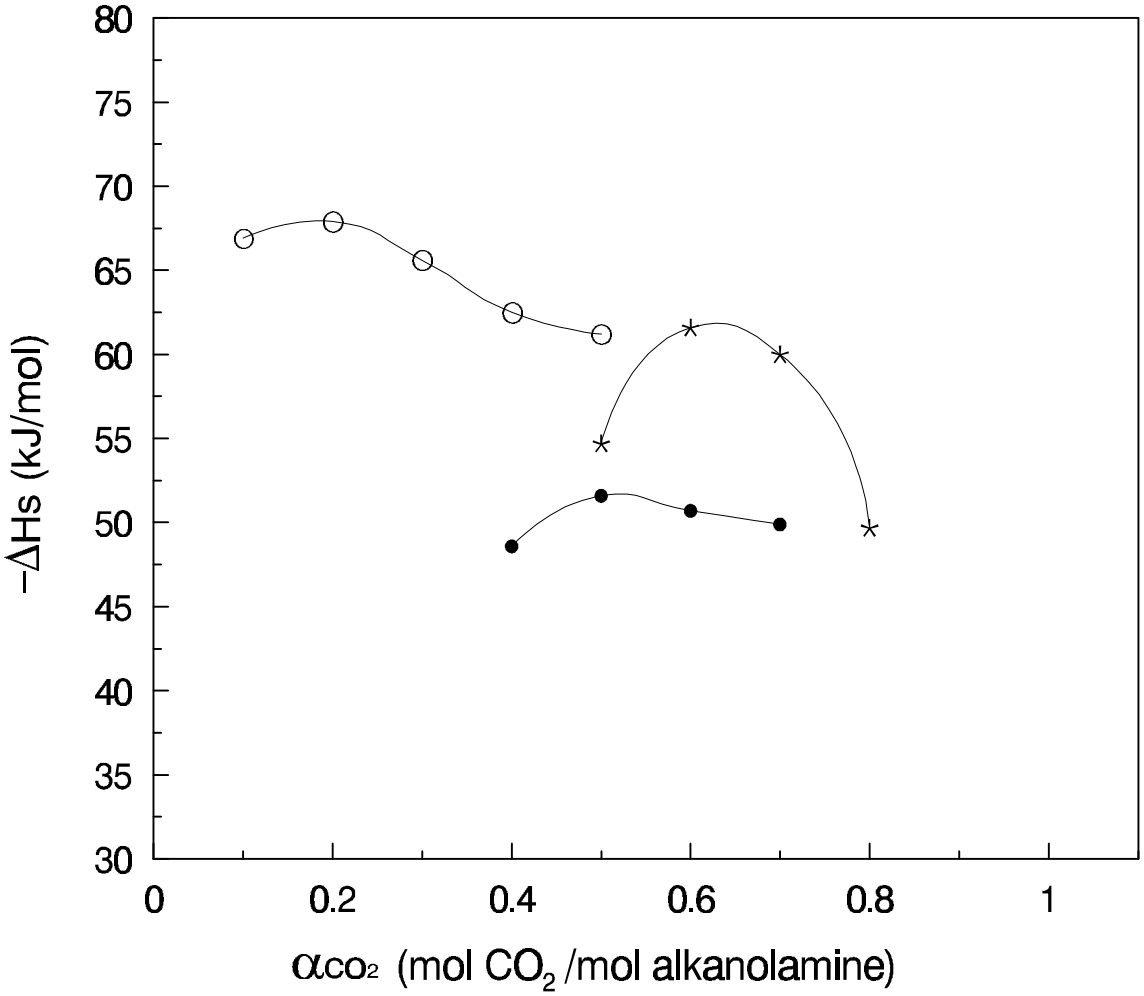
Figure 5. Effect of CO_2 loading in aqueos mixtures of DEA on the enthalpy of solution ΔHs: , DEA 30 wt. %, ∏, DEA 20 wt.% - AMP 10 wt.% and , DEA 10 wt.% - MDEA 20 wt.%.


3500
3000
2500
2000
1500
1000
500
0
p CO2 (kPa)
0
0.2
0.4
0.6
0.8
1
αco2 (mol CO2 /mol DEA)


3500
3000
2500
2000
1500
1000
500
0
p CO2 (kPa)
0
0.2
0.4
0.6
0.8
1
αco2 (mol CO 2/mol alkanolamine)


3500
3000
2500
2000
1500
1000
500
0
p CO2 (kPa)
0.2
0.4
0.6
0.8
1
αco2 (mol CO2/mol alkanolamine)


3500
3000
2500
2000
1500
1000
500
0
p CO2 (kPa)
0.2
0.4
0.6
0.8
1
1.2
αco2 (mol CO2 /mol alkanolamine)


80
75
70
65
60
55
50
45
40
35
30
−ΔHs (kJ/mol)
0
0.2
0.4
0.6
0.8
1
αco2 (mol CO2 /mol alkanolamine)