

# Solubility of Carbon Dioxide in Aqueous Mixtures of Monoethanolamine with Methyldiethanolamine

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**Solubility data of carbon dioxide in aqueous mixtures of monoethanolamine (MEA) with methyldiethanolamine (MDEA) have been measured at 40, 60, 80, and 100 °C and at partial pressures of carbon dioxide between 1.0 and 2000 kPa. The mixtures of alkanolamines studied are 30 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 24 wt % MEA + 6 wt % MDEA, and 30 wt % MEA aqueous solutions. The solubility of carbon dioxide in aqueous solutions are reported as functions of partial pressures of carbon dioxide at the temperatures studied.**

## Introduction

Alkanolamine aqueous solutions are frequently used for the removal of acidic gases, such as CO<sub>2</sub>, H<sub>2</sub>S, and COS, from natural, refinery, and synthesis gas streams. Aqueous MEA (2-aminoethanol, H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH) solutions have been used extensively due to their high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons (1). Due to the formation of rather stable carbamates by primary (or secondary) amine with CO<sub>2</sub>, the loading capacity of MEA cannot reach a value much beyond 0.5 mol of CO<sub>2</sub>/(mol of amine) (2). Aqueous MDEA (*N*-methyldiethanolamine, CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>) solutions are finding good acceptance in industry for the selective removal of H<sub>2</sub>S from gas streams which contain both CO<sub>2</sub> and H<sub>2</sub>S. Advantages of the use of MDEA solutions include their high loading capacity (about 1.0 mol CO<sub>2</sub>/(mol of amine)) and low heat of reaction with the acid gases (3). The lower heat of reaction leads to lower energy requirements for regeneration. Another advantage of MDEA is that it does not degrade readily. However, the low reaction rate of CO<sub>2</sub> with tertiary amines limits the use of MDEA solutions (2).

Recently the use of blended amines (a solution of two or more amines in varying compositions) in gas-treating processes is a subject of potentially major industrial importance (4). The use of blended amines, which contain a combination of the absorption characteristics of the amines, such as higher loading capacity and faster reaction rate, brings about a considerable improvement in absorption and a great savings in energy requirements. Blends of primary and tertiary amines, mixtures of MEA and MDEA, have been suggested for use in CO<sub>2</sub> removal (4). Absorption rates of CO<sub>2</sub> in aqueous solutions of mixtures of MEA-MDEA have been studied experimentally at 298 K (5). Besides reaction kinetics data, information on the equilibrium solubility of acidic gases in aqueous MEA/MDEA solutions is also required for the efficient design of treating units. The solubility of CO<sub>2</sub> in 2.0 kmol/m<sup>3</sup> MEA + 2.0 kmol/m<sup>3</sup> MDEA aqueous solutions were reported at 40 and 80 °C for partial pressures of CO<sub>2</sub> below 315 kPa (6). Other solubility data of CO<sub>2</sub> in MEA/MDEA aqueous solutions have not yet been reported in the literature. Thus, it is the objective of this research to study experimentally the solubility of CO<sub>2</sub> in aqueous MEA/MDEA solutions at temperatures of 40, 60, 80, and 100 °C and at partial pressures of CO<sub>2</sub> between 1.0 and 2000 kPa. The blended-amine aqueous solutions chosen for study are 30 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 24 wt % MEA

+ 6 wt % MDEA, and 30 wt % MEA.

## Experimental Section

In order to make CO<sub>2</sub> solubility measurements over the MEA/MDEA aqueous solutions at partial pressures of CO<sub>2</sub> from 1 to 2000 kPa, two vapor-liquid equilibrium apparatus have been set up in this study. For CO<sub>2</sub> partial pressures above 200 kPa, the equilibrium solubility of CO<sub>2</sub> was measured in a batch equilibrium cell, shown schematically in Figure 1. The cell is a stirred 0.5 dm<sup>3</sup> ZipperClave which is similar to that of Sartori and Savage (2). Approximately 350 mL of the solvent was fed by gravity to the equilibrium cell. The apparatus was then purged with CO<sub>2</sub> to remove traces of oxygen and was brought to the desired temperature. The partial pressure of CO<sub>2</sub> was adjusted to an amount indicated by the total pressure of the system in the range of 200-2000 kPa. The temperature of the cell was controlled by a temperature controller made by Autoclave Engineers. The pressure was indicated by a digital pressure indicator also made by Autoclave Engineers. The measurement accuracy of the digital pressure indicator is ±0.25% of the range 0-500 psig. On the basis of the manual provided by Autoclave Engineers for the calibration procedure, the zero and span adjustment of the digital pressure indicator were normally adjusted weekly. The pressure transducers were mounted outside the equilibrium cell. The temperature error due to the transducer of the digital pressure indicator is ±0.0075% / °F of the range. When the total pressure of the cell does not change for 4 h, the equilibrium is assumed to have been reached; it will normally take 20-24 h for the system to reach equilibrium. At equilibrium, three liquid samples (20-25 cm<sup>3</sup>) were withdrawn from the cell and analyzed for the solubility of CO<sub>2</sub> by using a titration method, described shortly. The CO<sub>2</sub> partial pressure was obtained by subtracting the partial pressure of water from the total pressure of the system. The partial pressure of water was obtained by using Raoult's law. For partial pressures of CO<sub>2</sub> below 200 kPa, the equilibrium solubility of CO<sub>2</sub> in blended amines was measured in a vapor-recirculation equilibrium cell, as shown in Figure 2. The equilibrium cell is a 1-dm<sup>3</sup> stainless steel sample cylinder made by Parker Hannifin Corp. Another stainless steel sample cylinder (0.3 dm<sup>3</sup>) is connected to the equilibrium cell to increase the volume of the vapor phase. Two cylinders were mounted vertically in a thermostated oil bath. The equilibrium setup is similar to that of Roberts and Mather (7). The temperature was controlled by an EX-810B basic immersion circulator, made by NESLAB Instruments Inc., to a stability within ±0.1 °C of the set-point temperature. The pressure of the system is indicated by an Ashcroft test gauge with the scale reading of 0.2 psi. The vapor-phase CO<sub>2</sub> was recirculated by using a diaphragm pump made by KNF Co. In the region of low partial pressures of CO<sub>2</sub>, nitrogen was introduced and mixed with CO<sub>2</sub>, and the partial pressure of CO<sub>2</sub> was determined by gas chromatography. Since the solubility of nitrogen is extremely small, is usually negligible, the introduction of nitrogen in the vapor phase to obtain the lower CO<sub>2</sub> partial pressures is a general procedure (7, 6, 7). A Shimadzu Model 8A GC equipped with a TCD (thermal conductivity detector) was used for analysis. The column was a 1/8-in.-diameter, 8-ft-length stainless steel column

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Table I. Solubility of CO<sub>2</sub> in 15.3 wt % MEA Aqueous Solution at 40 °C<sup>a</sup>

this study		Jones et al (8)		Lee et al.			
<i>p</i> /kPa	loading $\alpha$	<i>p</i> /kPa	loading $\alpha$	(9)		(10)	
<i>p</i> /kPa	loading $\alpha$	<i>p</i> /kPa	loading $\alpha$	<i>p</i> /kPa	loading $\alpha$	<i>p</i> /kPa	loading $\alpha$
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
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	3160.0	1.090
1000	0.900			488.0	0.808		
1370	0.942			929.0	0.897		
1900	0.992			1639.0	0.989		
2100	1.022			2873.0	1.072		
2550	1.049						
AAD/%	12.0		18.7		19.4		18.5
MAD/%	26.0		31.6		39.5		28.9

<sup>a</sup>*p*, partial pressure of CO<sub>2</sub>; loading  $\alpha$ , mol of CO<sub>2</sub>/(mol of amine); AAD%, average absolute percent deviation; MAD%, maximum absolute percent deviation.

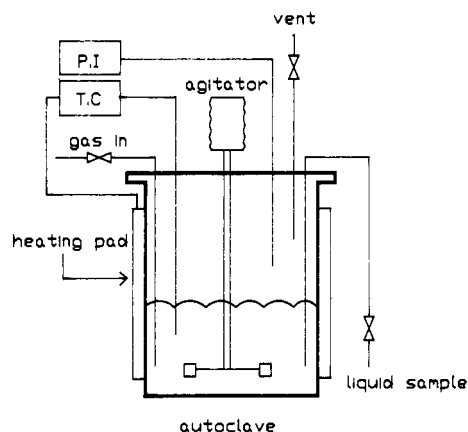


Figure 1. High-pressure vapor-liquid equilibrium apparatus.

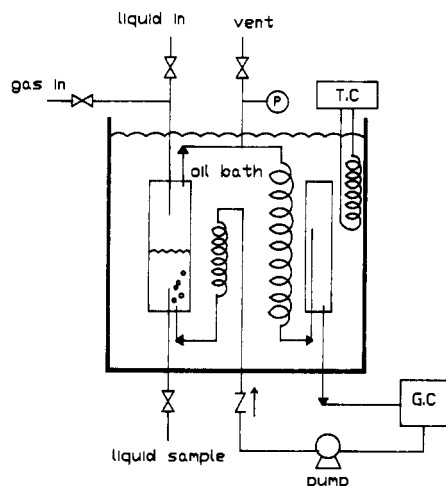


Figure 2. Low-pressure vapor-liquid equilibrium apparatus.

packed with 50/80 mesh Porapak Q, and it was connected in series with a column of the same size filled with 50/80 mesh Porapak R. The carrier gas was hydrogen. Temperatures were set at 100 and 180 °C for the column and the TCD detector, respectively. Before the introduction of the solution, the system was purged with nitrogen to remove traces of oxygen. The temperature of the thermostated oil bath was brought to the desired temperature. An aqueous alkanolamine solution of approximately 0.5 L was added to the cell. When necessary, nitrogen was introduced and mixed with CO<sub>2</sub> to maintain the system pressure at about 180 kPa and to obtain the desired

CO<sub>2</sub> partial pressures. The vapor phase was circulated by the diaphragm pump to reduce the time required for reaching the equilibrium. The vapor-phase composition was analyzed by the on-line gas chromatography for every 30 min. When compositions of the vapor phase do not change for 2 h, the equilibrium is assumed to have been reached. Normally, it takes about 4 h for the system to reach equilibrium. At equilibrium, the liquid samples were withdrawn and analyzed for the solubility of CO<sub>2</sub> using the titration method, and the partial pressure of CO<sub>2</sub> was calculated by the mole fractions of the vapor phase determined by gas chromatography.

As for the titration method, a liquid sample was withdrawn from the equilibrium cell into a vessel containing excess 1.0 M NaOH solution, thus converting free dissolved CO<sub>2</sub> into the nonvolatile ionic species. An excess amount of BaCl<sub>2</sub> solution is then added to the solution. The solution is shaken well to permit all absorbed (physically and chemically) CO<sub>2</sub> to precipitate the carbonate as BaCO<sub>3</sub>. The excess NaOH was titrated with HCl solution using phenolphthalein as the indicator. Using methyl orange as the indicator, a solution of HCl is then added. The amount of HCl added can be used to calculate the solubility of CO<sub>2</sub> in terms of the moles of CO<sub>2</sub> per mole of amine. NaOH, BaCl<sub>2</sub>, and HCl are products of Nihon Shiyaku Industries. MEA is Riedel-de Haën reagent grade with 99% purity and MDEA is Riedel-de Haën reagent grade with 98.5% purity. Alkanolamine aqueous solutions were prepared from distilled water. To determine the molarity of an alkanolamine aqueous solution, the solution was titrated with HCl using methyl orange as the indicator. In the 1990 catalog for Riedel-de Haën Laboratory Chemicals, MEA is marked as corrosive and MDEA as irritant; both MEA and MDEA are strong irritants of the eyes, are harmful in contact with skin, and are toxic by inhalation. When handling these chemicals, suggestions concerning the safety precautions have to be carefully followed. Also, before the amines are introduced into the equilibrium cell, it has to be definitely assured that there is no leakage found in the system.

## Results and Discussion

To confirm the sampling and analytical procedures and to test the two vapor-liquid equilibrium apparatus, we have obtained data for the system at which data had previously been reported in the literature. Solubilities of CO<sub>2</sub> in 15.3 wt % MEA aqueous solutions have been studied (8-10) at 40 °C and at partial pressures of CO<sub>2</sub> from 1 to 3000 kPa. Thus, solubilities of CO<sub>2</sub> in 15.3 wt % MEA aqueous solution at 40 °C have been measured in this work, and the results are presented in Table I. Comparison of the results is also shown graphically in Figure

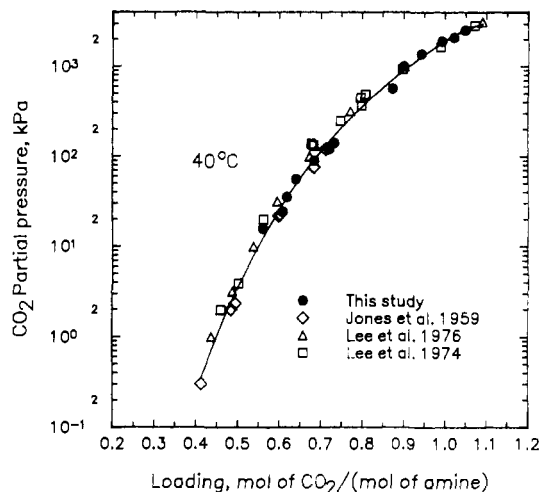


Figure 3. Solubility of CO<sub>2</sub> in 15.3 wt % MEA aqueous solution at 40 °C: points, experimental data; solid line, fitted values.

Table II. Solubility of CO<sub>2</sub> in 30 wt % MDEA Aqueous Solution<sup>a</sup>

<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$	<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$
40	1.2	0.244	80	1.7	0.155
	2.8	0.306		8.9	0.220
	6.5	0.401		18.1	0.261
	28.0	0.672		43.9	0.353
	72.8	0.811		82.8	0.400
	140.3	0.911		145.1	0.487
	208.5	0.919		376.0	0.538
	455.0	0.990		804.0	0.698
	834.0	1.016		1197	0.803
	1241	1.065			
60	1.1	0.189	100	3.0	0.186
	3.2	0.245		5.9	0.197
	7.7	0.312		9.5	0.208
	22.4	0.424		11.1	0.215
	44.7	0.499		17.8	0.234
	98.5	0.647		19.1	0.239
	163.6	0.738		52.9	0.299
	829.0	0.897		123.9	0.373
	1236	0.955		135.6	0.375
	1588	0.978		1022	0.508
1946	1.007	1187	0.524		
		1525	0.576		
		1890	0.644		

<sup>a</sup>*p*, partial pressure of CO<sub>2</sub>; loading  $\alpha$ , mol of CO<sub>2</sub>/(mol of amine).

3. As shown in Figure 3, the solubility data of Jones et al. (8) differ slightly from those of Lee et al. (both refs 9 and 10). Using the least-squares fit of all data points to a polynomial equation, a solid curve, as shown in Figure 3, is determined. The determined equation is as follows

$$\ln(p/\text{kPa}) = -19.2248 + 56.9016\alpha - 20.9694\alpha^2 - 32.5351\alpha^3 + 9.8811\alpha^4 + 31.4132\alpha^5 - 17.904\alpha^6$$

where *p* is the CO<sub>2</sub> partial pressure and  $\alpha$  the loading in terms of moles of CO<sub>2</sub> absorbed per mole of amine. The average and the maximum percent absolute deviations between the calculated and experimental CO<sub>2</sub> partial pressures are also presented in Table I. As can be seen from Figure 3, the solubility data obtained in this work from both the high-pressure and low-pressure vapor liquid equilibrium apparatus are generally in good agreement with the data of Lee et al. (9, 10) and Jones et al. (8).

The alkanolamine aqueous solutions studied are 30 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 24 wt % MEA + 6 wt % MDEA, and 30 wt % MEA. The CO<sub>2</sub> solubility data in

Table III. Solubility of CO<sub>2</sub> in 12 wt % MEA + 18 wt % MDEA Aqueous Solution

<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$	<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$
40	1.0	0.357	80	3.0	0.253
	3.7	0.441		4.8	0.290
	9.0	0.488		9.5	0.327
	17.4	0.536		21.0	0.359
	45.9	0.608		35.9	0.399
	107.4	0.684		82.6	0.480
	157.5	0.710		130.7	0.527
	448.0	0.781		419.0	0.593
	821.0	0.839		826.0	0.646
	1421	0.889		1226	0.700
60	1579	0.927	100	1612	0.749
	1966	0.947		1998	0.764
	0.9	0.278		2.1	0.197
	4.0	0.346		8.1	0.262
	10.7	0.417		12.0	0.287
	23.7	0.459		21.1	0.309
	46.6	0.512		46.8	0.353
	85.0	0.561		87.2	0.411
	145.4	0.605		769.0	0.532
	423.0	0.680		1169	0.576
816.0	0.742	1541	0.611		
1244	0.807	1934	0.645		
1623	0.840				
2016	0.872				

<sup>a</sup>*p*, partial pressure of CO<sub>2</sub>; loading  $\alpha$ , mol of CO<sub>2</sub>/(mol of amine).

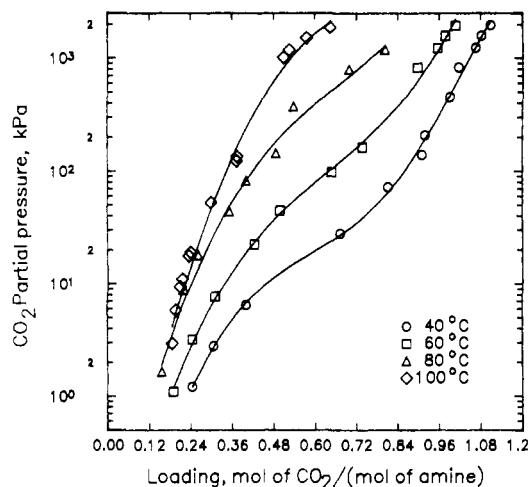


Figure 4. Solubility of CO<sub>2</sub> in 30 wt % MDEA aqueous solution at 40–100 °C: points, experimental data; solid lines, smoothed values.

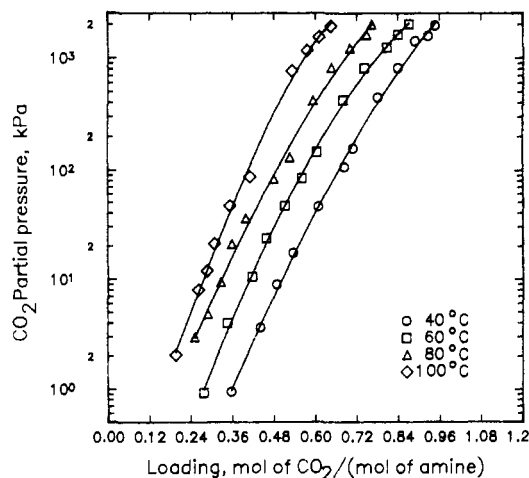


Figure 5. Solubility of CO<sub>2</sub> in 12 wt % MEA + 18 wt % MDEA aqueous solution at 40–100 °C: points, experimental data; solid lines, smoothed values.

**Table IV. Solubility of CO<sub>2</sub> in 24 wt % MEA + 6 wt % MDEA Aqueous Solution**

<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$	<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$
40	2.9	0.473	80	2.0	0.257
	6.6	0.500		4.6	0.332
	11.6	0.510		9.3	0.370
	29.4	0.549		18.4	0.407
	52.4	0.584		40.5	0.448
	82.2	0.612		64.6	0.474
	132.2	0.637		90.6	0.502
	449.0	0.678		401.0	0.545
	863.0	0.745		794.0	0.602
	1256	0.808		1187	0.625
1649	0.817	1580	0.646		
1987	0.849	1925	0.677		
60	1.5	0.355	100	4.0	0.235
	4.3	0.415		5.3	0.282
	12.0	0.448		15.6	0.334
	28.3	0.489		29.2	0.375
	48.7	0.524		60.9	0.417
	85.8	0.548		95.4	0.439
	117.2	0.566		140.0	0.457
	465.0	0.637		426.0	0.478
	823.0	0.672		764.0	0.520
	1244	0.703		1164	0.548
1595	0.719	1509	0.584		
1981	0.752	1943	0.620		

<sup>a</sup>*p*, partial pressure of CO<sub>2</sub>; loading  $\alpha$ , mol of CO<sub>2</sub>/(mol of amine).

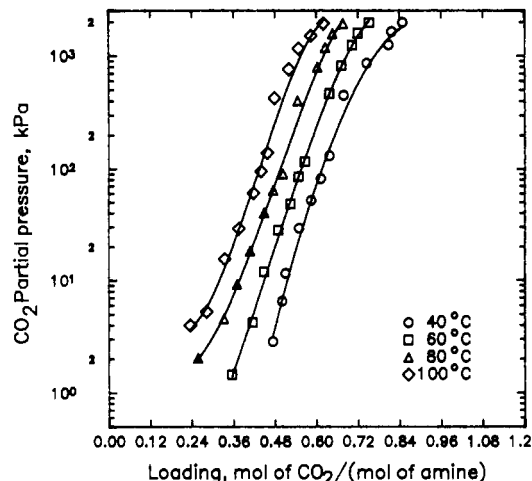
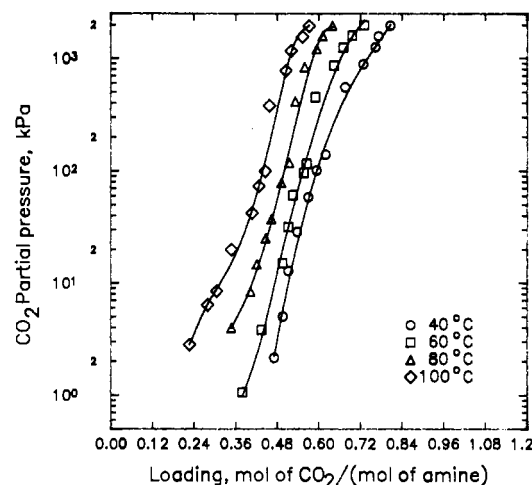
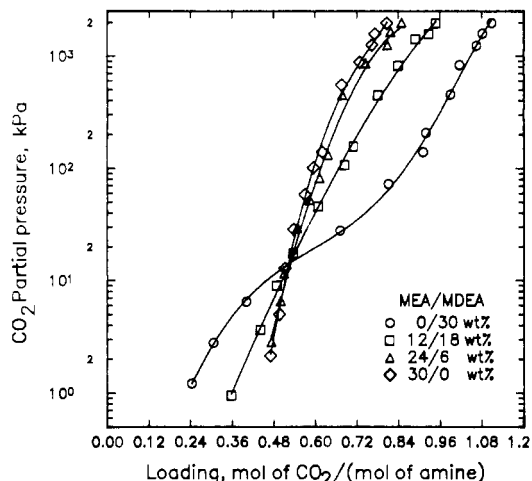
**Table V. Solubility of CO<sub>2</sub> in 30 wt % MEA Aqueous Solution**

<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$	<i>t</i> /°C	<i>p</i> /kPa	loading $\alpha$
40	2.2	0.471	80	4.0	0.347
	5.0	0.496		8.3	0.403
	12.8	0.512		14.7	0.421
	28.7	0.538		25.1	0.446
	58.4	0.570		37.5	0.463
	101.3	0.594		78.7	0.492
	140.1	0.620		117.9	0.515
	552.0	0.676		413.0	0.532
	883.0	0.728		834.0	0.559
	1256	0.763		1206	0.594
1580	0.772	1578	0.611		
1973	0.806	1964	0.639		
60	1.1	0.379	100	2.8	0.227
	3.8	0.435		6.4	0.279
	15.1	0.495		8.5	0.305
	31.8	0.512		19.9	0.348
	61.0	0.526		42.3	0.407
	96.5	0.557		73.4	0.427
	116.3	0.565		99.9	0.445
	451.0	0.590		379.0	0.457
	858.0	0.644		772.0	0.505
	1244	0.671		1165	0.520
1595	0.696	1551	0.553		
1975	0.731	1951	0.572		

<sup>a</sup>*p*, partial pressure of CO<sub>2</sub>; loading  $\alpha$ , mol of CO<sub>2</sub>/(mol of amine).

amine aqueous solutions at 40, 60, 80, and 100 °C are presented in Tables II–V. Plots of CO<sub>2</sub> partial pressures as functions of the CO<sub>2</sub> loading are given in Figures 4–7. For the 30 wt % MDEA aqueous solution, the solubility of CO<sub>2</sub> yields a value greater than 1.0 at 40 and 60 °C. As shown in Figures 4–7, the higher the CO<sub>2</sub> partial pressure, the higher the CO<sub>2</sub> loading obtained in the alkanolamine aqueous solutions. Generally, the solubility of CO<sub>2</sub> changes systematically with the temperature; the higher the temperature of the system, the lower the CO<sub>2</sub> solubility observed.

To investigate the effects of amine concentrations on CO<sub>2</sub> solubility, plots of solubility data in four alkanolamine aqueous solutions as functions of partial pressures of CO<sub>2</sub> at 40 and 80 °C are shown in Figures 8 and 9. As can be seen in Figure

**Figure 6. Solubility of CO<sub>2</sub> in 24 wt % MEA + 6 wt % MDEA aqueous solution at 40–100 °C: points, experimental data; solid lines, smoothed values.****Figure 7. Solubility of CO<sub>2</sub> in 30 wt % MEA aqueous solution at 40–100 °C: points, experimental data; solid lines, smoothed values.****Figure 8. Solubility of CO<sub>2</sub> in MEA/MDEA aqueous solutions at 40 °C: points, experimental data; solid lines, smoothed values.**

8, CO<sub>2</sub> solubilities vary systematically from 30 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, and 24 wt % MEA + 6 wt % MDEA to 30 wt % MEA, and all four solubility curves cross each other at the CO<sub>2</sub> partial pressure of 17 kPa. In Figure 9, CO<sub>2</sub> solubility curves also cross each other. Similar phenomena, crossing of the solubility curves, have been previously noted by Sartori and Savage (2).

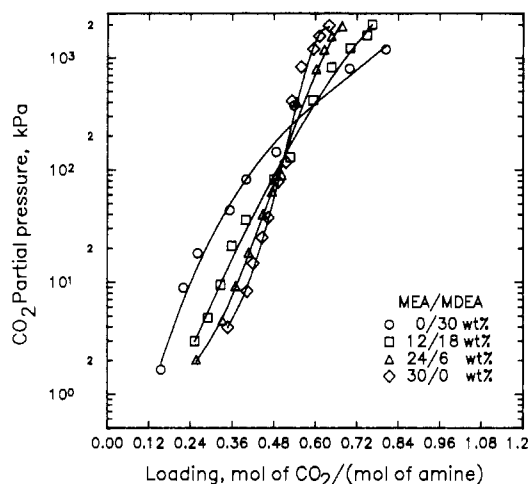


Figure 9. Solubility of CO<sub>2</sub> in MEA/MDEA aqueous solutions at 80 °C: points, experimental data; solid lines, smoothed values.

### Conclusion

The equilibrium solubility data of CO<sub>2</sub> into the blends of primary and tertiary amines, aqueous mixtures of MEA and MDEA, have been reported at temperatures of 40, 60, 80, and 100 °C and at CO<sub>2</sub> partial pressures from 1.0 to 2000 kPa. The mixtures of amines studied are 30 wt % MDEA, 12 wt % MEA +

18 wt % MDEA, 24 wt % MEA + 6 wt % MDEA, and 30 wt % MEA. Solubilities of CO<sub>2</sub> in 15.3 wt % MEA aqueous solution at 40 °C, previously reported by other investigators in the literature, have also been studied in this work to test the apparatus and to confirm the sampling and analytical procedures. The solubility data obtained in this work are generally in good agreement with the data reported by other investigators.

Registry No. MEA, 141-43-5; MDEA, 105-59-9; CO<sub>2</sub>, 124-38-9.

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## Solubility of Ethylene in Benzene at Pressures to 9 MPa and Temperatures from 353 to 433 K

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An experimental procedure for measuring the solubility of ethylene in benzene at elevated temperatures and pressures is described. The solubility has been measured as a function of pressure at six temperatures (353, 373, 393, 413, 423, and 433 K), and the results have been presented in tabular form and also in graphs. In addition an empirical equation has been developed which fits the measured data with an average error of 2.8%. Comparisons with the relevant literature data illustrate the significant differences which exist among the solubility data recorded by previous workers.

### Introduction

The studies described were prompted by commercial interest in optimizing the production process and product structures for some speciality products manufactured by copolymerizing ethylene with vinyl esters. In order to properly analyze kinetic data from polymerization experiments, values of the solubility of ethylene in benzene were required for a range of reactor operating conditions. A review of the relevant literature showed significant discrepancies among the reported solubility values. Consequently it was necessary to measure these values.

### Materials

The ethylene was purchased from Commonwealth Industrial Gases of Australia (a subsidiary of British Oxygen) as their

highest purity grade, which is better than 99.5 wt % pure. The benzene was purchased from B.D.H. Australia as their Univar grade, which was also rated as better than 99.5 wt % pure.

### Experimental Section

The general operating procedure is described first, and subsequently the details of the sampling and analyses for ethylene are presented.

The equipment diagram is shown as Figure 1. Experiments were carried out in a 1.0-L stainless steel reactor, fitted with a "Magnedrive" stirrer, which was set at 500 rpm for all runs. Temperature control was effected by means of an external heating element with a "Eurotherm" P.I.D. controller. Cold water was passed through an internal cooling coil to correct any overshoot of temperature which occurred. The temperature control was within  $\pm 1$  K. The maximum operating conditions of 9 MPa and 433 K were well below the rated maximum working conditions of the reactor, which were 34 MPa and 616 K. As an additional safety measure, the reactor was fitted with a rupture disk rated at 22 MPa at 295 K (the bursting pressure would be less than this at elevated temperatures). Whenever the reactor was dismantled and reassembled, the system was leak-tested with helium.

Each solubility measurement was initiated by first purging the reactor with ethylene. The reactor was then pressurized to approximately 5000 kPa with ethylene, and approximately 400 mL of benzene was pumped in. The Magnedrive stirrer was switched on and set to 500 rpm. The reactor was then brought