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Results and Discussion

The experimentally determined dew and bubble points for the carbon dioxide-propane mixtures are presented in Tables I-X and are shown graphically for two of the mixtures in Figures 3 and 4. Dew points for the ternary mixture of carbon dioxide, propane, and methane are presented in Table XI and shown graphically in Figure 5. The maximum uncertainty in pressure measurements was estimated to be ±0.015 MPa and the maximum uncertainty in temperature measurements was estimated to be ±0.05 K.

Pressure-composition diagrams were constructed for 10 isotherms by using the data from the literature and the dew and bubble point data obtained in this work. In order to incorporate the data of this work, the pressure values were taken from the intersection of the given constant-temperature lines with the dew and bubble point curves for each mixture. Figure 6 presents *P*-*x* curves for several temperatures and Figure 7 presents *P*-*y* curves for several temperatures. In general, good agreement was obtained between the data presented in this investigation and the data of the other investigators.

Solid formation experiments were conducted over the pressure range 0.124-0.165 MPa. The experiments were conducted for each of the binary mixtures investigated in this study. The temperature of a given mixture was lowered at constant pressure until solid crystals appeared. The mixtures were then heated at constant pressure until the solids disappeared. In general the appearance temperature was several degrees lower than the disappearance temperature. The temperatures at which solid appeared range from 183.1 to 198.3 K and the temperatures at which solid disappeared varied from 194.3 to 201.4 K. Solid formation temperatures increased as the carbon dioxide concentration increased.

Registry No. Propane, 74-98-6; methane, 74-82-8; carbon dioxide, 124-38-9.

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Solubility of Carbon Dioxide in Aqueous Diethanolamine Solutions at Elevated Temperatures and Pressures

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The solubility of carbon dioxide in 10, 20, and 30 wt % aqueous diethanolamine (DEA) solutions has been determined for elevated temperatures (100-205 °C) and CO_2 partial pressures (70-4000 kPa). The results were acquired by a simple experimental procedure and agree, on the average, within 10% of literature values reported for more moderate temperatures and pressures.

Introduction

Aqueous diethanolamine (DEA) solutions are used extensively for the removal of H_2S and CO_2 from raw natural gas and other light hydrocarbon mixtures. Knowledge of the equilibrium solubility of these acid gases in DEA solution is essential for the proper design and operation of absorption and desorption equipment. Furthermore, many gas treating plants experience problems with DEA degradation, i.e., the irreversible reaction of DEA with CO_2. To understand degradation, which is particularly serious at elevated temperatures and pressures, it is also necessary to have a good knowledge of CO_2 solubility in DEA solutions. The solubility data presented in this paper were acquired for use in a recent study on DEA degradation (*1*).

Data on CO_2 solubility in aqueous DEA solutions have been reported by several investigators, but no results have been published for elevated temperatures and pressures. Table I summarizes the ranges of experimental variables investigated by previous researchers. The present study provides CO_2 solubility data under the following conditions: DEA concentration 10-30 wt %; Temperature, 100-205 °C; CO_2 partial pressure, 70-4000 kPa.

Table I. Summary of Experimental Conditions Used by Previous Researchers

researcher	DEA concn, wt %	temp, °C	CO_2 partial press., kPa
Bottoms (*3*)	50	25-55	1.33-101.33
Mason and Dodge (*4*)	5-80	0-75	1.33-101.33
Reed and Wood (*5*)	25	100-140	241.3-1571.3
Dow (*6*)	5-40	20-100	1.33-400
Murzin and Leites (*7*)	5-80	20-90	0.0133-93.33
Lee et al. (*8*)	5-50	25-120	0.689-5707
Lawson and Garst (*9*)	25	38-121	2.0-4266

Apparatus

Aqueous DEA solutions were prepared by mixing distilled water and commercial-grade DEA which had a purity in excess of 98%. The carbon dioxide had a minimum purity of 99.5%.

The equipment used in this work consisted essentially of a 600-mL stirred, stainless steel autoclave (supplied by the Parr Instrument Co., Moline, IL, Model 4560; see Figure 1). The autoclave, which was equipped with an electric heating mantle, could be operated at temperatures ranging from ambient to 400 °C. The temperature was controlled to within ±0.5 °C by an automatic controller whose output was displayed on a digital

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Table II. Vapor Pressure of DEA Solutions as a Function of Temperature

	vapor press., kPa			
temp, °C	0% DEA[a]	10% DEA[a]	20% DEA[a]	30% DEA[a]
100	101.3	101.3	101.3	101.3
120	202.7	197.8	186.2	168.4
140	379.0	362.5	338.5	300.4
160	637.8	607.7	567.4	496.0
180	1027.1	985.0	919.0	837.3
200	1568.6	1525.8	1477.5	1352.4
210	1971.3	1885.3	1790.7	1677.5

[a] Weight percent.

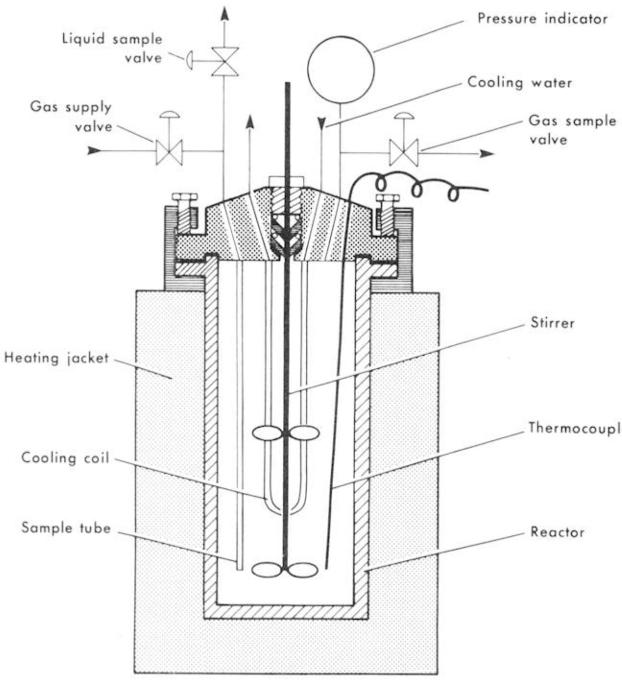

Figure 1. 600-mL autoclave used for high-pressure solubility studies.

thermometer and recorded by a strip chart recorder. The autoclave was capable of withstanding pressures up to 13 MPa at 400 °C.

Experimental Method

The experimental method may be summarized as follows:

(i) A 2-L high-pressure bomb was filled with pure CO_2 to a pressure of 5156 kPa. The filled bomb was then weighed to within ±0.2 g.

(ii) The 600-mL autoclave was charged with 450 mL of the desired DEA solution and closed. The autoclave was then heated to the desired temperature with the stirrer set at about 150 rpm.

(iii) The bomb was connected to the autoclave and CO_2 was admitted into the autoclave until the desired pressure was reached. After equilibrium was established, which was indicated by the attainment of a constant pressure and which usually took less than 15 min, the bomb was disconnected from the autoclave.

(iv) The bomb was reweighed and the quantity of CO_2 introduced into the autoclave was calculated from the weight change.

The amount of CO_2 in the DEA solution was determined from the total weight of CO_2 fed into the autoclave and the partial pressure of CO_2 in the autoclave. To calculate the latter, the vapor pressure of the aqueous DEA solution had to be known.

Table III. Solubility of CO_2 in 10 wt % DEA

temp, °C	total press., kPa	CO_2 partial press., kPa	CO_2 solubility, g of CO_2/g of DEA
205	4137.0	2451.9	0.283
	3103.0	1417.6	0.236
200	3826.7	2329.8	0.279
	2882.1	1385.2	0.246
	1896.0	488.9	0.185
190	3413.0	2214.7	0.290
	2502.9	1303.2	0.249
	1641.0	442.7	0.189
180	2971.7	2003.0	0.295
	2137.5	1168.7	0.257
	1365.2	369.5	0.191
170	3826.7	3067.6	0.338
	2620.1	1861.0	0.300
	1806.5	1047.4	0.262
	1123.9	364.7	0.193
160	3323.4	2731.8	0.352
	2289.1	1697.5	0.316
	1503.1	911.5	0.270
	896.4	304.8	0.196
150	4137.0	3678.5	0.423
	2868.3	2409.8	0.376
	1937.5	1479.0	0.334
	1248.0	789.5	0.279
	710.2	251.7	0.200
140	3675.0	3322.7	0.464
	2482.2	2040.2	0.396
	1599.6	1247.3	0.349
	1013.6	661.2	0.287
	551.6	199.3	0.200
130	3295.8	3031.0	0.482
	2151.2	1886.5	0.408
	1330.7	1066.0	0.355
	850.8	586.1	0.292
	427.5	162.7	0.205
120	3902.6	3711.6	0.558
	2999.3	2808.3	0.510
	1834.1	1645.1	0.430
	1123.9	932.9	0.370
	675.7	484.7	0.300
	324.1	133.1	0.200
110	3516.5	3375.8	0.580
	2702.9	2562.2	0.530
	1558.3	1417.6	0.435
	937.7	797.1	0.376
	558.5	417.8	0.303
	262.0	121.4	0.207
100	3192.4	3093.89	0.598
	2434.0	2334.4	0.540
	1324.0	1255.2	0.450
	827.4	728.8	0.382
	448.2	349.6	0.305
	200.0	105.5	0.208

The following experiments were performed to measure the vapor pressure. CO_2-free, aqueous DEA solutions were charged into the autoclave and heated to a specified temperature. The vapor pressure of the solution, which corresponded to the total pressure in the autoclave, was then measured with a precision pressure gauge. The temperature was subsequently raised and the pressure noted again. Table II summarizes the results of these experiments.

Calculation of CO_2 Solubility

From a knowledge of the total weight of CO_2 introduced into the autoclave, the total pressure in the autoclave, the vapor pressure of the CO_2-free DEA solution, and the temperature, the solubility of CO_2 in the liquid phase was calculated by the following method.

First, the amount of CO_2 in the vapor phase was determined by assuming that the phase obeyed Dalton's law; i.e., the total

Table IV. Solubility of CO_2 in 20 wt % DEA

temp, °C	total press., kPa	CO_2 partial press., kPa	CO_2 solubility, g of CO_2/g of DEA
205	4137.0	2539.4	0.195
	3102.8	1505.2	0.140
200	3861.2	2436.0	0.198
	2792.5	1367.3	0.152
	2116.8	691.6	0.112
190	3468.2	2331.9	0.200
	2358.1	1263.2	0.154
	1696.2	601.2	0.115
180	3006.2	2103.0	0.205
	1972.0	1069.4	0.159
	1475.5	573.0	0.123
170	3806.0	3106.2	0.255
	2606.3	1906.5	0.211
	1641.0	941.2	0.162
	1241.1	541.3	0.129
160	3371.7	2827.0	0.270
	2165.0	1620.3	0.226
	1310.1	765.3	0.168
	965.3	420.6	0.142
150	4137.0	3713.0	0.315
	2937.3	2513.2	0.280
	1765.1	1341.1	0.236
	1034.3	610.2	0.183
	744.7	320.6	0.144
140	3619.9	3293.7	0.330
	2509.8	2182.7	0.290
	1496.2	1156.3	0.240
	792.9	466.8	0.177
	565.4	239.3	0.146
130	3233.8	2990.4	0.339
	2075.4	2521.5	0.295
	1282.5	1039.1	0.248
	593.0	349.6	0.183
	420.6	177.7	0.148
120	3557.8	3378.6	0.381
	2827.0	2647.7	0.351
	1834.1	1654.2	0.306
	1075.6	896.4	0.257
	472.3	293.0	0.185
	324.1	144.8	0.150
110	3240.7	3106.2	0.391
	2530.5	2396.0	0.357
	1516.9	1382.5	0.315
	944.6	810.2	0.270
	375.8	241.3	0.190
	241.3	106.9	0.153
100	2854.5	2759.4	0.404
	2254.7	2159.5	0.365
	1372.1	1276.9	0.318
	784.6	689.5	0.275
	289.6	194.4	0.197
	186.2	91.0	0.156

Table V. Solubility of CO_2 in 30 wt % DEA

temp, °C	total press., kPa	CO_2 partial press., kPa	CO_2 solubility, g of CO_2/g of DEA
205	4137.0	2627.0	0.165
	3102.0	1592.7	0.114
200	3793.3	2762.9	0.183
	2792.5	1439.0	0.114
	1896.1	542.6	0.089
190	3240.7	2587.7	0.190
	2413.3	1340.0	0.120
	1627.2	553.7	0.081
180	2758.0	2417.4	0.192
	2034.0	1197.0	0.123
	1351.4	514.4	0.090
170	3585.4	2945.0	0.236
	2330.5	2138.2	0.202
	1689.3	1048.7	0.128
	1103.2	462.7	0.090
160	3136.5	2618.0	0.240
	2000.0	1728.6	0.200
	1334.5	846.0	0.132
	910.1	411.6	0.094
150	4137.0	3746.7	0.312
	2482.2	2078.2	0.240
	1723.8	1333.5	0.195
	1048.0	657.8	0.137
	723.9	333.7	0.104
140	3502.7	3203.4	0.328
	2006.4	1707.2	0.248
	1516.9	1217.7	0.209
	813.6	514.4	0.141
	572.3	273.0	0.106
130	3068.3	2845.6	0.330
	1654.8	1432.1	0.249
	1220.4	999.8	0.210
	620.6	393.0	0.144
	448.2	225.5	0.111
120	3826.7	3659.2	0.376
	2826.9	2659.4	0.330
	1379.0	1210.1	0.248
	965.3	797.8	0.212
	468.9	301.3	0.147
	313.7	146.7	0.111
110	3516.5	3388.2	0.381
	2689.1	2560.8	0.344
	1172.2	1043.9	0.256
	820.5	692.3	0.215
	365.4	237.2	0.149
	224.8	96.5	0.108
100	3275.1	3182.7	0.392
	2447.7	2355.3	0.355
	1034.3	941.9	0.264
	613.7	521.3	0.217
	275.8	183.4	0.149
	165.5	73.1	0.108

pressure exerted by the vapor phase equals the sum of the partial pressures of the individual components. The validity of this assumption was proved for the present experimental conditions by calculating the total pressure exerted by CO_2/water vapor mixtures with Dalton's law. The results were then compared with the pressures calculated by using the compressiblity factor method (*2*) based on the pseudocritical temperatures and pressures of the mixtures. The compressibility factors ranged from 0.92 to 1.00, which implies that Dalton's law is valid to within less than 8%. The partial pressure of CO_2 in the vapor phase was therefore simply taken as the difference between the total measured pressure and the vapor pressure of the CO_2-free, aqueous DEA solution, i.e.

$$\text{partial pressure of } CO_2 = \text{total pressure} - \text{vapor pressure of DEA solution} \quad (1)$$

Knowing the partial pressure of CO_2, the volume of the vapor phase (determined from the internal volume of the autoclave and the volume of DEA solution introduced), and the temperature, we could find the number of moles of CO_2 in the vapor phase by using an equation of state. The van der Waals equation was considered to be suitable for this purpose. Although more accurate equations of state are available, the van der Waals expression is useful for providing a simple, analytical representation of the behavior of a slightly nonideal gas. Furthermore, the amount of CO_2 in the vapor phase relative to that in the liquid phase is small. The loss of some accuracy in the CO_2 content of the vapor phase has therefore only a minor effect on the solubility of CO_2 in the DEA solution.

Once the number of moles of CO_2 in the vapor phase had been found, the mass of CO_2 in the DEA solution was obtained by substracting the mass of CO_2 in the vapor phase from the total mass of CO_2 fed to the autoclave, i.e.

Table VI. Comparison between CO_2 Solubilities in DEA Solutions Obtained in This and Other Studies

DEA concn, wt %	temp, °C	CO_2 partial press., kPa	CO_2 concn, g of CO_2/g of DEA: this study	CO_2 concn, g of CO_2/g of DEA: lit.	diff, %	ref
20	100	689.5	0.272	0.27	0.74	7
20	120	689.5	0.238	0.212	12.26	7
20	140	689.5	0.204	0.186	9.68	7
20	100	2178.8	0.366	0.348	5.17	7
20	120	2178.8	0.331	0.294	12.58	7
20	140	2178.8	0.29	0.25	16.00	7
25	107	591.6	0.22[a]	0.218	0.92	8
25	107	2185.7	0.31[a]	0.287	8.01	8
25	121	335.8	0.165[a]	0.143	15.38	8
25	121	1585.9	0.275[a]	0.248	10.89	8
25	121	2771.2	0.33[a]	0.3	10.00	8
					av = 9.24	

[a] Interpolated results from Figures 3 and 4.

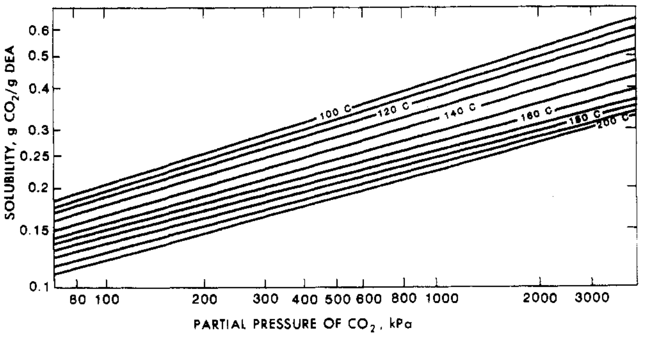

Figure 2. Solubility of CO_2 in a 10 wt % aqueous DEA solution.

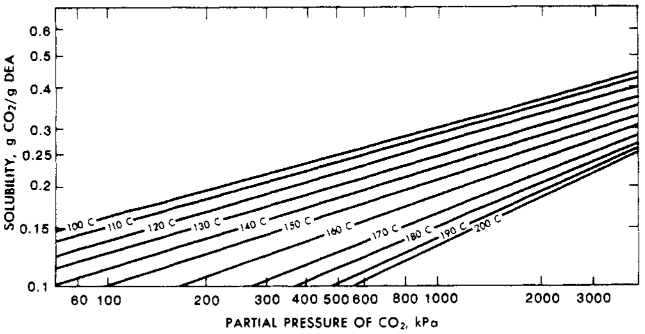

Figure 3. Solubility of CO_2 in a 20 wt % aqueous DEA solution.

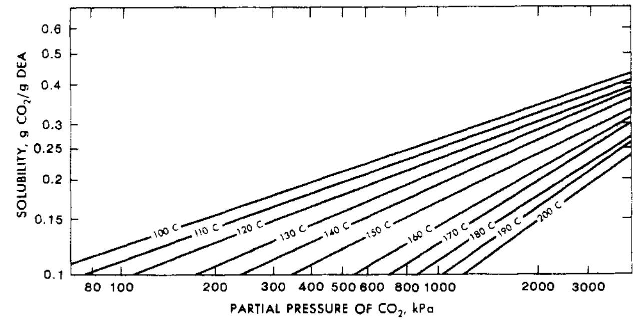

Figure 4. Solubility of CO_2 in a 30 wt % aqueous DEA solution.

$$\text{mass of } CO_2 \text{ dissolved} = \text{total mass of } CO_2 \text{ fed to autoclave} - \text{mass of } CO_2 \text{ in vapor phase} \quad (2)$$

From the mass of CO_2 dissolved in the aqueous DEA solution and the known mass of DEA in the autoclave, the solubility of CO_2 expressed as (g of CO_2)/(g of DEA) could be easily calculated.

Results

Tables III–V summarize the solubility data as a function of temperature, CO_2 partial pressure, and DEA concentration. For convenience, the corresponding, smoothed data are also presented in Figures 2–4. The solubility curves are virtually straight lines at elevated temperatures and pressures. Similar behavior had already been observed by others for comparable or milder conditions (*4–8*).

Accuracy of Data

It is realized that the method for determining the CO_2 solubility data is simple and somewhat approximate. To check the accuracy of the present method, the results were compared with literature values where possible. The comparisons are summarized in Table VI and show an average deviation of less than 10%.

The largest error probably arose from calculating the mass of CO_2 in the vapor phase. However, when it is noted that the mass of CO_2 in the vapor phase is generally less than 25% of the CO_2 dissolved in the liquid phase, an error of ±30% in the vapor phase mass causes an error of only ±10% in solubility. Such errors were considered to be acceptable for the purposes of our degradation studies.

Conclusions

The results obtained in this study extend the range of data on CO_2 solubility in aqueous DEA solutions beyond those reported previously. The data are in reasonable agreement (10% on the average) with the findings of other investigators under milder conditions. Furthermore, the present experimental method requires only simple equipment and is easy to perform.

Registry No. CO_2, 124-38-9; DEA, 111-42-2.

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