Densities and Solubilities of Solutions of Carbon Dioxide in Water + Monoethanolamine + *N*-Methyldiethanolamine

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Equilibrium solubilities of carbon dioxide in aqueous mixtures of monoethanolamine (MEA) with *N*-methyldiethanolamine (MDEA) have been studied experimentally at 40, 60, 80, and 100 °C and at partial pressures of carbon dioxide between 1.0 and 2000 kPa. The systems selected for study are 6 wt % MEA + 24 wt % MDEA and 18 wt % MEA + 12 wt % MDEA aqueous solutions. The equilibrium solubilities of carbon dioxide in aqueous solutions are reported as functions of the partial pressure of carbon dioxide for temperatures of 40–100 °C. The densities of the MEA/MDEA aqueous solutions at atmospheric pressure were also measured at temperatures ranging from 30 to 80 °C. The systems selected for density measurements are pure MEA, pure MDEA, 30 wt % MEA, 24 wt % MEA + 6 wt % MDEA, 18 wt % MEA + 12 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 6 wt % MEA + 24 wt % MDEA, and 30 wt % MDEA aqueous solutions.

Introduction

Alkanolamine aqueous solutions are frequently used for the removal of acid gases, such as CO_2 and H_2S, from gas streams in the natural gas and synthetic ammonia industries and petroleum chemical plants. Industrially important alkanolamine aqueous solutions are monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA), and *N*-methyldiethanolamine (MDEA). Aqueous MEA solutions have been widely used due to their high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons (*1*). For a gas stream that contains both CO_2 and H_2S, the aqueous MDEA solution is found to be an appropriate solution for the selective removal of H_2S from the gas stream. Advantages of the use of MDEA solutions include their high loading capacity (about 1.0 mol of CO_2/mol of amine) and low heat of reaction with the acid gases (*2*). However, the low reaction rate of CO_2 with tertiary amines limits the use of MDEA solutions (*3*).

Recently the use of blended amines, a solution of two or more amines in varying compositions, brings about a considerable improvement in absorption and a great savings in energy requirements (*4*). The use of blended amines intends to combine the absorption characteristics of the constituent amines; advantages of the use of the individual amine, such as the higher loading capacity and the faster reaction rate, are expected to contribute to the resulting solution. Blends of primary and tertiary amines, mixtures of MEA and MDEA, have been suggested to be used for CO_2 removal (*4*). Knowledge of the equilibrium solubility of acid gases such as CO_2 and H_2S in alkanolamine aqueous solutions is essential in the design of the gas absorption units for removing these acid gases from gas streams. The solubilities of CO_2 in 2.0 kmol/m^3 MEA + 2.0 kmol/m^3 MDEA aqueous solutions were reported at 40 and 80 °C for partial pressures of CO_2 below 315 kPa (*5*). For partial pressures of CO_2 up to 2000 kPa and at 40–100 °C, the solubilities of CO_2 in 30 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 24 wt % MEA + 6 wt % MDEA, and 30 wt % MEA aqueous solutions have been reported in our previous work (*6*). It is the purpose of this research to study experimentally the solubilities of CO_2 in 6 wt % MEA + 24 wt % MDEA and 18 wt % MEA + 12 wt % MDEA aqueous solutions at 40, 60, 80, and 100 °C and at partial pressures of CO_2 ranging from 1.0 to 2000 kPa. Also, at atmospheric pressure and at temperatures of 30–80 °C, the densities of the MEA/MDEA aqueous solutions are also measured on the basis of the ASTM standard test method. The systems selected for density measurements are pure MEA, pure MDEA, 30 wt % MEA, 24 wt % MEA + 6 wt % MDEA, 18 wt % MEA + 12 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 6 wt % MEA + 24 wt % MDEA, and 30 wt % MDEA aqueous solutions.

Experimental Section

*1. **Solubility Measurement.*** In order to make CO_2 solubility measurements over the MEA/MDEA aqueous solutions for partial pressures of CO_2 ranging from 1 to 2000 kPa, two vapor–liquid equilibrium apparatus have been set up and tested in this study. For partial pressures of CO_2 above 200 kPa, the equilibrium solubility of CO_2 was measured in a stirred 0.5-L ZipperClave batch equilibrium cell. A 1.0-L stainless steel vapor-recirculation equilibrium cell was used to measure the equilibrium solubility of CO_2 in aqueous amine solutions for partial pressures of CO_2 below 200 kPa. In the region of low partial pressures of CO_2, nitrogen was introduced and mixed with CO_2, and the partial pressure of CO_2 was determined by gas chromatography. The solubility (loading capacity) of CO_2 in amine solutions was determined by using the titration method. The materials, vapor–liquid equilibrium apparatus, and methods of analysis are essentially the same as those used in our previous work on the solubility of CO_2 in MEA/MDEA aqueous solutions (*6*).

*2. **Density Measurement.*** The densities of MEA/MDEA aqueous solutions were measured by using a 25-mL Gay-Lussac pycnometer. The procedure used to determine the density of the solution is based on the ASTM D 3505 standard test method (*7*). The temperature of the thermostat is controlled by a TU-16A immersion circulator, made by Techne Inc. to within ±0.01 °C of the desired temperature. The density of the solution is calculated by the observed weight of the sample and that of the degassed pure water (*7*). The densities of the pure water are adopted from the values reported in the *Chemical Engineers' Handbook* (*8*). The density measurements were made over the temperature range of 30–80 °C.

Results and Discussion

The sampling, analytical procedures, and vapor–liquid equilibrium apparatus in this work have been tested by obtaining CO_2 solubility data in a 15.3 wt % MEA aqueous solution, the system at which CO_2 solubility data had previously been reported (*9–11*). CO_2 solubility data obtained in this work are found to be in good agreement with the solubility data previously published (*6*). The CO_2 solubility data obtained at 40, 60, 80, and 100 °C are presented in Tables I and II for 6 wt % MEA

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Table I. Partial Pressure P of CO_2 in 6 wt % MEA + 24 wt % MDEA Aqueous Solution for Loading of CO_2, α (mol of CO_2/total mol of amine)

t/°C	P/kPa	α	t/°C	P/kPa	α
40	1.12	0.300	80	1.46	0.195
	3.59	0.381		6.07	0.254
	12.56	0.490		17.17	0.314
	22.86	0.583		26.83	0.359
	53.61	0.675		35.55	0.375
	108.1	0.761		82.75	0.439
	174.8	0.809		128.2	0.488
	442.0	0.878		397.0	0.598
	828.0	0.916		797.0	0.701
	1235.0	0.978		1225.0	0.757
	1579.0	0.989		1611.0	0.778
	2000.0	1.015		2080.0	0.816
60	2.05	0.282	100	2.88	0.185
	5.70	0.335		5.73	0.210
	10.01	0.372		10.30	0.236
	22.16	0.437		28.45	0.282
	45.40	0.533		41.40	0.320
	101.6	0.613		86.28	0.363
	167.6	0.692		134.8	0.416
	450.0	0.768		1168.0	0.634
	822.0	0.876		1540.0	0.646
	1222.0	0.903		1905.0	0.664
	1608.0	0.925			
	2029.0	0.945			

Table II. Partial Pressure P of CO_2 in 18 wt % MEA + 12 wt % MDEA Aqueous Solution for Loading of CO_2, α (mol of CO_2/total mol of amine)

t/°C	P/kPa	α	t/°C	P/kPa	α
40	2.04	0.415	80	1.73	0.232
	6.60	0.480		4.17	0.296
	13.91	0.517		11.25	0.363
	24.05	0.548		24.98	0.417
	46.22	0.582		34.35	0.440
	81.33	0.611		76.41	0.470
	144.0	0.650		117.3	0.504
	435.0	0.732		398.0	0.554
	835.0	0.762		791.0	0.605
	1242.0	0.820		1205.0	0.650
	1594.0	0.851		1557.0	0.667
	1973.0	0.881		1950.0	0.713
60	1.68	0.331	100	1.37	0.167
	5.35	0.409		2.22	0.188
	15.56	0.460		3.72	0.235
	26.68	0.481		9.57	0.264
	44.99	0.517		17.83	0.311
	91.16	0.559		33.49	0.360
	145.4	0.574		67.62	0.407
	423.0	0.654		83.80	0.415
	823.0	0.717		480.0	0.470
	1237.0	0.759		756.0	0.525
	1588.0	0.771		1177.0	0.549
	1933.0	0.793		1501.0	0.580
				1901.0	0.612

+ 24 wt % MDEA and 18 wt % MEA + 12 wt % MDEA, respectively. Plots of partial pressures of CO_2 as a function of the CO_2 solubility are shown graphically in Figures 1 and 2. As shown in Figures 1 and 2, the CO_2 loading capacities in alkanolamine aqueous solutions vary systematically with the partial pressures of CO_2. Also, the higher the temperature of the system is, the lower the CO_2 solubility observed. To investigate the effect of amine concentrations on CO_2 solubility, plots of solubility data in four MEA/MDEA aqueous solutions as functions of partial pressures of CO_2 at 60 and 80 °C are shown in Figure 3 and 4. The solubilities of CO_2 in 30 wt % MEA and in 30 wt % MDEA were adopted from our previous results (*6*). As can be seen in Figure 3, CO_2 solubilities vary systematically from 30 wt % MDEA, to 18 wt % MEA + 12 wt % MDEA, to 6 wt % MEA + 24 wt % MDEA, to 30 wt % MEA, and all four solubility curves cross each other at a point where the CO_2 partial pressure is about 45 kPa. In Figure 4, CO_2 solubility curves also cross each other.

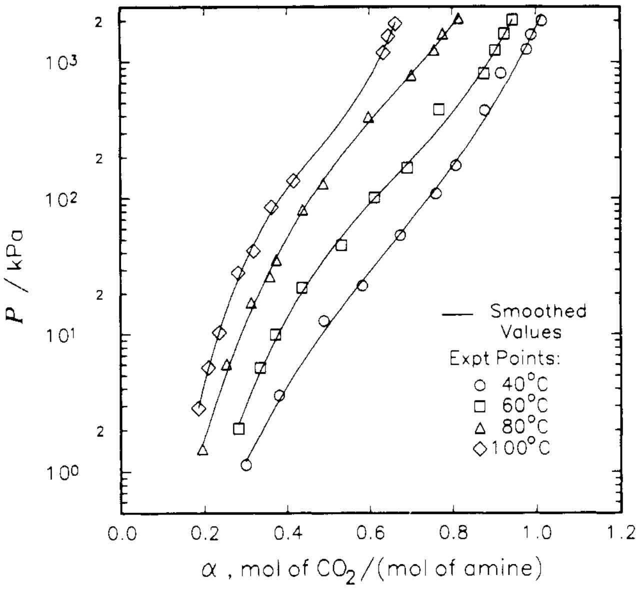

Figure 1. Partial pressure P of CO_2 in 6 wt % MEA + 24 wt % MDEA aqueous solution at various temperatures for various loadings α (mol of CO_2/total mol of amine).

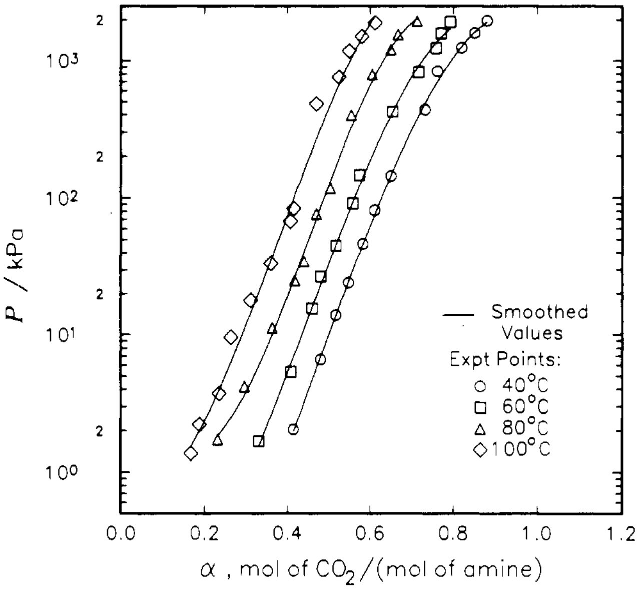

Figure 2. Partial pressure P of CO_2 in 18 wt % MEA + 12 wt % MDEA aqueous solution at various temperatures for various loadings α (mol of CO_2/total mol of amine).

The densities of the MEA/MDEA aqueous solutions at temperatures 30–80 °C are reported in Table III. In Figure 5, the plots of density versus the temperature for amine solutions are shown. For comparison the densities of the pure water, adopted directly from the values reported in the Chemical Engineers' Handbook (*8*), are also shown in Figure 5. As shown in Figure 5, the densities of the aqueous amine solutions change systematically from the 30 wt % MEA to the 30 wt % MDEA aqueous solutions.

Conclusion

The equilibrium solubilities of CO_2 in 6 wt % MEA + 24 wt % MDEA and 18 wt % MEA + 12 wt % MDEA aqueous solutions have been reported at temperatures of 40, 60, 80, and 100 °C and for partial pressures of CO_2 ranging from 1.0 to 2000 kPa. The densities of the MEA/MDEA aqueous solutions

Table III. Densities ρ of MEA + MDEA Aqueous Solutions

t/°C	ρ/(g cm^{-3}) of wt % MEA/wt % MDEA mixtures 0/30	6/24	12/18	18/12	24/6	30/0	ρ/(g cm^{-3}) of pure liquid MEA	MDEA	Water[a]
30	1.0223	1.0195	1.0167	1.0137	1.0111	1.0081	1.0098	1.0315	0.9957
35	1.0199	1.0172	1.0142	1.0114	1.0086	1.0060	1.0048	1.0279	0.9941
40	1.0171	1.0145	1.0115	1.0088	1.0061	1.0034	1.0009	1.0249	0.9923
45	1.0146	1.0118	1.0091	1.0062	1.0035	1.0007	0.9967	1.0213	0.9902
50	1.0116	1.0088	1.0062	1.0034	1.0007	0.9980	0.9929	1.0174	0.9881
60	1.0057	1.0032	1.0001	0.9975	0.9946	0.9921	0.9849	1.0098	0.9832
70	0.9991	0.9967	0.9938	0.9912	0.9886	0.9861	0.9771	1.0023	0.9778
80	0.9922	0.9897	0.9868	0.9841	0.9818	0.9790	0.9683	0.9946	0.9718

[a] Values reported by Perry and Chilton (*8*).

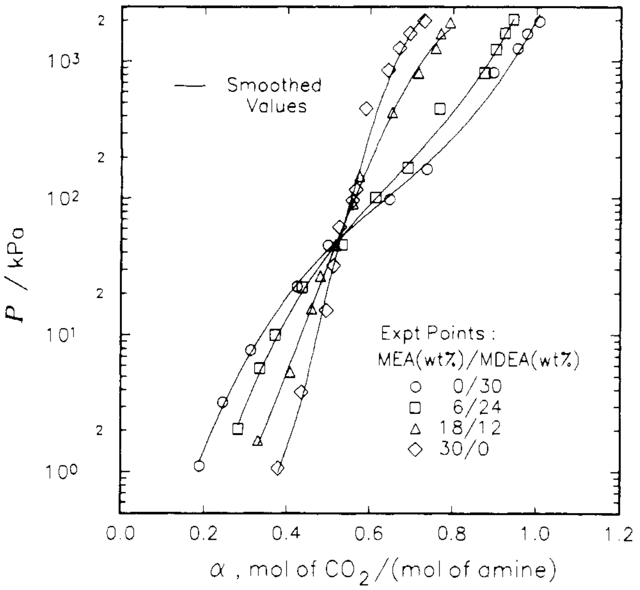

Figure 3. Partial pressure P of CO_2 in various MEA + MDEA aqueous solutions at 60 °C for various loadings α (mol of CO_2/total mol of amine). Data of 30 wt % MEA and 30 wt % MDEA are values reported by Shen and Li (*6*).

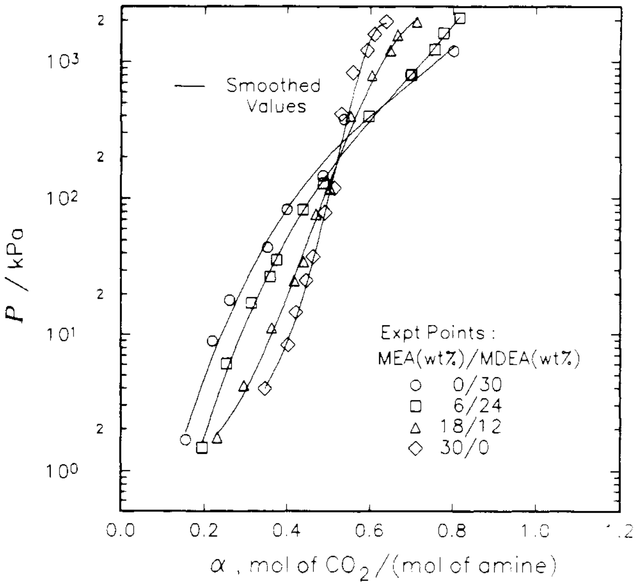

Figure 4. Partial pressure P of CO_2 in various MEA + MDEA aqueous solutions at 80 °C for various loadings α (mol of CO_2/total mol of amine). Data of 30 wt % MEA and 30 wt % MDEA are values reported by Shen and Li (*6*).

at atmospheric pressure for temperatures of 30–80 °C are also presented. The systems selected for density measurements are pure MEA, pure MDEA, 30 wt % MEA, 24 wt % MEA + 6 wt % MDEA, 18 wt % MEA + 12 wt % MDEA, 12 wt % MEA + 18 wt % MDEA, 6 wt % MEA + 24 wt % MDEA, and 30 wt % MDEA aqueous solutions.

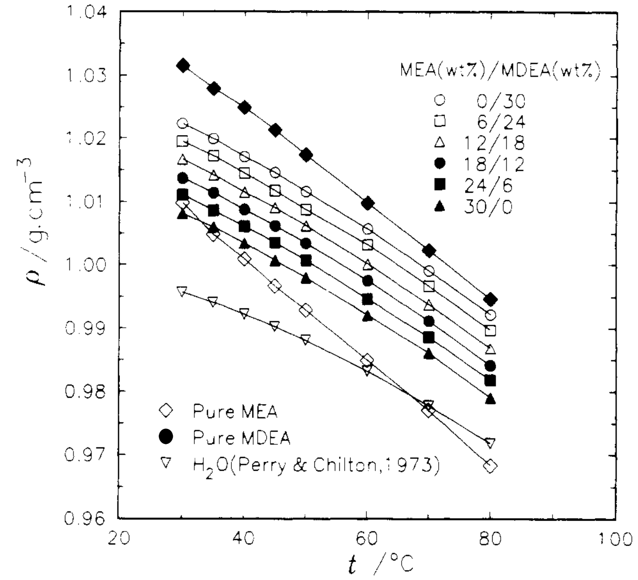

Figure 5. Densities ρ of MEA/MDEA aqueous solutions at temperature t.

Registry No. MEA, 141-43-5; MDEA, 105-59-9; CO_2, 124-38-9.

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