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Solubility of CO_2 in Aqueous Methyldiethanolamine Solutions

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For 5.0, 20.5, 50.0, and 75.0 mass % methyldiethanolamine (MDEA) aqueous solutions, solubilities of CO_2 were measured at 323.15, 348.15, and 373.15 K, respectively. Isothermal absorption capacities of CO_2 as a function of MDEA concentration are presented. Lastly, the absorption enthalpy of CO_2 in 50.0 mass % MDEA solution was calculated to be 54 $kJ \cdot mol^{-1}$ CO_2.

Introduction

Alkanolamines are the most commonly used chemical absorbents for the treatment of gas streams containing H_2S and CO_2. However, gas absorption utilizing alkanolamines has problems such as excessive foaming, thermal degradation, and corrosion of materials. To resolve such limitations, effort has been placed on developing improved absorbents that contain increased amounts of anticorrosive and antifoaming agents (Pauly et al., 1984; Kosseim et al., 1984).

Among works focusing on enhancing the physiochemical properties of alkanolamine absorbents, most of the solutions are based on specific methyldiethanolamine (MDEA) additives that improve the absorbent's reactivity with CO_2. The reaction rate on MDEA with CO_2 is in general very slow, and the absorption capacity of CO_2 in aqueous MDEA solution tends to be low at low concentrations of CO_2. However, since MDEA has a low vapor pressure, there is almost no evaporative loss of the absorbent during operation of the absorptive process. MDEA also shows favorable thermal and chemical stability. Furthermore, since MDEA shows low corrosive behavior, it can be employed at a high concentration in the absorption process. The use of highly concentrated MDEA solutions can lead to significant electricity savings compared to conventional absorbents due to lower circulation demands in the absorption process. Since MDEA does not directly react with CO_2 during the absorptive process, the stripping can easily be achieved by a simple pressure reduction. Accordingly, stripping energy requirements can be reduced compared to those of conventional absorption processes utilizing monoethanolamine (MEA) or diethanolamine (DEA) as the absorbent (Ball and Veldman, 1991).

This article reports experimental measurements of CO_2 solubility in aqueous MDEA solutions over a range of temperatures (323.15, 348.15, and 373.15 K) and concentrations of MDEA (5.0, 20.5, 50.0, and 75.0 mass %).

Experimental Section

Sample MDEA solutions were prepared from Aldrich reagent grade MDEA (99% purity) and demineralized water.

As shown in Figure 1, the experimental apparatus consisted of an SS316 vapor-recirculation equilibrium cell (420 cm^3), a gas reservoir (4045 cm^3) to increase the volume of the vapor phase, a CO_2 injection cell (1886 cm^3), a cylindrical piston pump, three precision pressure gauges, three pressure transducer−digital indicators, and four K-type thermocouples. A Walcom pressure transducer with an accuracy of 0.001 $kg_f \cdot cm^{-2}$ was installed in the equilibrium cell, the reservoir, and the CO_2 injection cell. The temperature of the contents of the cell was measured to within 0.1 K. Temperature and pressure were recorded with a 30 channel hybrid recorder (HR 2300, Yokogawa, Japan). The three cylinders were mounted vertically in a thermostated air bath controlled to within ±0.2 K. On the basis of the manuscript provided by the manufacturing company for the calibration procedure, the zero and span adjustments of the digital pressure/temperature indicators were adjusted weekly.

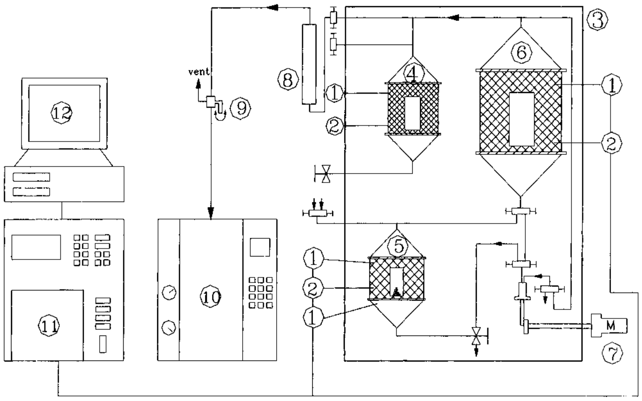

Figure 1. Systemic diagram of CO_2 absorption equilibrium apparatus: 1, thermocouple; 2, pressure transducer; 3, air bath; 4, CO_2 injection cell; 5, equilibrium cell; 6, gas reservoir; 7, piston pump; 8, condenser; 9, gas sampling valve; 10, GC; 11, hybrid record, 12, data acquisition system.

The gas−liquid contact and the transport of CO_2 to the MDEA solution were governed with a circulation pump. The pump serves to recirculate the vapor phase and bubble it through the liquid phase at a rate of up to 14.4 L/min. Packing with glass beads was used at the bottom of the cell for homogeneous dispersion of CO_2. To monitor the circulation of the gas stream, a view cell was installed.

The amount of absorbent charged into the equilibrium cell at the beginning of a run was determined by weighing on a digital balance with a precision of 0.01 g and heating the solution to a run temperature.

When thermal equilibrium was reached, equilibrium pressure was recorded. Thermal equilibrium pressure is

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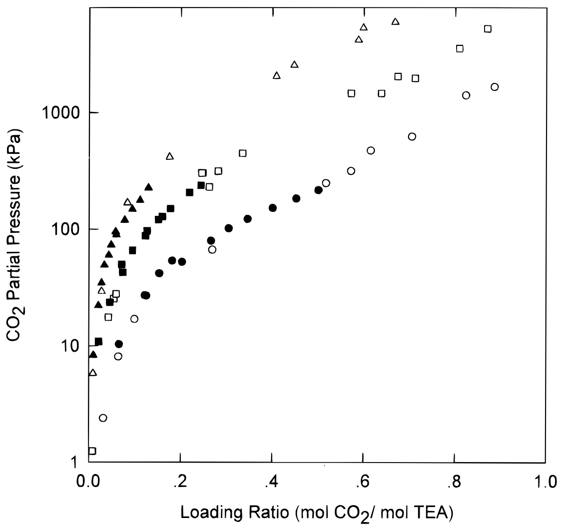

Figure 2. Comparison of the solubility of CO_2 in 50 mass % TEA solution. Open points, Jou et al. (1985): (○) 323.15 K; (□) 348.15 K; (△) 373.15 K. Solid points, this work: (●) 323.15 K; (■) 348.15 K; (▲) 373.15 K.

Table 1. Solubility of CO_2 in 5, 20.5, 50, and 75 mass % MDEA Solution at 323.15 K

mass fraction	loading ratio (mol CO_2/ mol MDEA)	P_{CO_2}/ kPa	mass fraction	loading ratio (mol CO_2/ mol MDEA)	P_{CO_2}/ kPa
0.05	0.068	1.051	0.50	0.0150	0.775
	0.1495	2.051		0.0442	2.474
	0.2375	2.750		0.0740	4.872
	0.3362	4.249		0.1315	11.66
	0.4287	6.847		0.1916	17.36
	0.5019	8.945		0.2420	24.45
	0.5585	11.84		0.3190	38.74
	0.6266	15.94		0.3854	53.03
	0.6843	20.63		0.4529	70.92
0.205	0.0451	1.141	0.75	0.0260	10.04
	0.1185	3.340		0.0708	24.83
	0.2223	5.738		0.1075	44.42
	0.3368	11.33		0.1457	62.20
	0.4332	19.42		0.1842	82.09
	0.4933	25.42		0.2246	106.0
	0.5899	39.71		0.2728	139.2
	0.6117	55.49			
	0.7149	72.18			
	0.7857	106.0			
	0.8478	146.8			

Table 2. Solubility of CO_2 in 5, 20.5, 50, and 75 mass % MDEA Solution at 348.15 K

mass fraction	loading ratio (mol CO_2/ mol MDEA)	P_{CO_2}/ kPa	mass fraction	loading ratio (mol CO_2/ mol MDEA)	P_{CO_2}/ kPa
0.05	0.0592	1.139	0.50	0.0162	3.624
	0.1320	2.938		0.0334	7.920
	0.2015	5.735		0.0420	9.721
	0.2655	9.432		0.0537	13.71
	0.3133	13.42		0.0770	21.31
	0.3796	19.22		0.1010	31.10
	0.4605	28.01		0.1330	45.39
	0.5354	39.70		0.1656	61.88
				0.1945	78.86
0.205	0.0710	4.526	0.75	0.0179	17.43
	0.1258	9.922		0.0326	39.21
	0.1938	18.01		0.0525	72.09
	0.2429	26.30		0.0750	112.1
	0.2526	27.10		0.0952	151.3
	0.2906	36.00		0.1103	184.2
	0.3415	48.39		0.1271	220.7
	0.3873	61.28		0.1480	268.3
	0.4432	79.66			
	0.5026	104.7			
	0.5551	132.5			
	0.6199	173.4			

Table 3. Solubility of CO_2 in 5, 20.5, 50, and 75 mass % MDEA Solution at 373.15 K

mass fraction	loading ratio (mol CO_2/ mol MDEA)	P_{CO_2}/ kPa	mass fraction	loading ratio (mol CO_2/ mol MDEA)	P_{CO_2}/ kPa
0.05	0.0300	1.841	0.50	0.0087	5.003
	0.0448	3.939		0.0164	11.39
	0.0905	7.336		0.0261	20.29
	0.1196	10.33		0.0350	30.38
	0.1475	14.73		0.0476	45.27
	0.2273	26.82		0.0656	68.45
				0.0827	95.83
				0.1080	140.3
0.205	0.0260	3.314	0.75	0.0643	21.71
	0.0547	9.609		0.0126	47.29
	0.0877	20.50		0.0202	83.46
	0.1164	30.29		0.0280	112.9
	0.1586	48.37		0.0342	154.9
	0.1937	68.06		0.0410	188.8
	0.2359	96.14		0.0492	235.5
	0.2853	132.7			
	0.3259	167.2			

the sum of vapor pressure of water, MDEA, and N_2 partial pressure. The equilibrium cell was then pressurized with CO_2 from the CO_2 injection cell. The charged amount of CO_2 to the equilibrium cell from the CO_2 injection cell was calculated from the pressure drop of the CO_2 injection cell using an ideal gas law.

Equilibrium is assumed when the pressure remains constant for 30 min; it will normally take 3−4 h for the system to reach equilibrium. The equilibrium cell was again pressurized with additional CO_2 until the final experimental solution loading ratio, or equilibrium vapor pressure of CO_2, was achieved. The entire experimental procedure was repeated several times for each solution until a set of vapor−liquid equilibrium data could be obtained.

For each charge of CO_2 to the reservoir, an equilibrium CO_2 partial pressure is calculated as the total pressure of the gas reservoir minus the thermal equilibrium pressure of the gas reservoir without CO_2 injection. Equilibrium solution loading is then calculated as the total moles of CO_2 charged to the autoclave from the CO_2 injection cell (calculated from CO_2 injection cell pressure drop) minus the moles of CO_2 remaining in the reservoir vapor space (calculated from gas reservoir equilibrium vapor pressure again).

Equilibrated concentrations of CO_2 of the vapor phase were analyzed by gas chromatography (15 ft × $^1/_8$ in. 60/80 Carboxen™−1000 column, Supelco) operating at 318.15 K for 5 min and then increased to 498.15 K at 20 K·min^{-1}. The thermal conductivity detector was set at 523.15 K, and 30 mL·min^{-1} helium flow. A 100 μL sample was injected into the gas chromatography at 420.15 K. GC was calibrated by standard gas that was composed of 3.06% O_2, 16.02% CO_2, and the balance N_2; the range of accuracy was within ±1.5% for the response of GC.

Results and Discussion

To determine the accuracy of the experimental apparatus, a brief absorption equilibrium test (using aqueous TEA solution at 50.0 mass % and conducted at 323.15, 348.15, and 373.15 K) as reported in the literature (Jou et al., 1985) was repeated. Moles of CO_2 absorbed per moles of TEA was defined as the equilibrium loading ratio. There was consistency between the two data sets (Figure 2). The reproducibility between the various experiments was always within ±5%.

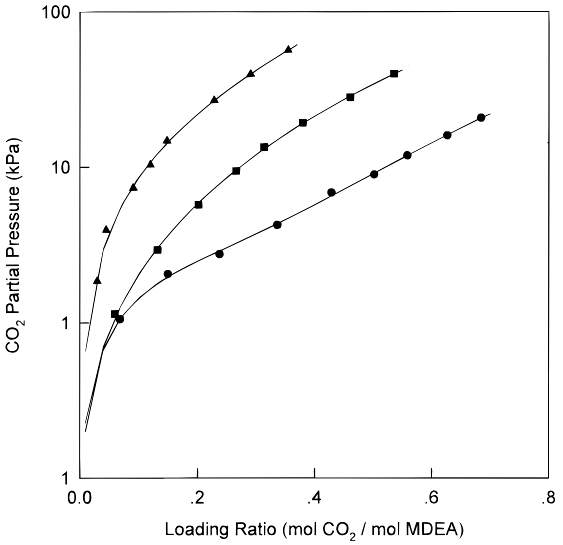

Figure 3. Equilibrium solubility of CO_2 in 5 mass % MDEA solution: (●) 323.15 K; (■) 348.15 K; (▲) 373.15 K; (solid line) smooth fitting.

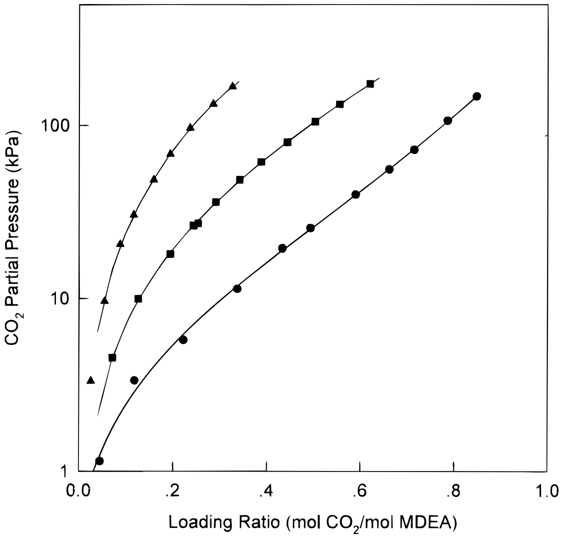

Figure 4. Equilibrium solubility of CO_2 in 20.5 mass % MDEA solution: (●) 323.15 K; (■) 348.15 K; (▲) 373.15 K; (solid line) smooth fitting.

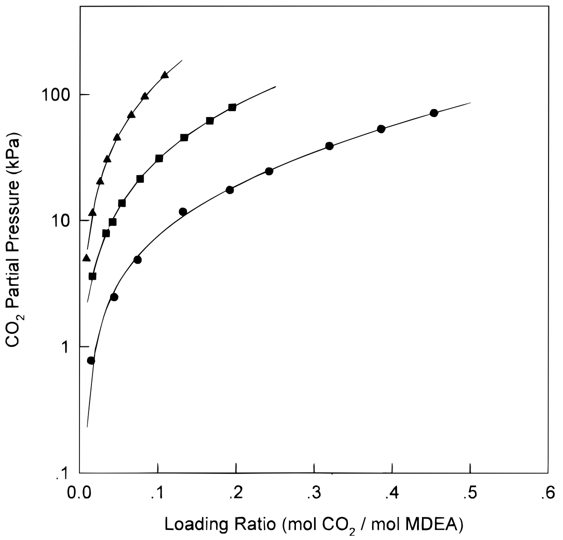

Figure 5. Equilibrium solubility of CO_2 in 50 mass % MDEA solution: (●) 323.15 K; (■) 348.15 K; (▲) 373.15 K; (solid line) smooth fitting.

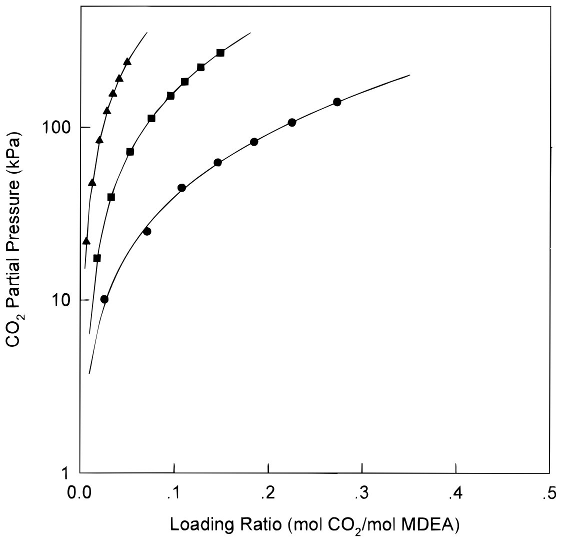

Figure 6. Equilibrium solubility of CO_2 in 75 mass % MDEA solution: (●) 323.15 K; (■) 348.15 K; (▲) 373.15 K; (solid line) smooth fitting.

In Table 1−3, the measured solubilities of CO_2 in aqueous solutions of 5.0, 20.5, 50.0, and 75.0 mass % MDEA at 323.15, 348.15, and 373.15 K are summarized. To determine the effect of temperature at fixed concentrations of MDEA on the solubility of CO_2, the partial pressures of CO_2 were plotted by the equilibrium loading ratio. These results are summarized in Figures 3−6.

The association of water with the MDEA molecule appears to be the critical role of the tertiary amines, since Versteeg and van Swaaij (1988) have shown that CO_2 does not react with MDEA in the absence of water. Water molecules dissolve MDEA through hydrogen bonding, and this association allows MDEA to catalyze the hydration of CO_2 as proposed by Barth et al. (1981). Thus, to illustrate the effect of MDEA concentration on the absorption capacity of CO_2, the absorption equilibria of CO_2 in MDEA solutions at four different concentrations are shown in Figure 7. The equilibrium loading ratio (α) decreases with increasing concentration of MDEA at fixed temperature and partial pressure of CO_2. Thus, on the basis of such plots, it is clear that MDEA needs to be maintained at a low concentration in order to increase the absorption capacity of CO_2 in aqueous MDEA solution. In this regard, we introduced the concept of absorption capacity, *A*, which is defined by the moles of CO_2 absorbed per unit volume of MDEA solution. The absorption capacity can be written by

$$A\frac{\text{mol CO}_2\text{ absorbed}}{\text{m}^3\text{ solution}} = \alpha\,\frac{\text{mol CO}_2\text{ absorbed}}{\text{mol MDEA}}\,C^0_{\text{MDEA}}\,\frac{\text{mol MDEA}}{\text{m}^3\text{ solution}} \quad (1)$$

Using eq 1, the variation of the absorption capacity with respect to MDEA concentration at 323 K was calculated and is shown in Figure 8. When the partial pressure of CO_2 is below 10 kPa, it is advantageous to employ a 20.5 mass % MDEA solution for the absorption of CO_2. When the partial pressure is above 10 kPa, it is better to employ a 50.0 mass % MDEA solution.

The absorption enthalpy of CO_2 in aqueous MDEA solution ($\Delta_{sol}H$) was calculated on the basis of the following

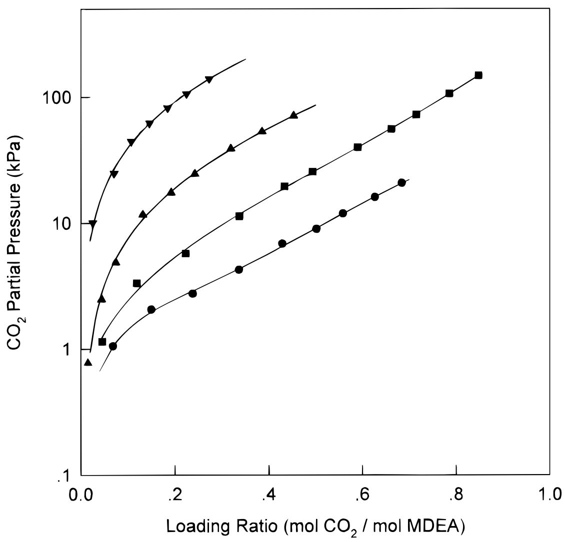

Figure 7. Equilibrium solubility of CO_2 in MDEA solutions at 323.15 K: (●) 5 mass %; (■) 20.5 mass %; (▲) 50 mass %; (▼) 75 mass %; (solid line) smooth fitting.

Gibbs–Helmholtz equation

$$\frac{\Delta_{\mathrm{sol}}H}{R} = \left(\frac{\partial \ln p_1}{\partial(1/T)}\right)_{x_1} \tag{2}$$

where the subscript 1 denotes CO_2 and x_1 is the mole fraction or equilibrium loading ratio of CO_2.

The enthalpy of absorption is dependent on the loading ratio. The average absorption enthalpy of CO_2 in 50 mass % MDEA solution was 54.6 kJ·mol^{-1} CO_2 in the range of equilibrium loading ratios from 0.01 to 0.10. This value is lower than 62 kJ·mol^{-1} CO_2, which was proposed by Jou et al. (1982) for 4.28 mol·cm^{-3} (51 mass %) MDEA, but is higher than Kohl and Riesenfeld's (1985) proposed 475 Btu·lb^{-1} CO_2 (48 kJ·mol^{-1} CO_2).

Conclusion

The absorption equilibrium data of CO_2 in aqueous MDEA solutions of 5.0, 20.5, 50.0, and 75.0 mass % MDEA were measured at 323.15, 348.15, and 373.15 K, respectively. Below a CO_2 partial pressure of 10 kPa, a 20.5 mass % MDEA solution showed a maximum absorption capacity of CO_2, and above 10 kPa, a 50.0 mass % MDEA solution was superior. Lastly, the absorption enthalpy of CO_2 in 50.0 mass % MDEA solution was 54.6 kJ·mol^{-1} CO_2 in the range of equilibrium loading ratios from 0.01 to 0.10.

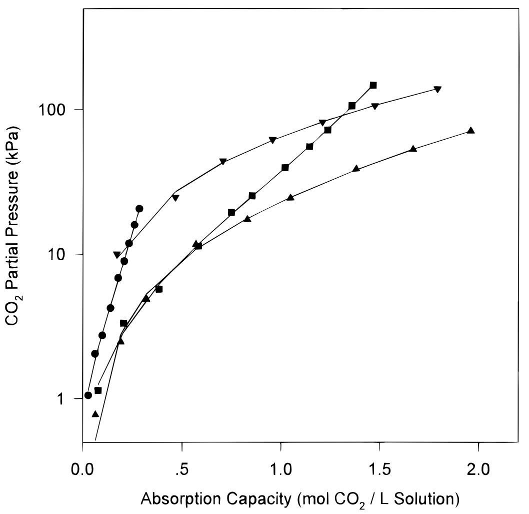

Figure 8. Absorption capacity of CO_2 in MDEA solutions at 323.15 K: (●) 5 mass %; (■) 20.5 mass %; (▲) 50 mass %; (▲) 75 mass %; (solid line) smooth fitting.

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