Solubility of Carbon Dioxide in Aqueous Mixtures of Alkanolamines

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The solubility of CO_2 in water + *N*-methyldiethanolamine + monoethanolamine (MDEA + MEA) and water + *N*-methyldiethanolamine + diethanolamine (MDEA + DEA) are reported at two compositions of 3.4 M MDEA + 0.8 M MEA or DEA and 2.1 M MDEA + 2.1 M MEA or DEA at temperatures from 70 to 180 °C and CO_2 partial pressures from 100 to 3850 kPa. The solubility of CO_2 in the blends decreased with an increase in temperature but increased with an increase in CO_2 partial pressure. At low partial pressures of CO_2 and the same total amine concentration, the equilibrium CO_2 loadings were in the order MDEA + MEA > MDEA + DEA > MDEA. However, at high CO_2 partial pressures, the equilibrium CO_2 loadings in the MDEA solutions were higher than those of the MDEA + MEA and MDEA + DEA blends of equal molar strengths due to the stoichiometric loading limitations of MEA and DEA. The nonadditivity of the equilibrium loadings for single amine systems highlights the need for independent measurements on amine blends.

Introduction

Aqueous solutions of primary, secondary, and tertiary alkanolamines are widely used to remove acid gases such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) from natural, refinery, and synthesis gases in reversible absorption–regeneration processes. The differences in the performance of these amines depend on their reactivities. Primary and secondary amines such as monoethanolamine (MEA) and diethanolamine (DEA), respectively, are very reactive and therefore exhibit high rates of acid gas removal. However, the formation of stable carbamates with CO_2 causes a stoichiometric loading limitation of 0.5 mol of CO_2/mol of amine. Tertiary amines such as *N*-methyldiethanolamine (MDEA) do not form stable carbamates and are therefore able to effect a high total CO_2 removal but at much lower rates. Consequently, they are primarily used for the selective removal of H_2S. Furthermore, the MDEA process, being less reactive with CO_2, is characterized by lower energy requirements compared to the MEA and DEA processes. Recently, attention has been focused on the use of amine blends to maximize the desirable qualities of the individual amines. The specific goal in this respect is to have solutions of tertiary + secondary or tertiary + primary amines that retain much of the reactivity of primary or secondary amines, offer low regeneration costs (similar to those of tertiary amine based plants), are less corrosive, and require lower circulation rates to achieve a desired degree of sweetening (or produce a sweeter gas for the same circulation rate).

Simulation studies with blends of MDEA + MEA and MDEA + DEA have indicated considerable improvements in absorption and/or appreciable savings in energy requirements compared with single amine systems (*1–3*). The realization of such benefits in practice is a function of proper equipment design which requires knowledge of the equilibrium solubility of acid gases in amine blends. Although simulation is an attractive approach to obtain such results in view of the large number and variety of possible blend formations, experimentation is still necessary to validate the vapor–liquid equilibrium (VLE) models for amine blends. This paper presents measurements of the solubility of CO_2 in 3.4 M MDEA + 0.8 M MEA or DEA and 2.1 M MDEA + 2.1 M MEA or DEA (corresponding to 19 and 50 mol % total primary or secondary amine substitutions, respectively) at temperatures ranging from 70 to 180 °C, and CO_2 partial pressures from 100 to 3850 kPa.

Table 1. Comparison of Present Results with Literature Values at 100 °C

concn (M) ([MDEA]/[MEA])	P_{CO_2} (kPa)	loading (mol of CO_2/mol of amine) this study	loading (mol of CO_2/mol of amine) lit. (ref)	dev (%)
2.06/1.0	134.8	0.33	0.416 (*4*)	−20.67
	1168.0	0.63	0.634	−0.63
	1540.0	0.67	0.646	+3.72
	1905.0	0.72	0.664	+8.43
				AAD = 8.36
4.28/0.0	558.0	0.269	0.305 (*5*)	−11.80
	1103.0	0.439	0.438	+0.23
	1900.0	0.565	0.585	−3.42
	2822.0	0.756	0.720	+5.00
	3611.0	0.823	0.815	0.98
				AAD = 4.29
4.28/0.0	558.0	0.269	0.350 (*6*)	−23.14
	1103.0	0.439	0.520	−15.58
	1900.0	0.565	0.665	−15.04
	2822.0	0.756	0.800	−5.50
	3611.0	0.823	0.900	−8.56
				AAD = 13.56

Experimental Procedure

The experiments were conducted using a 600-mL stainless steel batch reactor equipped with an insulating jacket, a Bourden-type pressure gauge (0–600 psi, in 5 psi subdivisions), and a variable-speed stirrer. Heat supplied to the reactor was controlled by a temperature indicator controller. The temperature in the reactor was monitored by a J-type thermocouple. Amine solutions of the desired strengths and compositions were prepared from mixtures of distilled water and the appropriate quantities of amine(s). The MEA, DEA, and MDEA were purchased from Aldrich Chemical Inc., Milwaukee, with stated purities of 99+%.

For a typical run, 250 mL of aqueous amine solution of the desired strength and composition was placed in the reactor. The reactor was then sealed, the stirrer was started, and nitrogen was introduced at low pressures for about 15 min to purge the reactor of oxygen. The reactor was then heated to the desired operating temperature. Once the temperature had stabilized, the vapor pressure of the solution indicated by the pressure gauge was recorded. Carbon dioxide (CO_2)

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Table 2. Experimentally Determined Solubilities of CO_2 in Various Amine Solutions

	aqueous 3.4 M MDEA + 0.8 M MEA		aqueous 2.1 M MDEA + 2.1 M MEA		aqueous 3.4 M MDEA + 0.8 M DEA		aqueous 2.1 M MDEA + 2.1 M DEA	
T (°C)	P_{CO_2} (kPa)	loading (mol/mol of amine)	P_{CO_2} (kPa)	loading (mol/mol of amine)	P_{CO_2} (kPa)	loading (mol/mol of amine)	P_{CO_2} (kPa)	loading (mol/mol of amine)
70	214	0.484	210	0.526	65	0.246	224	0.517
	775	0.707	589	0.660	241	0.501	741	0.688
	1860	0.803	1650	0.784	706	0.683	1929	0.814
	2660	0.859	2753	0.846	1781	0.801	2894	0.907
	3773	0.884	3717	0.917	2743	0.873	3756	0.928
					3807	0.911		
100	190	0.234	234	0.399	165	0.181	265	0.313
	569	0.383	782	0.536	630	0.365	758	0.450
	1306	0.545	1502	0.609	1227	0.509	1388	0.569
	2171	0.633	2181	0.694	2095	0.593	2171	0.663
	2980	0.753	2921	0.738	2808	0.692	3094	0.727
	3876	0.795	3859	0.769	3697	0.774	3845	0.779
120	206	0.157	138	0.235	262	0.126	248	0.185
	775	0.297	658	0.400	782	0.245	771	0.324
	1447	0.411	1412	0.492	1447	0.346	1430	0.420
	2205	0.491	2156	0.558	2064	0.460	2157	0.515
	2911	0.550	2894	0.604	2977	0.548	2949	0.590
	3610	0.589	3776	0.632	3707	0.624		
140	261	0.109	137	0.159	338	0.080	327	0.118
	806	0.215	602	0.298	796	0.160	792	0.219
	1364	0.289	1343	0.386	1433	0.230	1419	0.303
	2167	0.361	2108	0.448	2036	0.318	2112	0.374
	2839	0.408	2790	0.504	2863	0.381	2998	0.440
	3562	0.437	3590	0.536	3621	0.446	3711	0.489
160	220	0.058	151	0.094	234	0.042	293	0.079
	723	0.125	585	0.205	734	0.098	751	0.150
	1343	0.178	1219	0.280	1289	0.152	1275	0.217
	2025	0.224	2167	0.337	1957	0.214	1916	0.279
	2659	0.263			2635	0.259	2911	0.331
	3480	0.288			3449	0.298	3549	0.407
180	223	0.050	165	0.065	227	0.042	190	0.045
	568	0.090	482	0.129	568	0.077	538	0.090
	1092	0.132	1019	0.187	1068	0.114	1120	0.141
	1722	0.168	1674	0.236	1705	0.149	1792	0.196
	2377	0.206	2311	0.278	2491	0.185	2618	0.235
	3104	0.228	3035	0.315	3135	0.218	3187	0.291

Table 3. Experimentally Determined Solubilities of CO_2 in MDEA, MEA, and DEA Solutions

	4.28 M aqueous MDEA		4.2 M aqueous MEA		4.2 M aqueous DEA	
T (°C)	P_{CO_2} (kPa)	loading mol/mol of amine)	P_{CO_2} (kPa)	loading (mol/mol of amine)	P_{CO_2} (kPa)	loading (mol/mol of amine)
100	162	0.123	455	0.541	93	0.299
	558	0.269	1330	0.622	486	0.469
	1103	0.439	2264	0.675	1110	0.595
	1900	0.565	3039	0.708	2019	0.660
	2822	0.756	3863	0.723	2660	0.684
	3611	0.823			3742	0.725
120	276	0.091				
	827	0.202				
	1482	0.288				
	2153	0.369				
	2894	0.433				
	3832	0.497				

was passed from a pressurized cylinder at a fixed delivery pressure into a stainless steel bomb. The initial mass of the bomb was determined using a Mettler balance (0–2000 ± 0.1 g) before it was connected to the reactor. Necessary valves were opened to transfer CO_2 from the bomb to the reactor. A one-way valve and a heater fitted to the CO_2 line prevented back-flow of materials as well as the freezing of CO_2, respectively. Following the contact of CO_2 with the amine solution, the total system pressure dropped gradually, and equilibrium was deemed to have been attained when the system pressure did not change for times ranging from 15 min at 180 °C to at least 1 h at 70 °C. At equilibrium, the inlet valve to the reactor was closed and the system pressure recorded. The CO_2 bomb was then disconnected and its final mass determined. Subsequently, the CO_2 bomb was refilled at a higher pressure, reweighed, and reconnected to the reactor to obtain another pair of pressure/loading data. By repeating this procedure, it was possible to use the same amine solution at a fixed temperature to obtain a series of loadings at increasing pressures. The maximum pressure was limited by either the pressure gauge or the CO_2 pressure in the bomb. The reactor was then shut down and cleaned for another set of runs.

In addition to the main experiments that were performed under the aforementioned conditions, other experiments were conducted with water + MEA, water + DEA, water + MDEA, water + MDEA + MEA, and water + MDEA + DEA.

Results and Discussion

The partial pressure of CO_2 in the reactor was calculated from the difference between the total pressure and the vapor

Table 4. Comparison of CO_2 Loadings in Single Amines and Mixed Amine Systems Containing 50 mol % (or 2.1 M) DEA at 100 °C

	mol of CO_2 in liquid				
P_{CO_2} (kPa)	2.1 M DEA	2.1 M MDEA	total (a) (4.2 M)	2.1 M MDEA + 2.1 M DEA (b)	ratio (a/b)
758	1.40	1.28	2.68	1.89	1.42
1388	1.61	1.57	3.18	2.38	1.33
2171	1.77	1.77	3.54	2.78	1.27
3094	1.89	1.94	3.83	3.05	1.26
3845	1.97	2.05	4.02	3.27	1.23

Table 5. Comparison of CO_2 Loadings in Single Amine and Mixed Amine Systems Containing 19 mol % (or 0.8 M) DEA at 100 °C

	mol of CO_2 in liquid				
P_{CO_2} (kPa)	0.8 M DEA	3.4 M MDEA	total (a) (4.2 M)	3.4 M MDEA + 0.8 M DEA (b)	ratio (a/b)
630	0.63	1.29	1.92	1.53	1.49
1227	0.77	1.70	2.47	2.14	1.45
2095	0.90	2.10	3.00	2.49	1.43
2808	0.98	2.38	3.36	2.91	1.41
3695	1.06	2.62	3.68	3.25	1.40

pressure of the amine solution at the operating temperature. The mass of CO_2 fed to the reactor was determined as the difference between the initial and final masses of the CO_2 bomb, less the mass of CO_2 lost in the transfer line. The latter was determined experimentally and correlated by the polynomial expression

$$CO_2\ \text{lost/g} = 0.001948 + 2.325 \times 10^{-4}(P_t/\text{kPa}) + 5.6309 \times 10^{-7}(P_t/\text{kPa})^2 - 1.32713 \times 10^{-10}(P_t/\text{kPa})^3 + 2.01542 \times 10^{-14}(P_t/\text{kPa})^4$$

where P_t is the total system pressure.

For any run within a set (i.e., those conducted with the same solution), the mass of CO_2 fed to the reactor is the cumulative mass of CO_2 fed to the reactor in the set. The volume of the gas phase was calculated as the difference between the internal volume of the reactor and the volume of amine solution. By using the pressure, volume, and temperature values and the Peng–Robinson equation of state, it was possible to determine the moles of CO_2 in the gas phase. This value was then subtracted from the CO_2 discharged to the reactor to obtain the amount of CO_2 dissolved in the amine solution. The latter was then expressed as moles of CO_2 per mole of amine.

It is recognized that errors in pressure readings, the mass of the CO_2 bomb, and the determination of the CO_2 content of the gas phase affect the accuracy of the solubility values. An estimate of the error was obtained by comparing the results with literature values (Table 1). There is consistency with the literature values (*4–6*) particularly at CO_2 partial pressures above 500 kPa where the absolute average deviations (AAD) range from 4 to 13.5%. This suggests that the present experimental equipment and procedure are better suited for moderate to high pressure/loading measurements. Repeat experiments indicated reproducibilities of ±1.5%. The measured solubilities are listed in Tables 2–5.

Effect of Temperature and Pressure. Figures 1–4 show the effects of temperature and pressure on the equilibrium CO_2 loadings in the amine blends. In general, the equilibrium loadings decrease with temperature and increase with pressure.

Effect of Components. Figure 5 shows that, at 70 °C and within the pressure range investigated, the choice of MEA or DEA in the mixture did not make any difference in the equilibrium solubility of CO_2. At higher temperatures, the MDEA + MEA solution recorded higher loadings than the MDEA + DEA solution, suggesting that a lower energy may be required to regenerate the latter solution. A similar observation was reported by Austgen et al. (*7*) at 80 °C. However, data at 40 °C for loadings below 0.5 mol/mol of amine indicate that the MDEA + MEA solution is better suited for sweetening such low-pressure gases (*7*). This advantage must be weighed against the higher regeneration

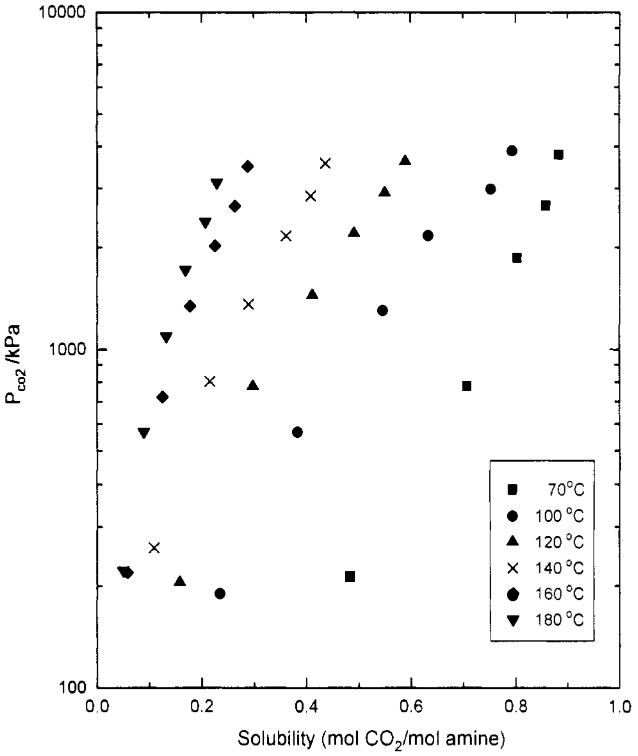

Figure 1. Effect of temperature on the equilibrium solubility of CO_2 in aqueous solutions of 3.4 M MDEA + 0.8 M MEA.

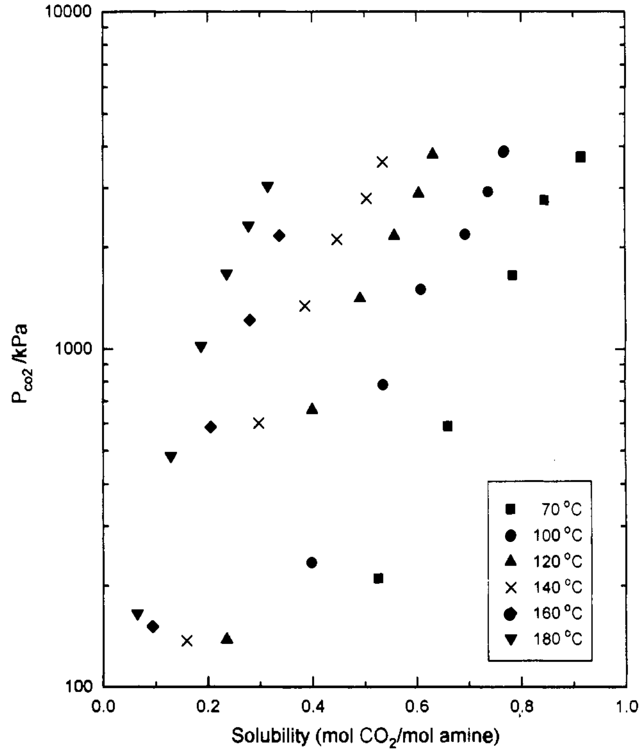

Figure 2. Effect of temperature on the equilibrium solubility of CO_2 in aqueous solutions of 2.1 M MDEA + 2.1 M MEA.

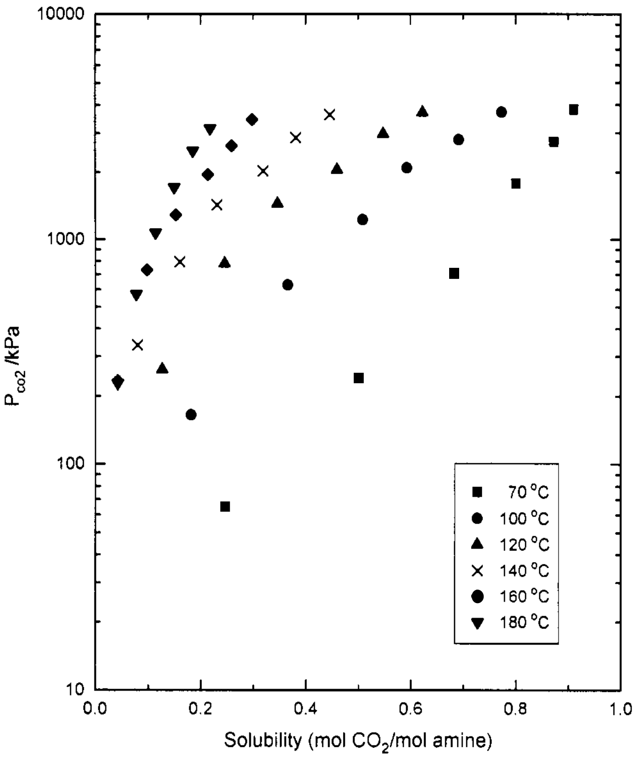

Figure 3. Effect of temperature on the equilibrium solubility of CO_2 in aqueous solutions of 3.4 M MDEA + 0.8 M DEA.

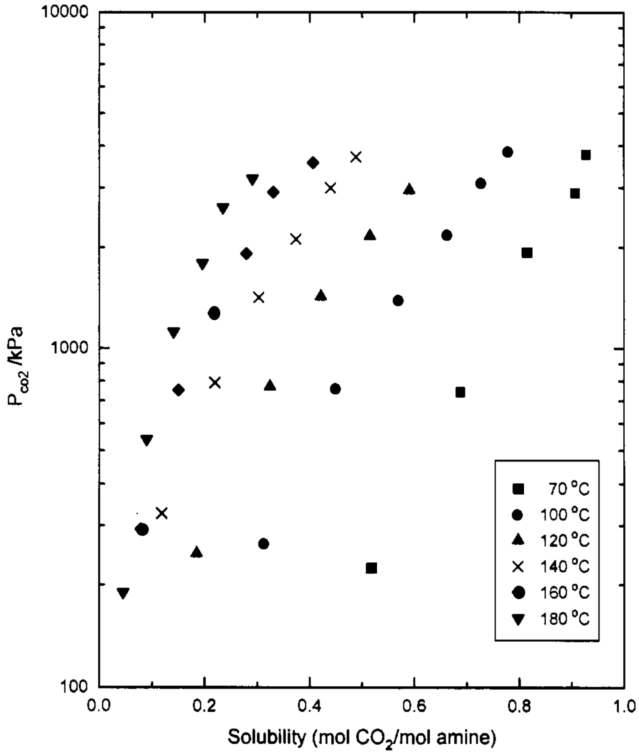

Figure 4. Effect of temperature on the equilibrium solubility of CO_2 in aqueous solutions of 2.1 M MDEA + 2.1 M DEA.

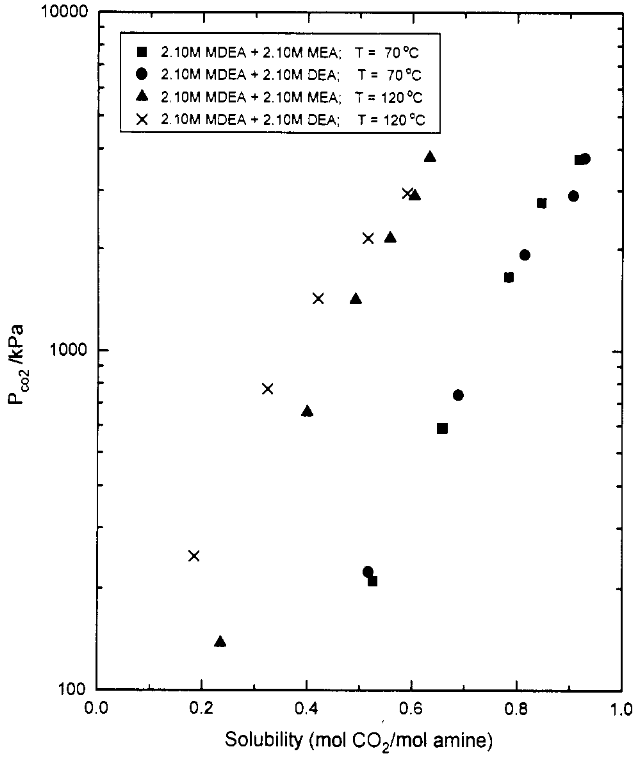

Figure 5. Effect of amine components on the equilibrium solubility of CO_2 at 70 and 120 °C.

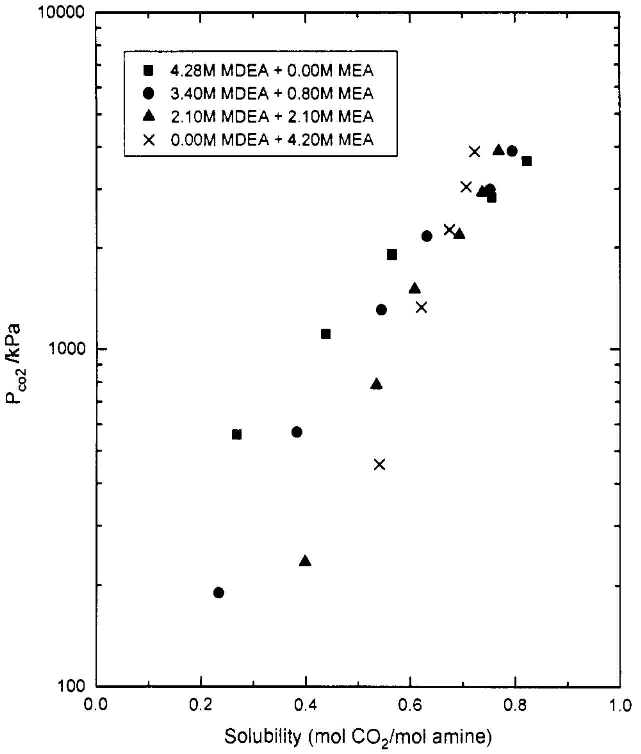

Figure 6. Effect of amine composition on the equilibrium solubility of CO_2 in aqueous MDEA + MEA solutions at 100 °C.

energy requirement associated with the MDEA + MEA solution.

Effect of Composition. The effect of composition on the equilibrium loadings is shown by Figures 6 and 7. At low pressures, the influence of the primary or secondary amine is pronounced, resulting in CO_2 loadings that increase with MEA or DEA concentration but decrease with increasing MDEA concentration, for solutions of equal molarity. At higher CO_2 pressures, the stoichiometric loading limitation associated with the absorption of CO_2 into MEA and DEA hinders the absorption in the amine blends. In this region, MDEA solutions which have no stoichiometric limitations provide higher loadings than MDEA + MEA and MDEA + DEA blends. A similar observation was reported previously (*6, 8*).

Tables 4 and 5 show substantial deviations between the experimental solubility data for the amine blends and the

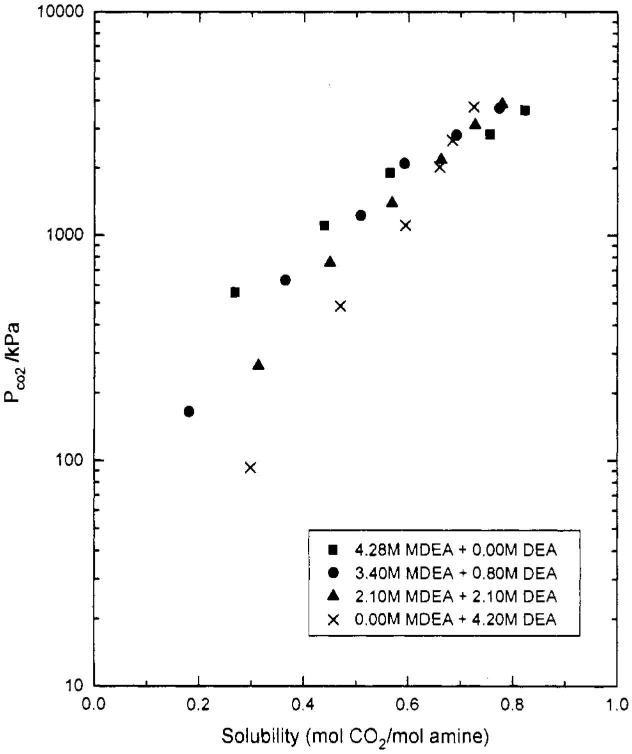

Figure 7. Effect of amine composition on the equilibrium solubility of CO_2 in aqueous MDEA + DEA solutions at 100 °C.

sum of the solubilities for the corresponding single amine systems. Such deviations underscore the need for experimental data on blended amine systems.

Conclusions

The solubility of CO_2 in aqueous blends of *N*-methyldiethanolamine with monoethanolamine and diethanolamine (MDEA + MEA and MDEA + DEA) have been measured at two compositions of 3.4 M MDEA + 0.8 M MEA or DEA and 2.1 M MDEA + 2.1 M MEA or DEA, temperatures from 70 to 180 °C, and CO_2 partial pressures from 100 to 3850 kPa. The CO_2 solubility decreases with increasing temperature but increases with CO_2 partial pressure. The results also indicate that the influences of amine components and composition depend on the extent of substitution, temperature, and CO_2 partial pressure. Furthermore, the nonadditivity of solubilities based on single amine systems highlights the necessity for experimental determination of equilibrium loadings in blended amine systems.

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